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Review

Directed assembly metallocyclic supramolecular systems for molecular recognition and chemical sensing

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Abstract

In recent years there has been immense interest in metallo-supramolecular architectures and their functional properties. The incorporation of metal centers into supramolecules opens up new possibilities for designing more robust receptors for chemical sensing purposes of ionic and neutral molecules. This review focuses on the advances made in the functional properties of the metallocyclic supramolecules with an emphasis on their potential use in the area of molecular recognition and sensing. We have also tried to cover, to some extent, the use of metallocyclic supramolecules in solid-state thin films for size-selective and chemical composition selectivity of volatile organic guest compounds.

Keywords: Supramolecular chemistry; Transition-metal complexes; Self-assembly; Metallocycles; Molecular recognition; Sensors; Chromophore; Luminescence

1. Introduction

A sensor is generally understood to be a device that transforms an event into an analytically useful and measurable signal for the presence of matter or energy [1]. The signals generated by such an event should ideally be detectable both in close vicinity as well as at remote distances. It should be different from any signal generated from the unspecific background and the unbound sensor. Moreover, a rational approach implies that the desired information is only reported on request. Random and uncontrolled generation of the output must be avoided and nature utilizes biomolecules for this purpose, e.g., in the case of an enzyme or antibody. Such biomolecules are typically sensitive to pH, oxidizing agents and heat, while artificial sensors can be synthesized from more robust components. Artificial sensors can, in principle, be tailored for various analytes, and their physical properties can be adjusted to meet the specific requirements. Important aspects of designing a sensor include analytical affinity, choice of chromophore or fluorophore, the binding selectivity, the signaling mechanism

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and the immobilization method [2–7]. The analyte affinity is a matter of primary concern in the design of a sensor. Artificial receptors bind guest molecules by a combination of fundamental electrostatic, hydrogen bonding and van der Waals interactions. The molecular forces can be controlled to effect molecular recognition by means of host–guest complementarity and host preorganization [8]. The preorganization leads to stronger and more selective binding as well as increasing rigidity. The sensor rigidity can hinder the analyte to the binding site, hence slowing equilibration considerably. Therefore, the sensor rigidity should be balanced with flexibility. Furthermore, the binding site and the event reporter should be structurally integrated as much as possible in order to maximize the communication.

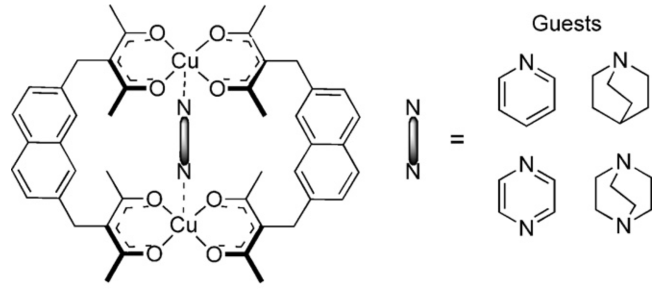
A versatile means of communication to generate such an event is provided by metallo-supramolecules. In metallo-supramolecules, the necessary components can be easily incorporated according to the needs of the analyte to generate analytically useful and observable signals. The extensive studies on macrocyclic 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 supramolecular chemistry [9]. The design and preparation of novel macrocycles, and the exploitation of their application, have attracted considerable attention from the scientific community in the past three decades. Because of the harsh reaction conditions and low yields of the desired supramolecules, the conventional kinetically controlled organic synthetic procedures are not very suitable for the preparation of macrocycles. However, the directional and coordinate bonding nature of the metals has been successfully exploited to design the desired macrocycles with relative ease [10–13]. It is well documented that through directional coordinate bonding, two- and three-dimensional self-assembly architectures are readily available by the reaction of metal starting materials with appropriate organic ligands. This novel strategy of metal mediated self-assembly has been successfully applied to construct numerous metallo-supramolecular structures with interesting functions. Although several excellent review articles on the metallo-supramolecular chemistry are available [10–13], there appears to be no review articles that deal exclusively with the functional properties of metallocyclic supramolecules, particularly with respect to their sensing/recognition capability. However, there are a few recent review articles that describe to some extent their use in chemical sensing [14–16].

Substantial progress has been made in the past few years in the area of functional metallo-supramolecular assemblies and their use as recognition units, in general. As a result of constraints imposed by coordinate bonding, metallocyclic supramolecules 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 $\mathrm{kJ\,mol^{-1}}$ per interaction, which lie between strong covalent bonds (ca. 400 $\mathrm{kJ\,mol^{-1}}$) and other weak noncovalent interactions, such as hydrogen bonding and van der Waals interactions ($<40\,\mathrm{kJ\,mol^{-1}}$). Additional attractive features of metallocyclic supramolecules are their suitability for various functional properties and their potential use for various applications. Firstly, functionalities can easily be introduced into the metallocyclic supramolecular structure by employing functional ligands and/or metal centers in the assembly. Upon formation of the superstructures, these metal centers may interact, thus leading to a higher level of functionality and the cavities created may accommodate guest molecules. Secondly, the macrocycles containing transition metals are generally more sensitive and responsive on electro- and photochemical stimuli compared to metal-free organic macrocyclic molecules. The most significant features, which arise upon the formation of the architecture, include encapsulation of guest molecules, luminescence and redox activity. Depending on the size and nature of the cavities, these structures can act as a host for various types of guest molecules of different sizes and shapes. A combination of the differing host–guest behavior of various metallocyclic supramolecules with their arising luminescent or electronic properties can, thus, be exploited for sensing purposes. The inherent potential of metallocyclic supramolecules thereby provides new opportunities to develop novel molecular devices. In this review, we highlight the recent advances made in functional metallocyclic supramolecules and, in particular, focus on their potential applications with respect to chemical sensing.

2. Molecular recognition

2.1. Molecular recognition by metallocyclic supramolecules via noncovalent interactions

Since cavities of different sizes are easily accessible with metallocyclic supramolecules by complexation of a broad range of organic molecules and metal components, then it follows that they can act as hosts for various types of guest molecules. One of the first metallocyclic supramolecules, **1**, was reported to act as a host by Maverick et al. [17]. The binuclear copper(II) cycle **1** acts as a host for various nitrogen bases such as pyrazine, pyridine, quinuclidine, and diazabiclo-[2,2,2]octane (DABCO). The olive green solution of **1** changes to turquoise on addition of nitrogen bases. The binding constants of the nitrogen bases with **1** were determined spectrophotometrically in chloroform at room temperature. The authors compared the binding constants for **1** with monofunctional and bifunctional Lewis bases such as pyridine ($K_a = 0.5\,\mathrm{M^{-1}}$), quinuclidine ($K_a = 7\,\mathrm{M^{-1}}$), pyrazine ($K_a = 5\,\mathrm{M^{-1}}$) and DABCO ($K_a = 220\,\mathrm{M^{-1}}$) in chloroform solutions, and concluded that the larger binding constant for the bidentate coordinating ligands were consistent with internal coordination in the cavity. This conclusion was also supported by the crystal structure of the DABCO with **1**:

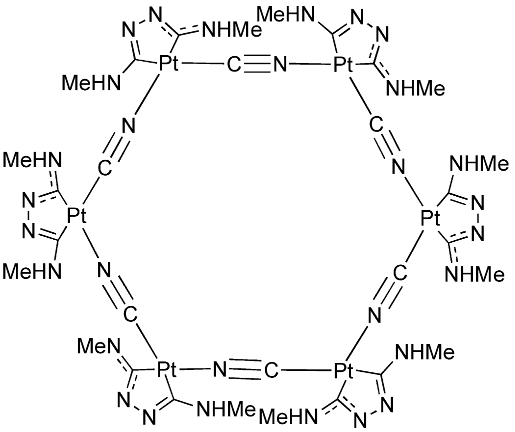


1

The cyclic trimetallic copper complex **2** has been known for some time [18], but its luminescence and host–guest chemistry was first reported by Provencher and Harvey [19]. They found that compound, **2**, emits strongly in solution ($\lambda_{em} = 540$ nm, $\tau_{em} = 89 \pm 9$ μs at 298 K in ethanol), which is described to be phosphorescence from an excited-state delocalized throughout the tricopper frame. Interaction of **2** with carboxylates (either acetate or 4-aminobenzoate) quenches the luminescence, apparently because of the formation of a host–guest exciplex. The quenching constants were found to be 1.65×10^8 and 5.10×10^8 M^{-1} s^{-1} for acetate and benzoate, respectively.

Che and coworkers reported a hexametallic platinum metallocycle **3** complexed with chelating dicarbene and cyanide ligands to create a hexagonal cavity in the supramolecule [20]. The platinacycle luminesces at 514 nm when subjected to MLCT (Pt–π* (carbene)) excitation in the near-UV region. They observed that the emission was quenched by *N*,*N*′-dimethyl-4,4′-bipyridinium hexafluorophosphate:

The quantitative self-assembly of a Pd(II)-based molecular square **4** was reported by Fujita et al. [21]. The invention of this metallocyclic supramolecule boosted the interest of scientific community towards the metallocyclic supramolecular self-assembly. The X-ray structure of the **4** showed an almost perfect square with the pyridine rings slightly twisted. The side-to-side distance in this square was approximately 8 Å. This molecular square showed the unique ability of molecular recognition of neutral aromatic guests such as benzene, naphthalene, etc. For instance, the square **4** encapsulates the electron rich guest 1,3,5-trimethoxybenzene into the cavity in water (D_2O) to form a 1:1 host–guest complex. The ^{1}H NMR chemical shift change of 1.56 ppm for the aromatic protons and 0.59 ppm shift for methyl protons in D_2O at room temperature were observed. Analysis of the chemical shift change by Benesi–Hildebrand and a least squares procedure gave an association constant, $K_a = 750\ M^{-1}$ at 25 °C. During the binding process, both the hydrophobic and electrostatic interactions contribute to the formation of host–guest complexes. Later they found that the square **4** showed smaller binding constant with smaller molecules such as *p*-dimethoxybenzene ($K_a = 330\ M^{-1}$), *m*-dimethoxybenzene ($K_a = 580\ M^{-1}$) or *o*-dimethoxybenzene ($K_a = 30\ M^{-1}$) [22]. Stang et al. reported similar positively charged molecular squares, **5** and **6**, that recognize 1,5-dihydroxynaphthalene in deuterated methanol to give corresponding inclusion complexes [23]. For example, a significant upfield shift of ~0.11 ppm for *ortho* protons and 0.2 ppm for *meta* protons of 2,5-dihydroxynaphthalene was observed as a function of concentration in the ^{1}H NMR titration with **5**:



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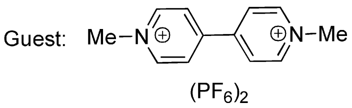

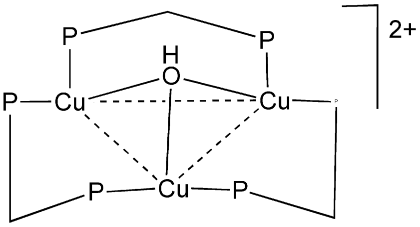

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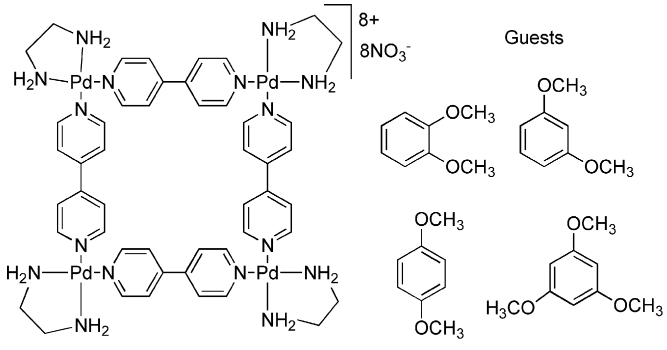

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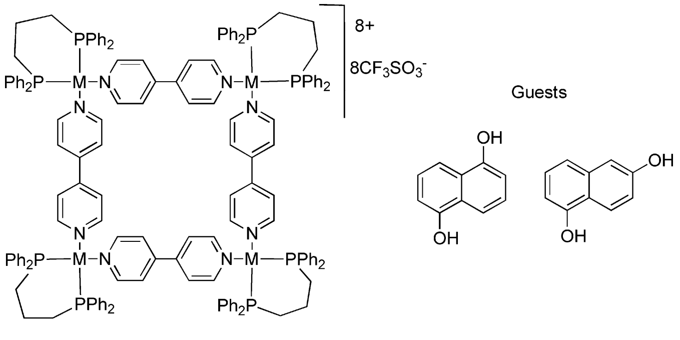
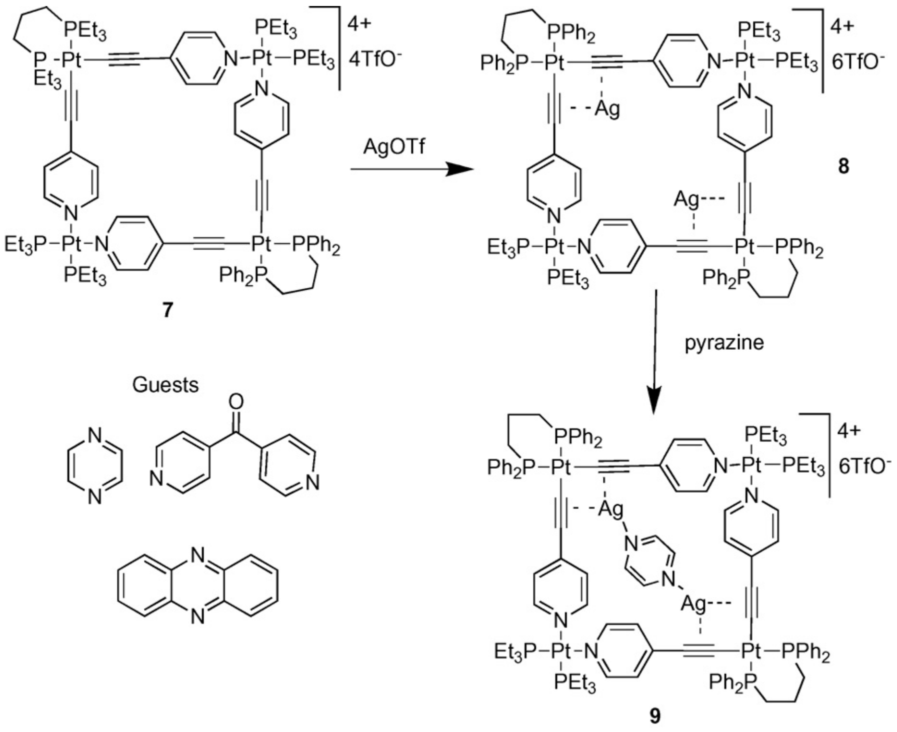


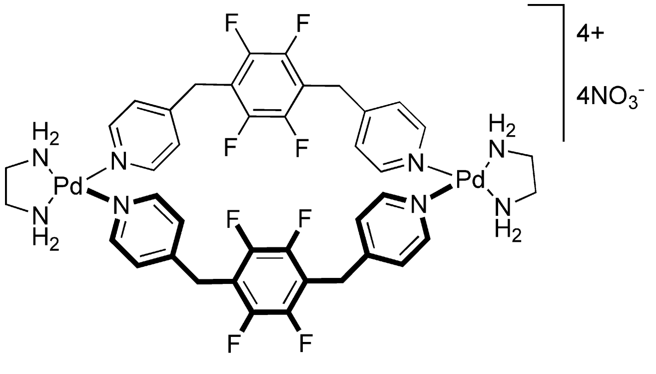
M = Pd (5), Pt (6)

Thus, the rational design of efficient hosts for molecular recognition involves the introduction of specific recognition sites into the assembly. Stang et al. have designed some molecular squares with Lewis base receptor sites, which show a variety of metal-binding capability and geometrical predictability. X-ray crystallography provided new insight into molecular recognition design of the Lewis acid–base host–guest molecular square **7** with phenazine [24]. There are several interesting structural features evident for this complex. The overall geometry of the perimeter for this complex is almost planar with the guest phenazine oriented nearly orthogonal to the Pt–Pt^{2+}–Pt plane. The π-complexed silver atoms are located in a pseudo-*trans* arrangement with respect to the Pt–Pt^{2+}–Pt plane, resulting in a C_i-symmetric relationship. Interestingly, the acetylene moieties in the backbone of the molecular square **7** interact with 2 equiv. of silver triflate to give a host–guest complex, **8**, with considerable stability in solution. Further, the metallocylic square, **8**, serves as a receptor to bind Lewis basic guests with the appropriate size being achieved through the π-complexed silver cations. The reaction of **8** with equimolar amount of Lewis bases such as pyrazine, phenazine or 4,4′-bipyridyl ketone in CH_2Cl_2 at room temperature, results in the formation of corresponding ternary complexes, **9** (see Scheme 1). The coordination of silver was monitored by a significant change in the intensity and shape of the CD absorption bands, while the stoichiometric addition of respective guests to the receptors was observed by the subsequent decrease in the absorption intensities and variation of the signal shape.

The molecular loop **10** was shown to bind electron rich aromatic guests in water with strikingly high affinity [25,26], which is ascribed to the incorporation of an electron-deficient perfluorinated benzene unit. It was also capable of binding 1,3,5-trimethoxybenzene, *p*-dimethoxybenzene, *m*-dimethoxybenzene, and *o*-dimethoxybenzene with association constants $K_a = 2500$, 2680, 1560, and $1300\,M^{-1}$, respectively. For larger guests, such as *N*-(2-naphthyl)-acetamide, only a weak host–guest interaction was observed ($K_a = 15\,M^{-1}$):



Scheme 1.



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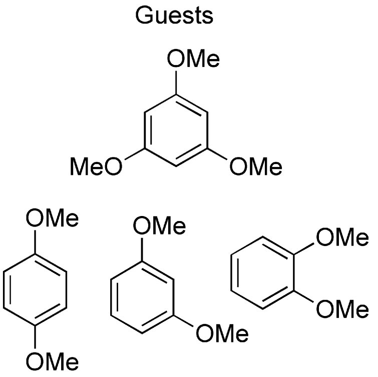
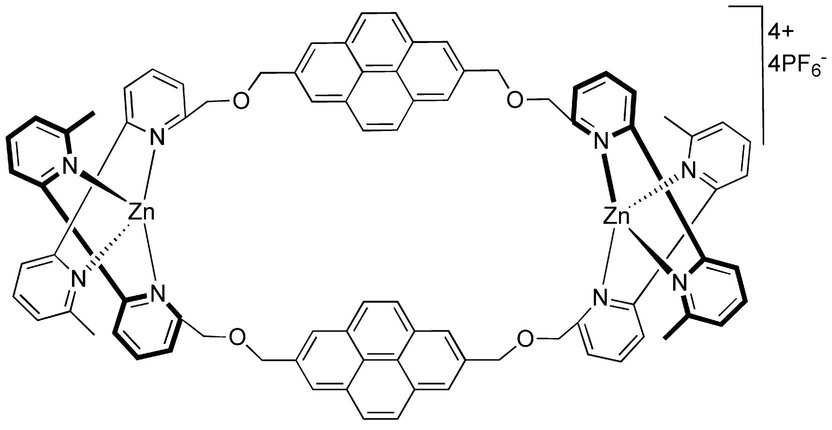
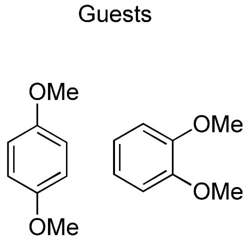


Bilyk and Harding reported the encapsulation of 1,4-dimethoxybenzene and 1,2-dimethoxybenzene into the electron-deficient cavity of the dinuclear metallocyclic Zn complex **11**. The X-ray structure of the corresponding complexes with the cycle has definitively established the inclusion of the guest within the cavity [27,28]:

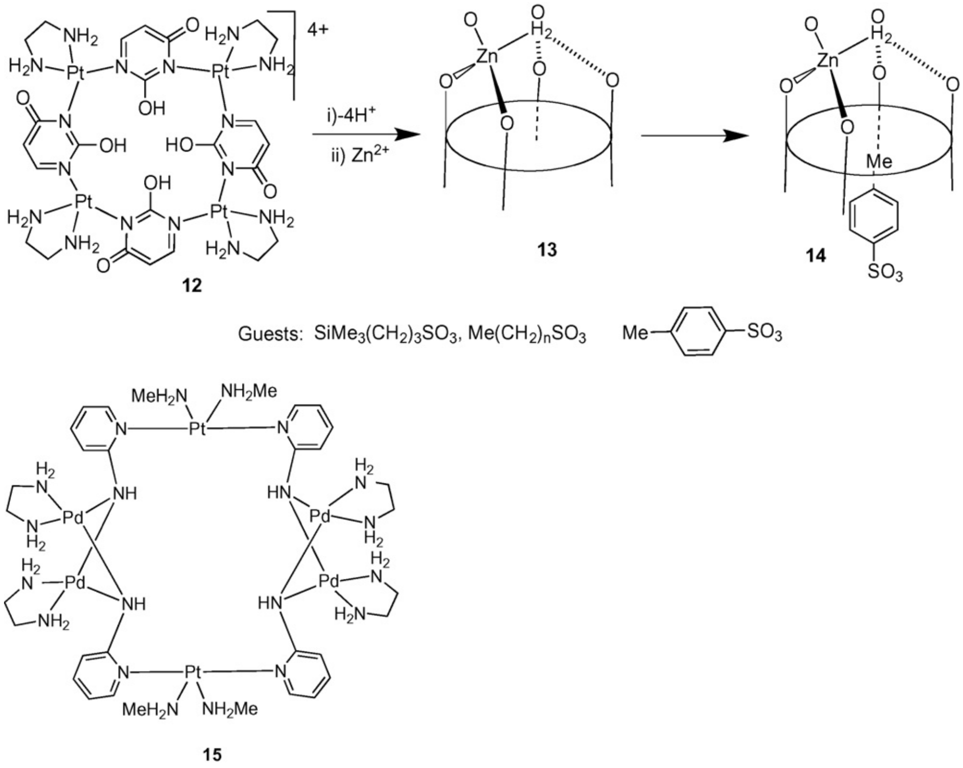


11

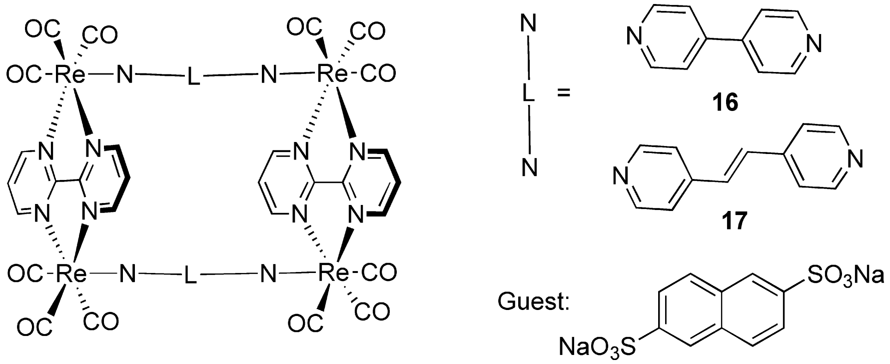


Metallocyclic supramolecule **12** reported by Lippert and coworkers was believed to be a metal analogue of calix[4]arene [29]. The metallocycle consists of four Pt atoms, four 1,2-diaminoethane and four uracil bases. After deprotonation, the oxo surface formed by the four O^{2-} exocyclic atoms of the uracil nucleobases are capable of encapsulating additional metal ions and can include only one metal ion in the cone. The titration of the deprotonated platinum cone with Zn^{2+}, Be^{2+} and La^{3+} ions (see Scheme 2) caused a significant chemical shift change in the ^{1}H NMR spectra. Moreover, the species (such as **13**) formed with the inclusion of the metal ions in the cavity can further act as a host for organic anions, such as *p*-toluenesulfonate and 3-(trimethylsilyl)-1-propanesulfonate to form an inclusion complex **14**. The association constants (K_a) were found in the range of 13–159 M^{-1}. The organic anion complexation is probably due to the cooperativity induced between the positive charge introduced by the coordinated metal cation and the hydrophobic nature of the cone cavity in aqueous solution. A similar cycle **15** showed an affinity towards the oxalate guest. The ^{1}H NMR titration revealed that the NH_2 group interacts with the oxalate guests and are concentration dependent [30].

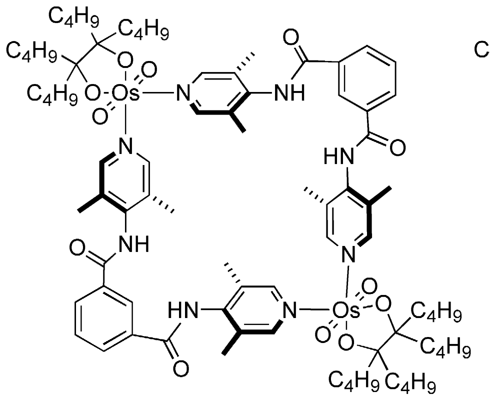
Hupp and coworkers studied the affinities of the rhenium–bipyridine rectangles **16** and **17** [31]. The dimension of the cavity in the metallocyclic rectangle **16** is 5.89 Å × 11.55 Å. Proton NMR studies for the rectangles **16** and **17** with bis-sodium salt of 2,6-naphthanenedisulfonic acid gave association constants of 2.3×10^3 and $2.4 \times 10^3\ M^{-1}$, respectively, assuming the formation of a 1:1 host–guest complex. The roughly spherical tetraphenylborate anion showed no binding with **17**. The authors concluded that the binding involves columbic interactions in addition to van der Waals interactions:



Scheme 2.



Besides Lewis acid–base sites, hydrogen-bonding sites have also been extensively introduced into the metallocyclic molecular assemblies for the recognition of amide like guests. Jeong et al. have designed a series of osmium(IV) bridged molecular squares to explore their host–guest chemistry [32]. The cavities are enclosed by aromatic walls, while the hydrogen-bond donating amide units on the inner surface of the squares offer binding sites to the complementary hydrogen bonds of guests with suitable dimensions. Among the guests of the various sizes and shapes studied, the square, **18**, very strongly binds adipamide and terephthalamide, selectively. The authors found downfield chemical shifts for adipamide by1.5 ppm ($K_a = 3.6 \times 10^4\ M^{-1}$) and for terephthalamide of 1.23 ppm ($K_a = 2 \times 10^4\ M^{-1}$) in ^1H NMR. The strong binding of the diamides occurred because both hydrogen-bonding pockets of the host, **18**, simultaneously interacted with size matching diamide guests. The monoamides showed negligible hydrogen binding affinities with the host, further supporting the above fact. Similarly, the larger analogue **19** was found to bind larger guest amides, such as biphenyldicarboxamide, preferentially and strongly. The analysis of the ^1H NMR chemical shift change gave a binding constant of $K_a = 4.5 \times 10^4\ M^{-1}$. It was also found that the introduction of different substituents (e.g., OMe or NO_2) at the *para*-position of the corner pyridine rings affected the electron density on the pyridine nitrogen, and consequently the binding strength towards the amide guests:



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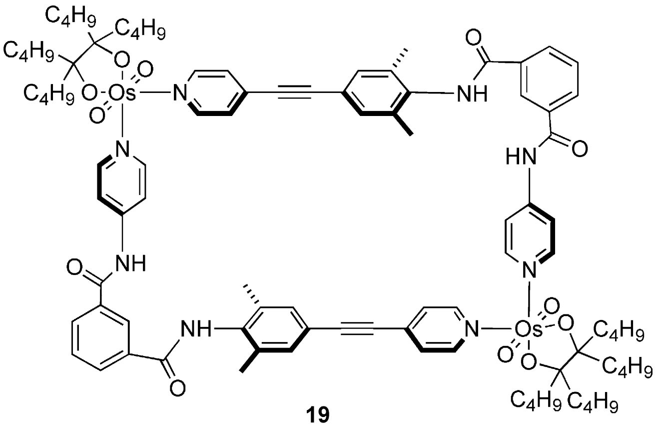
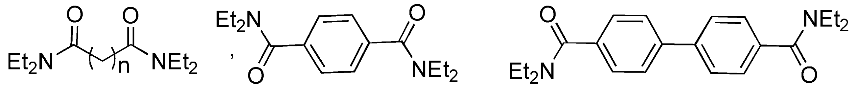


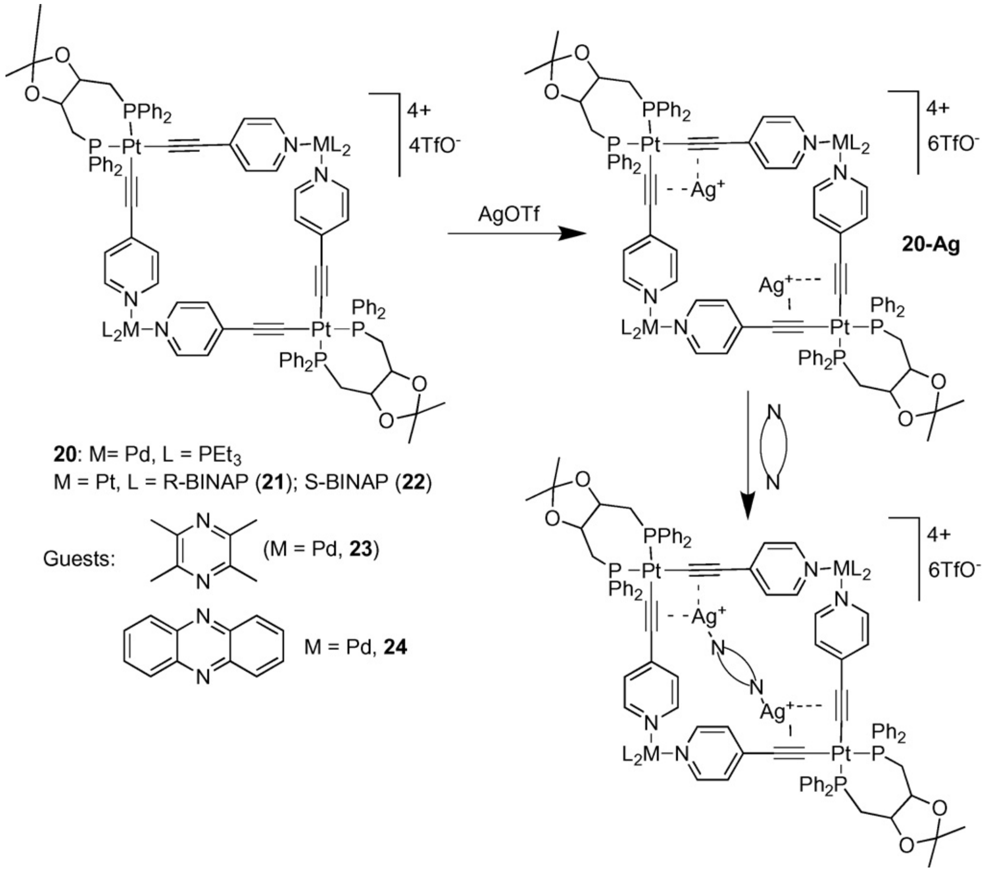
19

Guests:



2.2. Chiral recognition and sensing by metallocyclic supramolecules

The chirality in the supramolecule can be introduced either by (i) use of chiral auxiliary coordinated metal complex, (ii) use of an inherently chiral octahedral metal complex, (iii) use of optically active linker ligands, or (iv) use of a combination of the above methods [33]. The use of chiral phosphine ligands, such as 2,2′-bis(diphenylphosphino)-1,1-binaphthyl (BINAP) or 2,3-*O*-diisopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (DIOP), into the molecular assembly made it possible to monitor the host–guest interaction via circular dichroism (CD) spectroscopy along with other spectral studies [34]. CD spectroscopy has been used extensively as a powerful tool to study substrate binding in the biological systems [35]. A series of chiral molecular squares (see Scheme 3)

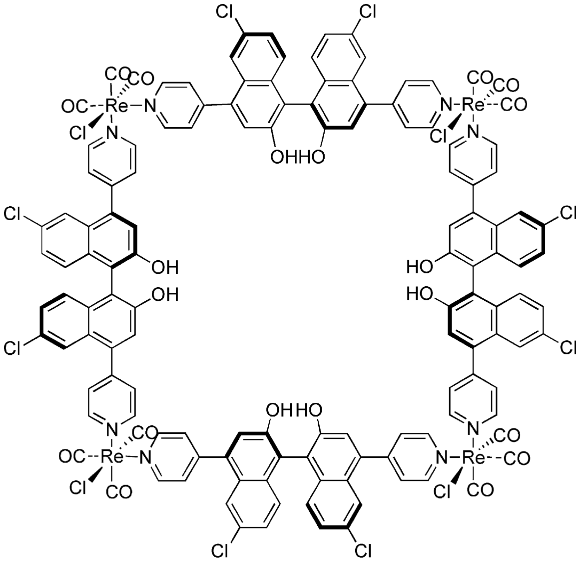


Scheme 3.

was reported by Stang and coworkers [34]. Interaction of the chiral squares with silver cation was monitored by a significant change in the intensity and shape of CD absorption, while the stoichiometric addition of respective guests to receptors was followed by the subsequent decrease in absorption intensities and variation of signal shape.

For example, upon addition of 2 equiv. of silver triflate, a decrease in Cotton effect and absorption intensity was observed for the square **20** ($\Delta\varepsilon = -15\,\mathrm{L\,M^{-1}\,cm^{-1}}$ at 336 nm). This change of intensity upon coordination of silver to the square **20** qualitatively correlates to large binding constant as expected for the π-complex **23·Ag** [36]. The subsequent coordination of guest molecules such as teramethylpyrazine or phenazine, resulting in corresponding inclusion complexes, **23** and **24**, continued to decrease absorption intensity and Cotton effect ($\Delta\varepsilon = -7$ and $-6\,\mathrm{L\,M^{-1}\,cm^{-1}}$at 336 nm, respectively). Small blue shifts in absorption spectra (11 and 1 nm, respectively) were also observed, indicating further delocalization of electron density afforded by neutral guests and silver complexation [37]. Moreover, introduction of another chiral ligand in molecular squares such as BINAP showed a more prominent decrease of Cotton effect and intensity because BINAP is conformationally more rigid having a Cotton effect approximately double than that of diphosphine. For example, Pt/Pt squares **21** and **22** showed maxima shift of about 15 and 12 nm on π-complexation of silver triflate. These π-complexed silver–platinum squares showed large intensity decreases (15–20 $\mathrm{L\,M^{-1}\,cm^{-1}}$) on inclusion of nitrogen bases. Similarly, pronounced effects were observed in the case of Pt/Pd squares too.

Lin and Lin wisely incorporated chiral ligands in a Re(I)-based molecular square **25** [38]. The luminescent, enantiopure, chiral molecular squares were able to interact with chiral amino alcohols, which resulted in chirality-based quenching of their luminescence. For example, the Stern-Volmer luminescence quenching constants of **(R)-25**, were found to be $K_{\mathrm{SV}} = 7.35$ and $6.02\,\mathrm{M^{-1}}$ for (*S*)-2-amino-1-propanol and (*R*)-2-amino-1-propanol, respectively, giving an enantioselectivity factor $K_{\mathrm{SV}}(R\text{–}S)/K_{\mathrm{SV}}(R\text{–}R)$ of 1.22 for luminescence quenching, which favors (*S*)-2-amino-1-propanol. Similarly, an opposite trend in the enantioselectivity factor for luminescence quenching was observed for **(S)-25** by the same guest molecules. Thus, the luminescence quenching of chiral molecular square **25** by 2-amino-1-propanol is dependent on the absolute configuration of the square ligand as well as the analytes. On the basis of these observations, it can be concluded that the square ligand and analyte of opposite configuration constitute the match pair for effective luminescence quenching. Moreover, the magnitude of the enantioselectivity for square **25** was significantly higher than that of the ligand, suggesting a better-defined chiral environment was conferred by the square structure. Therefore, the confinement of chiral ligands in metallocyclic supramolecules seems to be a promising approach to enantioselective recognition of chiral substrates:

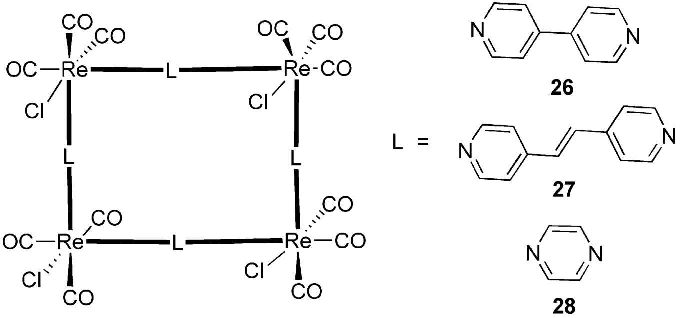


(S)-25 and (S)-25

2.3. Optical sensing of guest molecules by chromogenic and/or luminescent metallocyclic supramolecules

Introduction of chromogenic or luminescent properties is especially interesting in metallocyclic supramolecular assemblies since this might be used as an alternative to conventional NMR spectroscopy in the detection of guest inclusion [39]. In addition, photoluminescence allows examination of excited-state behavior of the host–guest complexation. Here it should be mentioned that informative optical effects generally result from changes in molecular structure, including proton transfer, charge transfer, and isomerization. The luminescence is much more sensitive to subtle changes in the geometry and medium environment. Luminescent compounds with internal cavities have been demonstrated as having potential applications in sensing devices [40–42]. Many macrocyclic complexes have been studied for their molecular recognition capabilities toward small aromatic molecules or inorganic ions based on their complementary cavity sizes and intermolecular forces such as hydrogen bonding, hydrophobic or electrostatic interactions [11,43]. The above requirements of a structurally important entity can be easily achieved by incorporating luminescent metal-organic chromophores in metallocyclic supramolecules [11,39,42]. Additionally, the vast literature available on the photophysical and photochemical properties of metal complexes are advantageous in designing such metallocyclic supramolecular assemblies.

An example of luminescent molecular assembly was provided by Hupp and coworkers by using luminescent Re(I)-based cyclophanes [44]. The directed assembly molecular squares **26**–**28** were emissive both in solution and solid state with the luminescence originating from the triplet metal-to-ligand charge transfer (MLCT) transition. The available square cavity sizes range from 3 Å (**28**) to 14 Å (**27**). One general and particular interesting feature in these Re(I)-based directed assembly cyclophanes is their tendency to form one-dimensional open channels not only in the macroscopic single crystals but also in the microcrystalline thin films [45]. As shown in several examples later in this review, the induction of nanometer scale porosity and permeability could provide significant implications in terms of selective molecular sensing and related applications:



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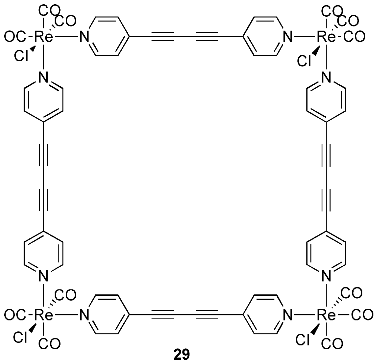
An extension of similar luminescent Re(I)-based cyclophanes has been reported by Sun and Lees [46]. For example, square **29**, was shown to be an effective probe for molecular sensing of nitroaromatics—surrogating trinitrotoluene (TNT), an explosive. A series of nitro-substituted aromatic compounds have been found to effectively quench the thin film luminescence of molecular square **29** but exhibit little effect on its corresponding corner molecule **30**. The quenching phenomenon was attributed to the porosity that exists in the film of square **29**, which provides cavities for binding the quencher molecules:



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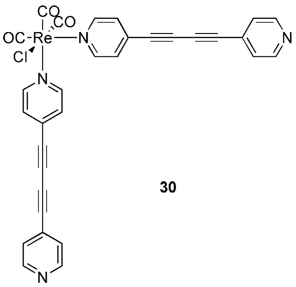
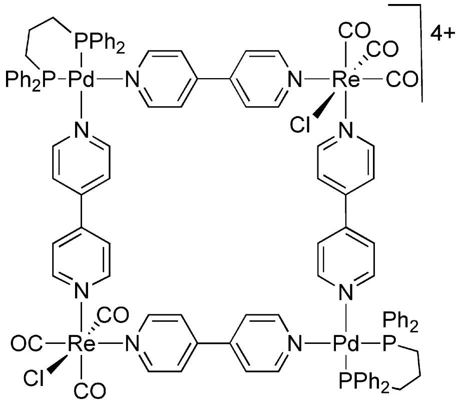


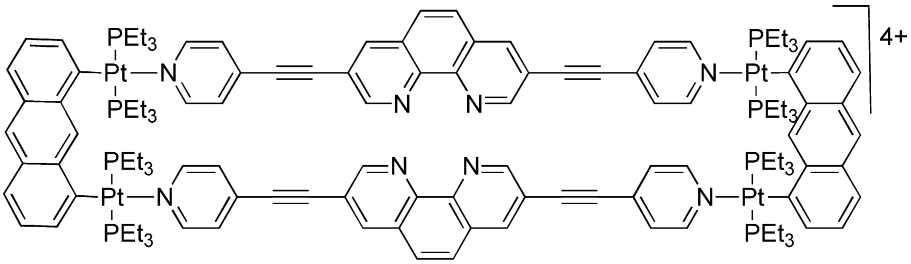
30

Hupp and coworkers reported a heterometallic molecular square, **31**, with alternating Re(CO)$_3$Cl and Pd(dppp)$_2$ (dppp = 1,3-bis(diphenylphosphino)propane) corners and with bridging 4,4′-bipyridine [47]. In acetone solution, emission from the ^{3}MLCT state is detected at 610 nm. It was expected that this molecule would act as a host for anions, because of cationic nature of the inorganic cyclophane **31**. Addition of ClO_4^- to the solution of **31** did indeed increase the luminescence intensity and excited-state lifetime. The enhancement effect was believed to originate from anion encapsulation-induced inhibition of oxidative quenching by Pd(II) sites. On the other hand, addition of BF_4^-, which binds more strongly than ClO_4^- ($K_a = 6000\,M^{-1}$ compared to $900\,M^{-1}$), induces a larger enhancement of luminescence, while addition of trifluoromethanesulfonate, which has a binding constant of intermediate value ($3000\,M^{-1}$), enhances the luminescence to a degree between that observed for BF_4^- and ClO_4^-:



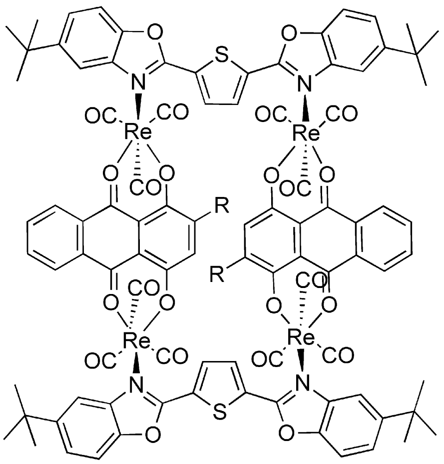
31

The rectangle **32**, reported by Stang and coworkers, acted as a chromatic sensor that was sensitive to the micromolar concentrations of Ni^{2+}, Cd^{2+}, and Cr^{3+} [48]. A change in UV–vis spectra was observed when a solution of rectangle **32** was treated with either $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}6H_2O$ or $Cr(NO_3)_3{\cdot}4H_2O$ up to a 1:1 host–guest ratio. The binding constants were found to be 2.01×10^7, 3.39×10^4, and $7.53 \times 10^3\,M^{-1}$ for Ni^{2+}, Cd^{2+}, and Cr^{3+}, respectively. The above observed equilibrium constants follow the same trend for the affinity as those for free 1,10-phenanthroline with the same ions:



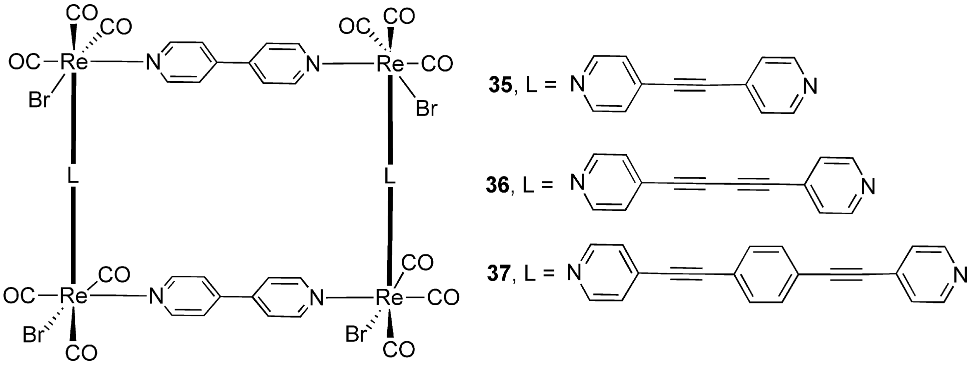
32

Very recently Lu and coworkers reported gondola-shaped tetra-rhenium metallocyclic compounds, **33** and **34** [49]. The metallocycles consist of a hydrophobic cavity of dimensions 5.6 Å × 7.0 Å × 17.8 Å and showed strong luminescence. The authors studied the host–guest property of the metallocycle with a number of metal ions and the rectangle showed selectivity for Hg^{2+} over other inorganic cations. A decrease in emission maxima at 438 nm and formation of a new emission band at 490 nm were observed when titrated with Hg^{2+}. The metallocycle forms a 1:1 host–guest complex, determined by plotting $1/\Delta I$ versus $[G]^{-1}$ at 495 nm, and the binding constant was determined as $1.3 \times 10^3\ M^{-1}$ for Hg^{2+}. Notably, the binding constant did not change with different counter anions:

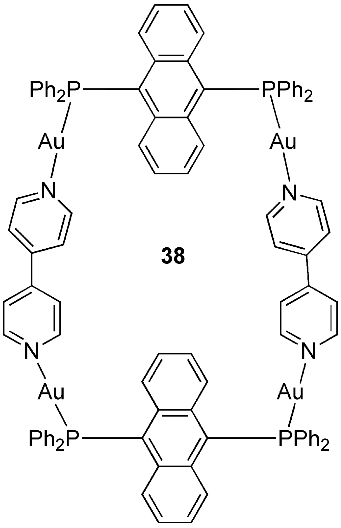


R = H, **33**; OH, **34**

Lu and coworkers reported photoluminescence electron-transfer quenching of the ^{3}MLCT state of Re(I)-based rectangles **35**–**37** by several amines [50]. The amines with lower oxidation potential showed a higher quenching constant suggesting that it is an electron-transfer process. This is further supported by a linear plot of log K_q versus oxidation potential. The binding constants for larger amines such as *N*,*N*,*N*′,*N*′-tetramethylphenylene diamine to the three different rectangles **35**–**37** were found to be 2.3×10^4, 2.6×10^2 and $6.4 \times 10^1\ M^{-1}$, respectively. These values suggest that the rectangle **35** is a better host for the larger amines. They also reveal the formation of an amine radical in the ^{3}MLCT excited-state electron-transfer reaction in the Re(I) rectangle supramolecules with amine:



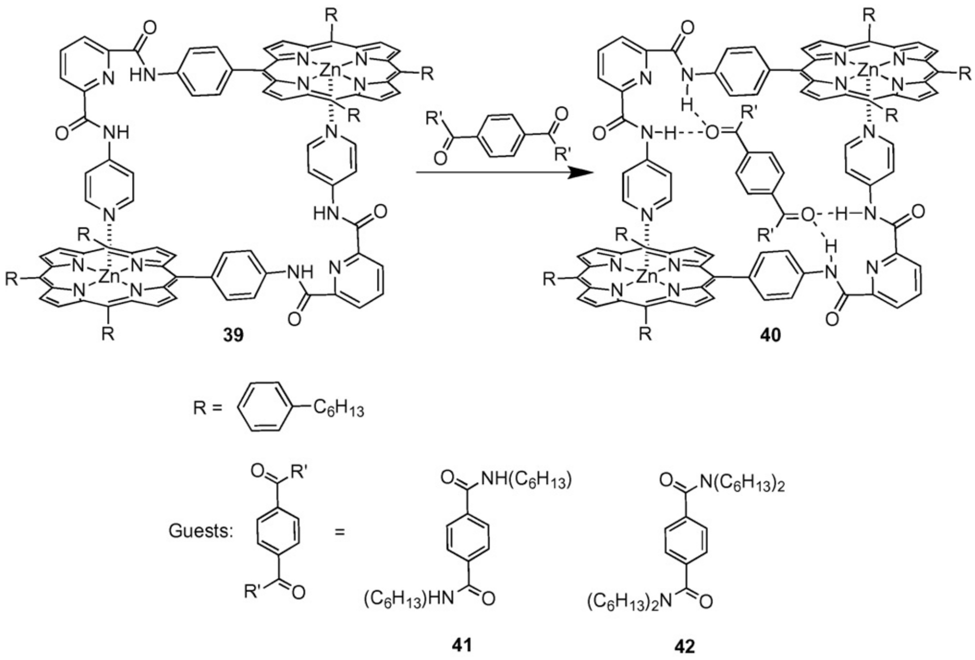
Yip and coworkers reported a new luminescent Au(I)-based self-assembly rectangle **38** with 9,10-bis-(diphenylphosphino)anthracene and 4,4′-bipyridine as the bridging ligands [51]. The rectangle exhibited a cavity size of 7.92 Å × 16.73 Å. The emission of rectangle **38** was quenched in the presence of aromatic guests. The solvophobic and ion–dipole effects are attributed to the effective formation of host–guest inclusion complexes between **38** and aromatic guests:



38

2.4. Porphyrin-based metallocyclic supramolecules for molecular recognition and sensing

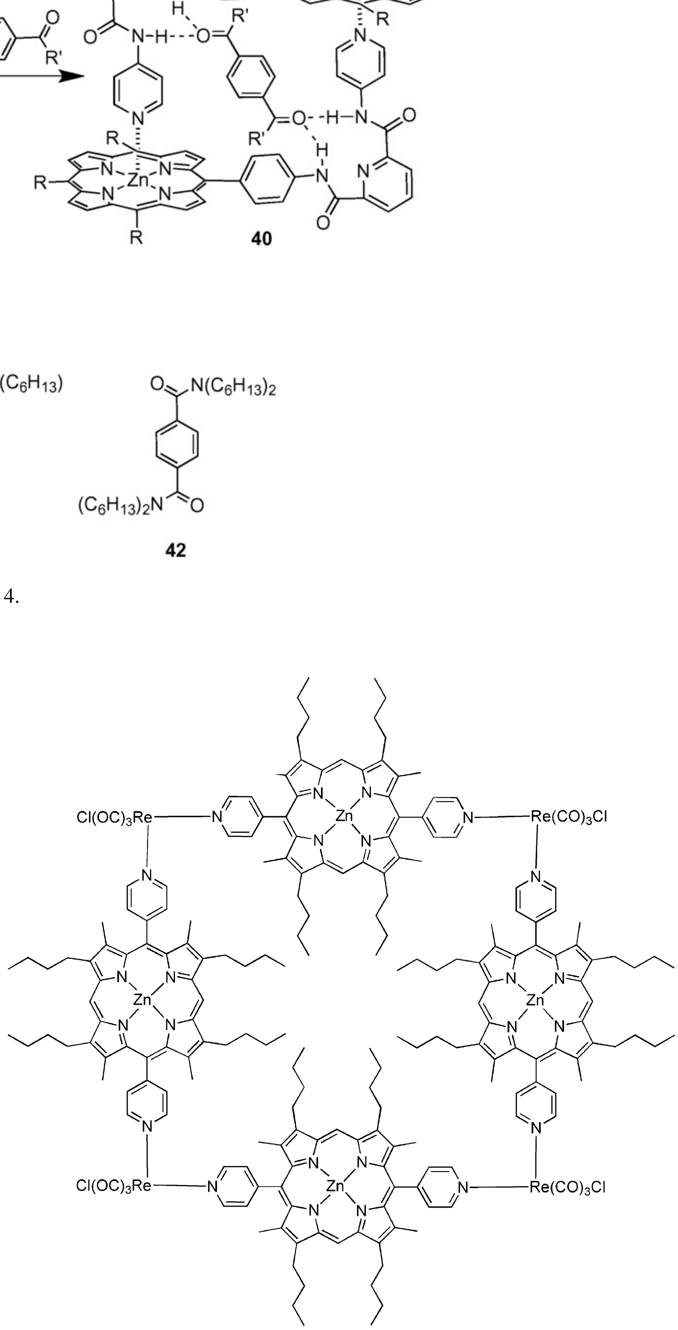
The rich photochemistry of porphyrins can be utilized to construct metallocyclic supramolecules, in which significant change in absorption as well as luminescence properties can take place upon guest encapsulation. The zinc(II) metalloporphyrin cycle **39** is reported by Hunter and Sarson, where a functionalized macrocyclic cavity is created through a Lewis acid–base interaction between the Zn(II)-porphyrin and pyridine [52]. The intramolecular hydrogen bonding between the



Scheme 4.

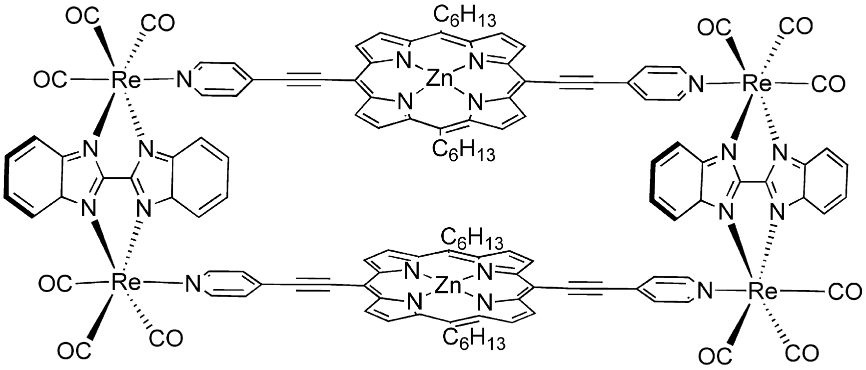
central pyridine and amide N–H ensures the approximate right angle in the supramolecular assembly [53]. The porphyrin cycle was able to encapsulate appropriate terephthalmide derivatives (**41** and **42**) with strong hydrogen binding provided by the amide functionality of the ligand (see Scheme 4). The association constants ($K_a = 1400$ and >1400 for **41** and **42**, respectively) were determined by titration in $CDCl_3$ monitored by ^1H NMR spectroscopy. The terephthalic ester and bulky groups around the carbonyl moieties showed weak interaction. Similarly, isophthalic acid derivatives bound very weakly, since the distance between the carbonyl groups is too short for the simultaneous formation of the hydrogen bonds with amide groups at both ends of the cavity.

The zinc(II) metalloporphyrin square, **43**, showed strong luminescence quenching with bipyridyl guests [54]. A nanomolar solution of the square, **43**, was subjected for titration with the flexible bipyridyl base, bis-1,4-(4-ethylpyridyl)benzene as the guest. More than 90% of the porphyrin absorption intensity was quenched following the addition of 2 equiv. of above bipyridyl guest to a solution of the square **43** in CH_2Cl_2. The UV–vis absorption spectrum showed a shift of the Soret and Q bands to longer wavelength by ca. 10 nm, as expected for binding to the Zn(II)-porphyrin portions of the host [55]. The fluorescence of square **43** was quenched on addition of the bipyridyl guest. The binding constant of bipyridine guest with square **43** is $\sim 2.4 \times 10^8\ M^{-1}$. A control study of the same bipyridyl base with ZnTPP (TPP = tetraphenylporphyrin) showed no measurable change in luminescence intensity of the host, ZnTPP. A lower binding constant was expected, though, based on the ability to achieve only one stabilizing interaction per assembly:



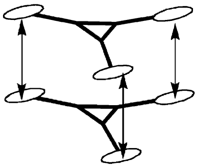
43

Hupp and coworkers reported the flexible nature of a porphyrin moiety in the rectangular assembly **44** [56]. A single crystal structure of **44** showed especially striking inward bowing of two of the four ethynylpyridine linkages. The driving force for the cavity collapse is apparently van der Waals interactions between the porphyrins as the cavity of the rectangle is too narrow to bind large guest. A strong difunctional Lewis base, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), bound to **44** in a 2:1 stoichiometry with a binding constant of $K_a = 5 \times 10^4\ M^{-1}$, whereas the monofunctional Lewis base, quinuclidine, also bound **44** in a 2:1 stoichiometry with a binding constant of $K_a = 2 \times 10^5\ M^{-1}$, four times larger than the binding constant for DABCO. This observation suggests that the guest molecules were bounded to the exterior of **44**, consistent with the strong van der Waals interaction between the two long axes bridging ligands that prevent an open-cavity internal binding event:

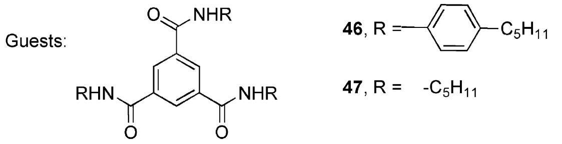


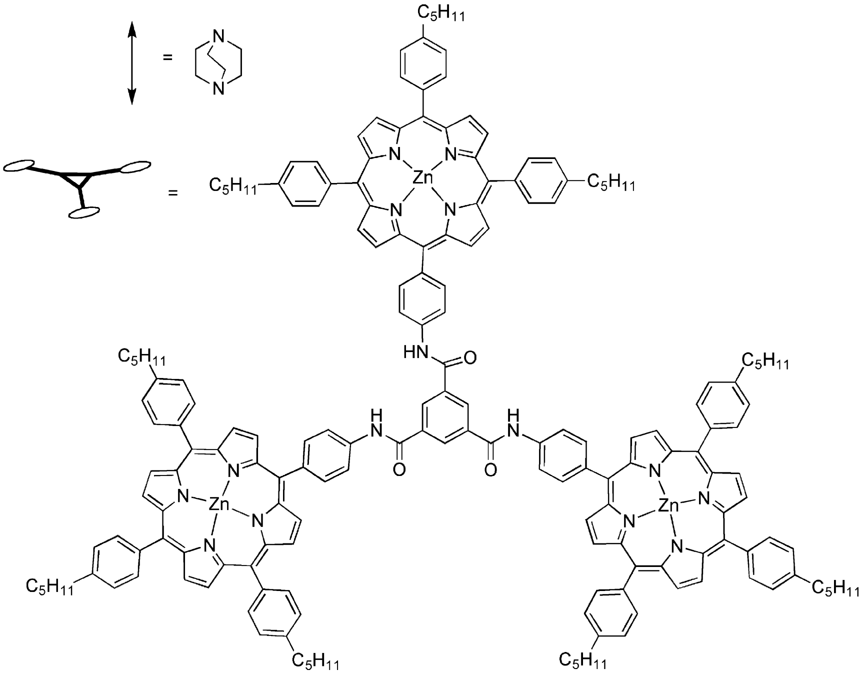
44

Recently Hunter and coworkers reported the self-assembly of Zn-trisporphyrin induced by coordination of 1,4-diazabicyclo[2.2.2]octane (DABCO) to form a stable 2:3 double-decker molecular coordination cage **45** [57]. The cage showed a flexible nature, which allows breathing of the cavity height between dimensions of 0 and 7 Å. Such a large flexibility enabled the recognition of large molecules of complementary size and shape through an induced-fit mechanism. It was found that the cage **45** was able to recognize benzene-1,3,5-tricarboxamides, **46** and **47**. The tricarboxamides bound inside the central cavity of the cage complex form a triple helical hydrogen-bonding motif. The driving force for recognition of tricarboxamides is probably the formation of six N–H···O=C hydrogen bonds, in addition to other aromatic interactions. The formation of such a structural motif was monitored by ^1H NMR titration of the cage **45** and the tricarboxamide guest **47**. The downfield shift of 0.1 ppm observed for both NH protons of cage **46** and tricarboxamide **47** indicated the formation of a hydrogen-bonded complex. Additionally the aromatic protons of the tricarboxamide were upfield shifted, indicative of aromatic stacking. The isothermal titration calorimetry (ITC) was employed to determine the binding constant of the cage **45** with the guests, **46** and **47**. Analysis of the ITC data for both guests **46** and **47** suggested the formation of a 1:1 host–guest complex and the binding constants of 9×10^3 and $14 \times 10^3\ M^{-1}$, respectively:



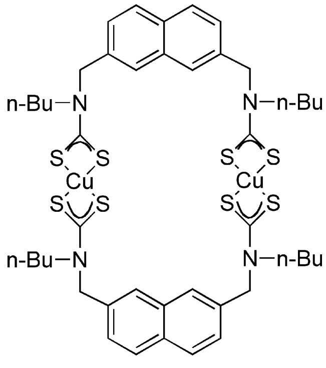
45





2.5. Metallocyclic supramolecules for electrochemical sensing

In addition to Lewis acid–base and luminescence properties, the electrochemical behavior of a metallocyclic supramolecular host can be influenced by the guest encapsulation. Beer et al. reported dinuclear copper(II) metallocyclic supramolecules, which showed quasi-reversible oxidation potentials [58]. They found that the interaction of metallocycles with various anions showed cathodic shifts in the oxidation potential on host–guest complex formation. In the case of the larger metallocycle **48**, significant cathodic shifts were observed in the presence of tetrahedral anions such as dihydrogenphosphate and perrhenate (∼85 mV), while the smaller anions such as chloride, bromide or nitrate did not yield a noticeable effect. In contrast, the smaller metallocycle **49** showed substantial cathodic shifts in presence of smaller anions such as chloride (20 mV), with little or no response to the larger anions. This indicates that these metallocycles are size-selective anion sensors:



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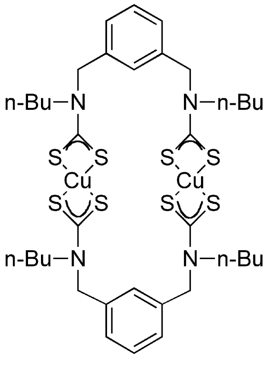
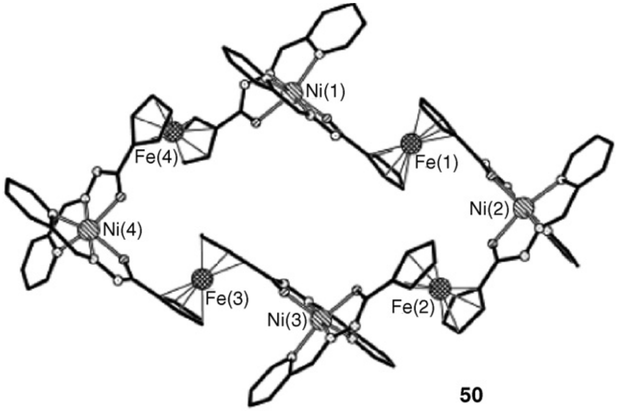


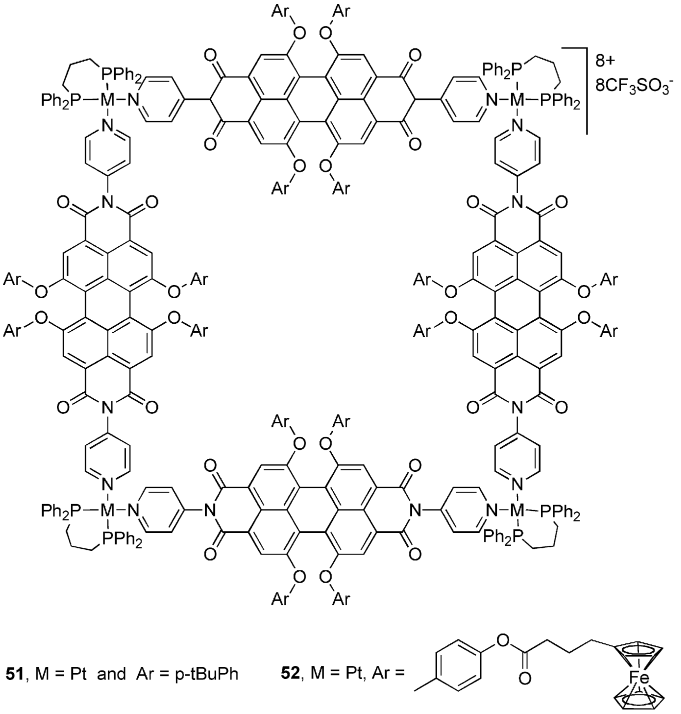
49

Li et al. reported a fairly large but uncommon cathodic shift (∼380 mV) in oxidation potential for octanuclear metallocycle (Ni_4Fc_4) **50** on encapsulation of the Mg^{2+} cation in solution as well as in the solid state [59]. The unusual cathodic redox-potential shift upon cation binding is opposed to an intuitive anodic shift, and is ascribed to the electronic reorganization of the metallocycle:



50

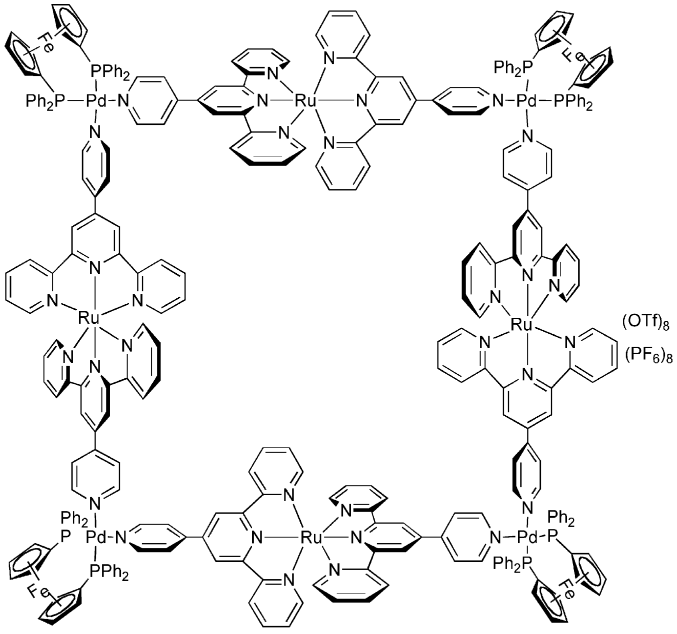
Perylene bisimide-based supramolecules were found to be excellent luminescent as well as redox active materials [60]. The perylene bisimide-based metallocycle **51** displayed two reductive waves ($E_{1/2} = -1.01$ and -1.14 V versus Fc/Fc^+), which were attributed to the monoanionic and dianionic perylene bisimide species. Both reductions are shifted by about −70 to −90 mV with respect to the bridging perylene bisimide ligand. Notably, it was possible to reversibly oxidize perylene bisimide units in **51** at potential $E_{1/2} = +0.93$ V. However, the free ligand was irreversibly oxidized and adsorbed onto the platinum electrode. This is attributed to the coordination of the pyridine nitrogen to platinum, thereby blocking the nitrogen lone pair in a way that the metallocycle is no longer susceptible to adsorption and facile oxidation:



51, M = Pt and Ar = p-tBuPh **52**, M = Pt, Ar =

The above-mentioned perylene bisimide scaffold was organized with redox active ferrocene units to make the three-dimensional metallocyclic superstructure **52** by Würthner et al. [61]. Incorporating ferrocene is an excellent choice for probing electron-transfer processes at electrode surfaces due to the excellent stability of the ferrocenium cation. The metallocycle **52** contains 20 redox active units in the structure. The two reversible four-electron reductive processes for the inner scaffold of perylene bisimide units were little influenced by the supramolecular arrangement in the cyclic voltametry. On the other hand, it was found that the redox properties of the 16 peripheral ferrocenyl subunits are strongly affected by sterical constraints imposed by the square type architecture, causing signal splitting for the redox potential of ferrocenes. In total, 24 charges are loaded onto this nanosize assembly. The interior cavity of this nanosize assembly with redox active units organized in a three-dimensional superstructure has the strong potential to act as a redox active functional material.

Ferrocene units have also been used on the metal center for architecting supramolecules for electrochemical studies. The heterometallic (Pd/Ru) molecular square **53**, reported by Sun and Lees, is particularly an interesting assembly from an electrochemical point of view because it incorporates four redox active terpyridyl metal complexes as bridging units in addition to other four ferrocene units at corners [62]. A DMF solution showed a reversible wave for the ruthenium center oxidation (Ru^{2+}/Ru^{3+}, $E_{1/2} = 0.7$ V) and an irreversible oxidation wave at 0.88 V for Fc/Fc^+. However, no appreciable communication between the metal centers was observed in this assembly. When the Pd corners were replaced by $Re(CO)_3Br$ corners, the oxidation potential for ruthenium center was anodically shifted due to the electron-withdrawing nature of the rhenium corner. This observation implies the redox potential of the bridging metal complex can be modulated by subtle environmental variations and suggests that the square **53** could be a potential redox sensing material:



53

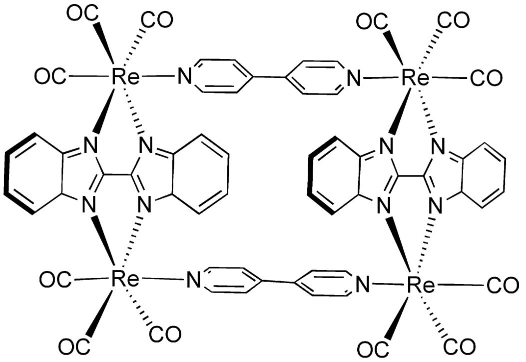
2.6. Thin films based metallocyclic supramolecules for chemical sensing

Simple molecular-aggregate type films of cyclic supramolecules have proven surprisingly effective as molecular sieves, due to the presence of a one-dimensional open channel in the films [63]. The advantage of the amorphous thin films is their strongly adherence and insolubility in aqueous medium. Another advantage is the capability of a higher uptake of the guests. The electrochemical studies revealed that the material is exceptionally porous for small molecules while it blocks large molecules [64].

Willner and coworkers have demonstrated an interesting concept to realize electrode surfaces, which are covered with stepwise assembling three-dimensional array of the molecular squares [65]. A very stable interface containing defined numbers of layers was generated by stepwise treatment of 3-aminopropyltriethoxysilane-modified indium-doped tin oxide (ITO) conductive glass with solutions of 12 nm gold nanoparticles solution and solutions of the Pd(II)-based molecular square **4**. The superstructure acts as a π-acceptor receptor for complexation of π-donor substrates, such as dialkoxybenzene, as was found for molecular square **4** in solution. Binding of analytes such as *p*-hydroquinone to the receptor units increases the local concentration at the electrode surface, and allows its electrochemical sensing by the three-dimensional conductive Au array. Therefore, the Au-nanoparticle/square **4** assembled superstructure acts as a functional interface to concentrate π-donor analytes and enable their electrochemical sensing. It was found that the electrochemical response was enhanced upon increasing the number of layers.

Another approach for the electrochemical sensing of substrates by molecular square sensory layers on the basis of size selectivity was introduced by Belanger and Hupp [45]. In their studies, thin films of neutral rhenium molecular squares (such as **26**) 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 through the film, depending on the cavity size of the metallocyclic supramolecule.

The sensing properties in the presence of volatile organic compounds (VOCs) of the self-assembled rectangle **54** in the solid state were studied [66]. The emission of thin films containing the complex were quenched upon exposure to *p*-toluidine vapor (which is a known reductant), but the emission was enhanced and shifted to higher energy when the film of rectangle **54** was exposed to THF vapor. The THF exposure also increased the luminescence lifetime from 620 to 950 ns. Both film-based emission study and crystal structure analysis suggested that rectangle **54** might behave as a high internal surface area mesoporous host material. The guest molecules were taken up into the film voids in the rectangle aggregate. The selectivity of this film-based mesoporous material **54** can be assessed by quantitative quartz crystal microgravimetry (QCM) measurements. The results showed that (a) the binding affinity increased with the film thickness as expected if the guest uptake is based on the permeation into the voids rather than simple physical adsorption, (b) the host/guest ratio exceeded 1:1 with high concentration of guest implying both intra- and intermolecular cavities were occupied, and (c) the aromatic guests with electron-withdrawing substituents diminished the affinity, whereas aromatic guests with electron-donating substituents enhanced the affinity:



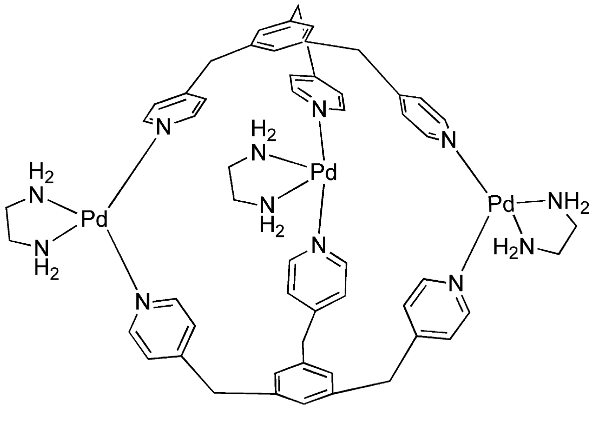
54

A similar study from the same group also used the thin film of molecular squares **26** and **28** for VOC sensing [67]. The films exhibited preference for aromatic guests (benzene) over aliphatic substrates (cyclohexane) and for good electron donors over poor ones. Size selectivity of the films was demonstrated with the uptake of cyclic ethers of various sizes, such as dioxane (size ~4.5 Å) and the large 18-crown-6 cyclic ether (size ~7.5 Å). This study showed that the amount of 18-crown-6 uptake was one to two orders of magnitude less than the amount of dioxane uptake, depending on the film thickness. The quantitative assessments of VOCs uptake were achieved via QCM for thin-film arrays. The VOC uptake process is reversible. Regeneration of the films after VOC uptake was achieved by placing the loaded films under vacuum at ambient temperature for 10 min.

Micropatterned porous films of molecular square **43** have been shown to diffract visible light [68]. The diffraction efficiency depended on the guest uptake and the extent of modulation scaled with the amount of guest taken up into film as determined separately from QCM measurements. However, many of the analytes were sorbed nonspecifically.

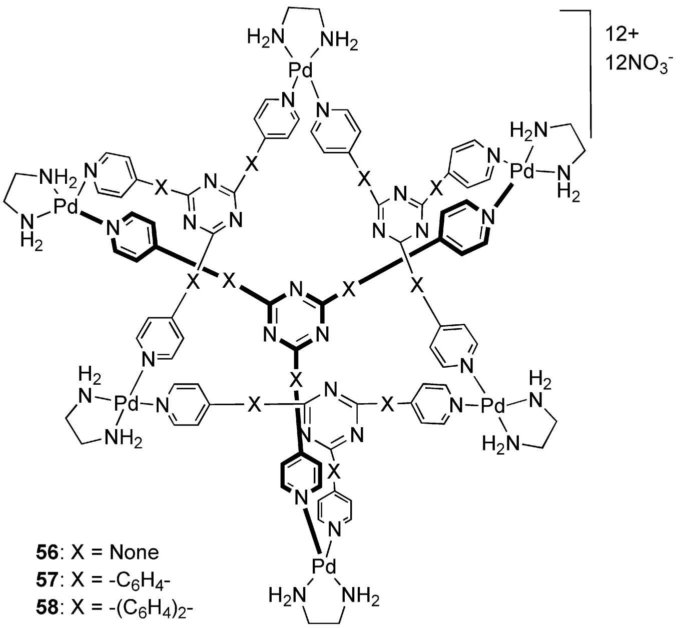
2.7. Three-dimensional metallo-cages for molecular recognition and sensing

Current understanding of molecular recognition in biological systems is based on the “induced-fit” mechanism, in which the substrate induces the organization of the recognition site of the receptor, rather than by a lock and key model [69,70]. Most examples of induced-fit models use flexible artificial hosts, which show restricted conformation only if they organize a specific guest [71,72]. One of the few examples of induced-fit models, in which the guest molecule induces the organization of the host itself, is provided by Fujita et al.’s metallocyclic supramolecular cage **55** [69]. They found that the host (cage **55**) binds 4-methoxyphenylacetate as a guest in 1:1 stoichiometry in aqueous solution. Analysis of the ^{1}H NMR data not only confirmed the presence of the guest molecule within the cavity but also confirmed the D_{3h} symmetry necessary for a trigonal prism. Interestingly, in the absence of the specific guest, the self-assembly resulted in the formation of a considerable amount of oligomeric product, this disappeared on addition of the guest leading to the formation of the cage-like complex:



55

Variations of the guest showed that bulky hydrophobic moieties such as 1-phenylethyl or adamantyl groups favor the formation of cage structure, whereas less hydrophobic substrates such as dicarboxylates or acetates showed hardly any effect. Similar, nanoscopic three dimensional molecules, **56–58**, with the shape of truncated tetrahedra were reported by Fujita et al. [73]. These molecules were soluble in water capable of encapsulating up to four guests, such as adamantane carboxylates. The assembly formed the host–guest complex with four molecules of adamantyl carboxylate and no intermediate inclusion complexes with one, two, or three were observed. This was confirmed by X-ray crystallographic structure of the cage **56** with adamantyl carboxylate as well as by ^{1}H NMR studies in aqueous solution. This is likely due to the allosteric effect: the hydrophobicity of the cavity increases with the inclusion of guest molecules in the cavity thereby increasing the number of guests inside the cavity:

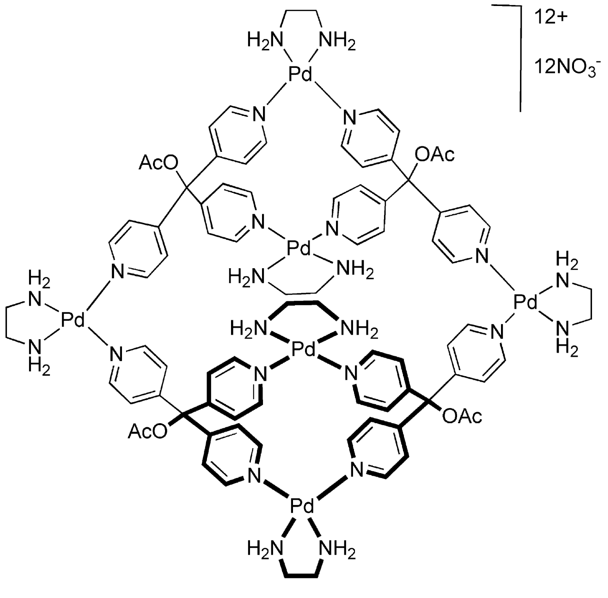


56: X = None
57: X = $-C_6H_4-$
58: X = $-(C_6H_4)_2-$

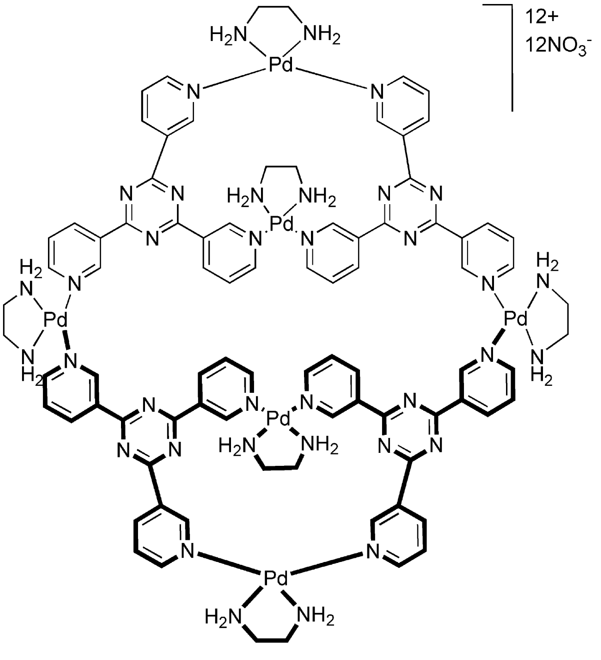
The homologous Pt(II) complex was isolated in the presence of template guest, such as adamantyl carboxylate molecules under harsh conditions, while only traces of the platinum cage was formed in the absence of such guest. The cage showed remarkable kinetic stability, because of the relatively inert Pt–pyridine bond. In contrast to its palladium counterpart, the platinum cage is stable under highly acidic and basic conditions and is not destroyed by strong nucleophiles. As a result the compound was used to design a pH responsive host–guest system. Under basic conditions, *N*,*N*-dimethylaniline was effectively bound in the hydrophobic cavity in a 1:4 (host:guest) ratio, whereas under acidic conditions, the guests were immediately liberated due to decreased hydrophobic interactions as well as cationic repulsion between the host and protonated *N*,*N*-dimethylaniline [74].

Besides the inclusion of charged molecules, the cage molecules were also able to encapsulate large neutral molecules into the approximately 2 nm wide cavity [75]. On mixing a hexane solution of *o*-carborane with aqueous solution of **56**, 4 equiv. of the *o*-carborane were transferred into the aqueous phase and encapsulated within the cavity of **56**. The 1:4 stoichiometry was confirmed by integration of the host and guest signals in the ^{1}H NMR spectrum. Inclusion of 1- and 2-admantanol showed that the interior of the cage has highly hydrophobic characteristics, which resulted in the outward pointing of the hydroxyl groups in the admantanol. For molecules that were slightly larger than the portal of **56**, encapsulation of just one guest was very slow as a result of a thermally induced slippage. Once the guest is inside the cavity, it did not escape from the cavity even when treated with organic solvents [75].

It was also shown that the two macrocyclic structures, **59**, and **60**, are capable of incorporating dicarboxylate anions such as sodium terephthalate and 1,4-benzodicarboxylate. The host–guest interaction is interpreted by electrostatic interaction of the positively charged cage and the negatively charged dicarboxylate [76]:

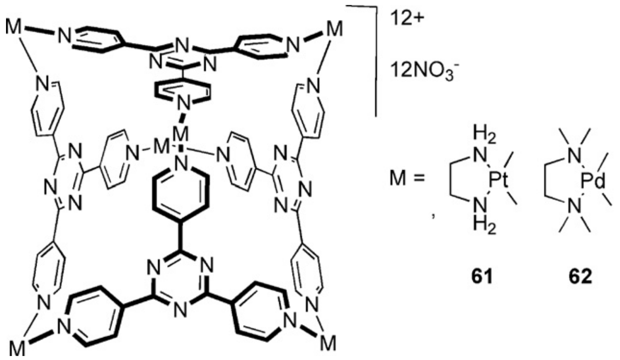


59

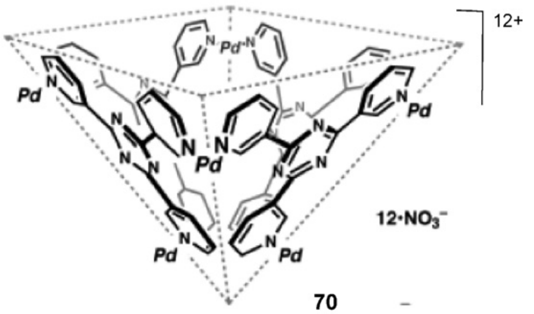


60

Tashiro and Fujita studied the interaction of cationic cages, **61** and **62** with various peptides [77,78]. The platinum cage **61** bound Ac-Trp-Trp-Ala-NH$_2$, **63**, very strongly in water. The solution color of the complex **61·63** was orange due to charge transfer from the indole rings to the electron-deficient triazine ligand of **61**. The association constant obtained on the analysis of this charge transfer was found $K_a = 1.5 \times 10^5\ \mathrm{M}^{-1}$, which was slightly smaller than the palladium analogue **62** ($K_a > 10^6\ \mathrm{M}^{-1}$). These cages were also capable of binding Ac-Trp-Ala-Trp-NH$_2$, **64**, over Ac-Ala-Trp-Trp-NH$_2$, **65**, and Ac-Trp-Trp-Gly-NH$_2$, **66**. Moreover, the cages can recognize hexapeptides. For example, Ac-Ser-Gly-Ala-Trp-Trp-Ala-NH$_2$, **67**, possessing an additional Ser-Gly-Ala sequence at the N-terminal of **63**, bound in cage **61** with high affinity ($K_a > 10^5\ \mathrm{M}^{-1}$). However, Ac-Ala-Trp-Trp-Ala-Gly-Ser-NH$_2$, **68**, having additional sequence at both terminals of **63**, showed poorer affinity than **67** ($K_a = 7.2 \times 10^4\ \mathrm{M}^{-1}$). Namely, cage **61** discriminated between two similar hexapeptides consisting of the same residues in different sequences. This selectivity is explained by the fact that the stable conformation of **61·63** is disturbed by steric repulsion between the cage and the elongated sequence at the C-terminal. Due to the highly cationic nature of the cage **61** (12+), charged peptides were strictly discriminated by electrostatic attraction and repulsion in various pH conditions. For example, the binding affinity of the non-protected tripeptide H-Trp-Trp-Ala-OH, **69**, was dramatically affected by pH. In an acetate buffer (pH 4.8), tripeptide **69** showed poorer affinity than **63** ($K_a = 4.7 \times 10^4\ \mathrm{M}^{-1}$) while under basic conditions showed strong binding ($K_a > 10^6\ \mathrm{M}^{-1}$):



61 **62**



70

In contrast to **69**, the affinities of the protected peptide **63** were not affected by pH conditions. Further, it was also found that the neutral and anionic peptides were bound by cage **61** more than 100-times stronger than cationic peptides. Thus the cage **61** recognized peptide containing Trp residues with high selectivity and affinity and discriminated longer peptides by means of electrostatic, charge-transfer, and steric repulsion between the cage and peptides. Moreover, the selectivity of the charged peptides can be controlled by pH conditions due to the cationic nature of the cage **61**.

Similarly, the bowl-shaped host **70** can recognize aromatic peptides [78]. For example, **70** bound the hexapeptide **68** more strongly than cage **61** (for **70·68** $K_a = 1.3 \times 10^5\ M^{-1}$). The bowl-shaped cage **70** can cover a large area and is expected to employ a pinpoint recognition of protein surface that often mediates protein–protein interactions.

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