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Conjugated shape-persistent macrocycles via Schiff-base condensation: New motifs for supramolecular chemistry*

Mark J. MacLachlan

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada

Abstract: Shape-persistent conjugated macrocycles are challenging synthetic targets with interesting properties and potential for a number of applications. In contrast to the standard kinetic approaches to macrocycles, reversible Schiff-base condensation offers a one-step, thermodynamic route to large macrocycles. These macrocycles, which feature "salen"-type coordination environments and an interior that resembles a crown-ether have interesting properties themselves and are novel substrates for supramolecular chemistry. This short review article places conjugated [3+3] Schiff-base macrocycles in the context of shape-persistent macrocycles and discusses their synthesis. In addition, specific examples of supramolecular chemistry with these macrocycles highlight their unique behavior when compared to conjugated carbon-based macrocycles and flexible crown-ethers.

Keywords: macrocycles; Schiff-base; supramolecular chemistry; synthesis; self-assembly.

INTRODUCTION

The scientific theory I like best is that the rings of Saturn are composed entirely of lost airline luggage.

—Mark Russell

Rings, on account of their high symmetry, hold an inherent beauty that is rivaled by few other simple shapes. They are symbols of continuity, with no beginning and no end, that have captured our imaginations in both real life and in popular culture. The cross-section of a ring, a flattened ring, is also aesthetically pleasing. Of course, this latter shape is married to Saturn's rings and to flying saucers of science fiction, but it is also associated with many practical inventions—tires, computer discs, and 45s.

Ring-shaped molecules are found in nature, as exemplified by cyclodextrins and cyclic peptides, Fig. 1. As cyclodextrins are relatively rigid and have a hydrophobic interior, they can reversibly bind guests [1]. These saccharides have been studied extensively and have even been used in practical applications. For example, they are used as storage containers for the slow release of scent molecules in some cleaning products, and as nets for capturing odorous molecules in other products [2]. Short cyclic peptides are also rigid and yield pores on their interior. Ghadiri has demonstrated that synthetic cyclic D,L-peptides can self-assemble via intermolecular hydrogen bonding to give rigid 1D nanotubular structures, Fig. 2 [3]. These assemblies are being explored as antibiotics [4].

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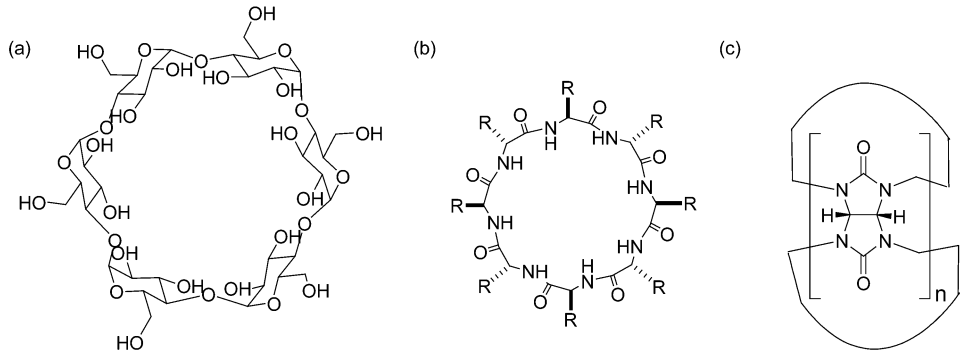


Fig. 1 Structures of some common rigid macrocycles: (a) cyclodextrin; (b) cyclic peptide; and (c) [n]cucurbitural.

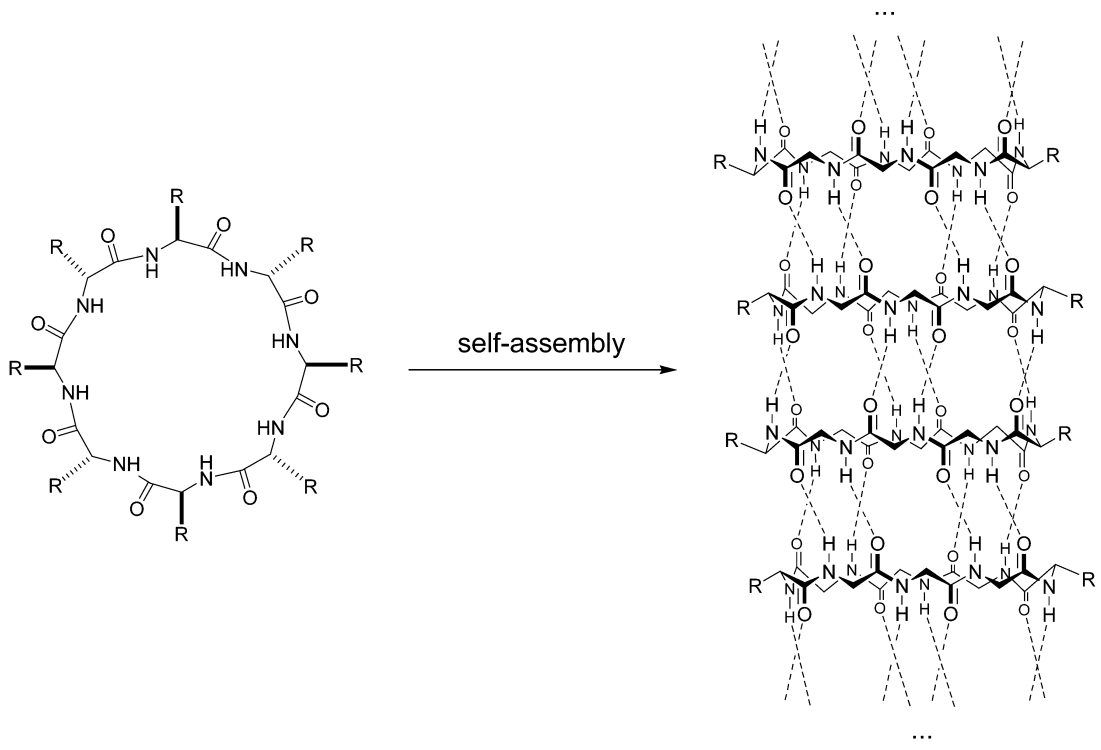
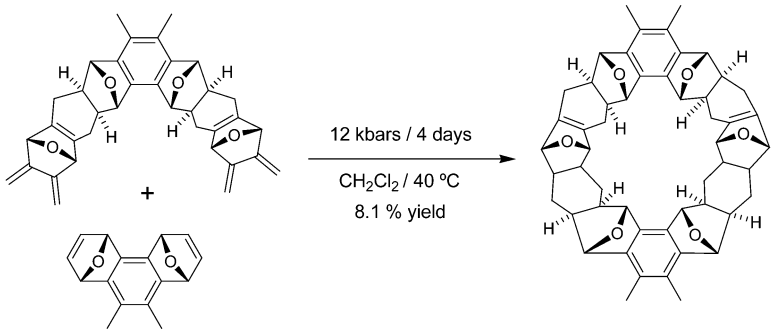


Fig. 2 Organization of cyclic D,L-peptides into hydrogen-bonded assemblies gives 1D polymeric structure with a channel.

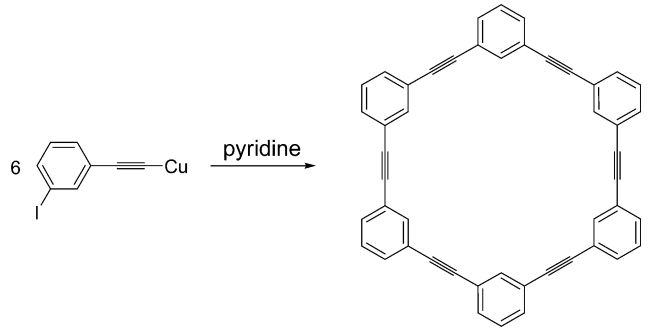
Although small rings formed by cyclodextrins and peptides are relatively rigid, larger rings do not show the same degree of shape-persistence due to conformational flexibility. One way to overcome this is by preparing macrocycles with rigid, shape-persistent precursors. Molecular belts have been prepared by Stoddart and coworkers using a sequence of repetitive Diels–Alder reactions. For example, Scheme 1 shows the synthesis of one of the many rings they have synthesized [5]. It is noteworthy that the ring-closing step gives only 8.1 % yield of the macrocyclic product, necessitates high pressures, and requires chromatographic separation. Cucurbiturals (Fig. 1) are a class of container molecules with tunable diameters [6]. The smallest [n]cucurbiturals (n = 5–8) are now commercially available, and higher analogs (n = 9–10) have been synthesized. Other approaches to large, rigid

macrocycles have been attempted with varied degrees of success, but most require either iterative procedures with the use of protecting groups, or high dilution to favor the formation of macrocycles over oligomers and polymers [7].

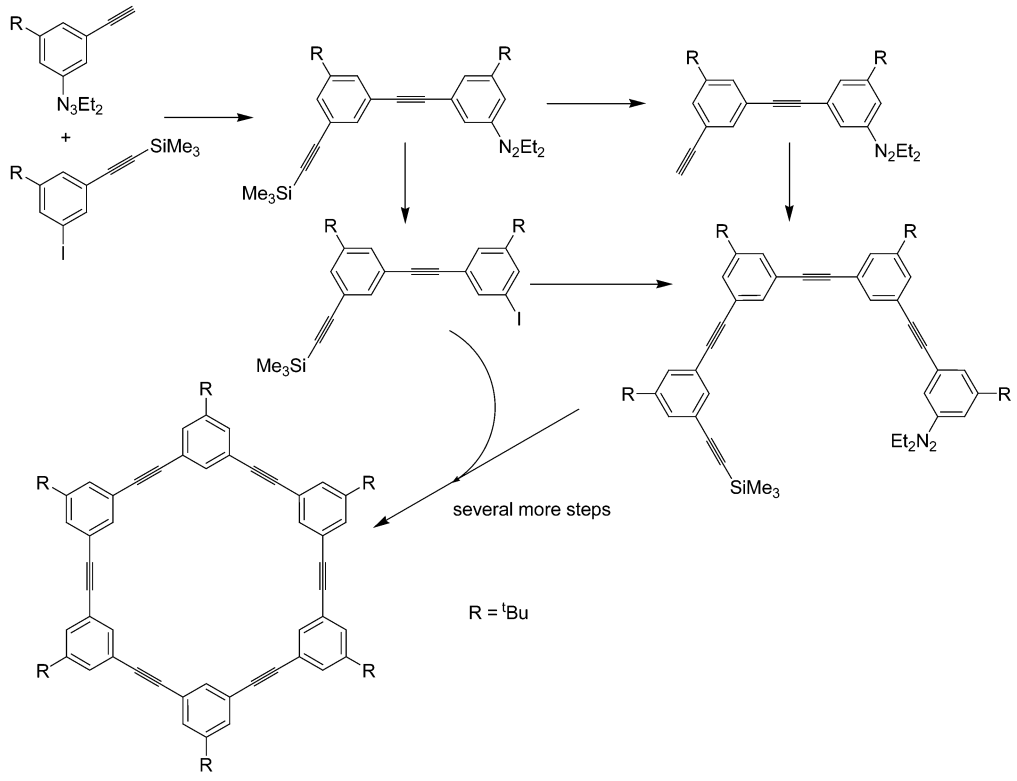


Scheme 1 Synthesis of a molecular belt via Diels–Alder cyclization reaction.

One class of conjugated macrocycles that has been studied extensively is the cyclic phenyleneethynylenes with alternating benzene rings and alkyne spacers [8–10]. In 1974, Staab reported the first example of these conjugated macrocycles, prepared in 4.6 % yield by a single-step intermolecular, sixfold Stephens–Castro coupling of the copper salt of *m*-iodophenylacetylene as shown in Scheme 2 [11]. Although beautiful in structure, these macrocycles were obtained in low (statistical) yield, and must be separated from oligomeric, polymeric, and other cyclic byproducts. Due to the low yield of this synthesis few studies were performed on this system until 1992, when Moore reported a new, step-wise route to these macrocycles having a 75 % yield, Scheme 3 [12]. This was a significant improvement in yield over the statistical approach, but the reaction required multiple steps and chromatography.



Scheme 2 Staab's original synthesis of shape-persistent phenyleneethynylene macrocycles.



Scheme 3 Moore's step-wise synthesis of phenyleneethynylene macrocycles.

The kinetic approach to shape-persistent macrocycles has been explored by numerous researchers and has given rise to a large body of research in this field [7,13]. Significant developments in shape-persistent macrocycles have taken place in the past decade, and numerous researchers have made important contributions. Many of the advances in this field have been highlighted in review articles referenced herein, so I only cite a few representative examples (Fig. 3) here. Moore has examined the aggregation behavior of conjugated phenyleneethynylene macrocycles in liquids that are poor solvents for the aromatic backbone [14]. They have demonstrated that π–π interactions between the macrocycles are important for mediating this aggregation. Tobe reported a series of giant phenylenebutadiyne macrocycles which are analogous to the phenyleneethynylene macrocycles, but with each alkyne replaced by a butadiyne moiety. These macrocycles also undergo self-association in aromatic and polar solvents [15]. Höger recently described discotic liquid crystals with a nematic phase based on phenyleneethynylene macrocycles where the flexible chains are located on the *interior* of the ring [16]. Although it has been long known that macrocycles with peripheral flexible groups may form discotic liquid crystals [17], liquid crystallinity in rigid rings with intrannular substituents was previously unknown. Schlüter prepared cyclic polyphenylenes containing 12 aromatic rings by a step-wise procedure [18]. Schlüter has also reported functional macrocycles incorporating bipyridine ligands into a rigid, conjugated scaffold [19]. These macrocycles can complex to transition metals (e.g., Ru(II)) and have been incorporated into polymers by free radical and ring-opening metathesis (ROMP) polymerizations. Macrocycles with exoannular coordinating groups were reported by Tykwinski and, in collaboration with Stang, they demonstrated that these macrocycles can be linked in the solid state using coordination chemistry to form extended macrocyclic frameworks [20]. Clearly, there have been many exciting developments in the field of organic shape-persistent macrocycles, many more than I have summarized

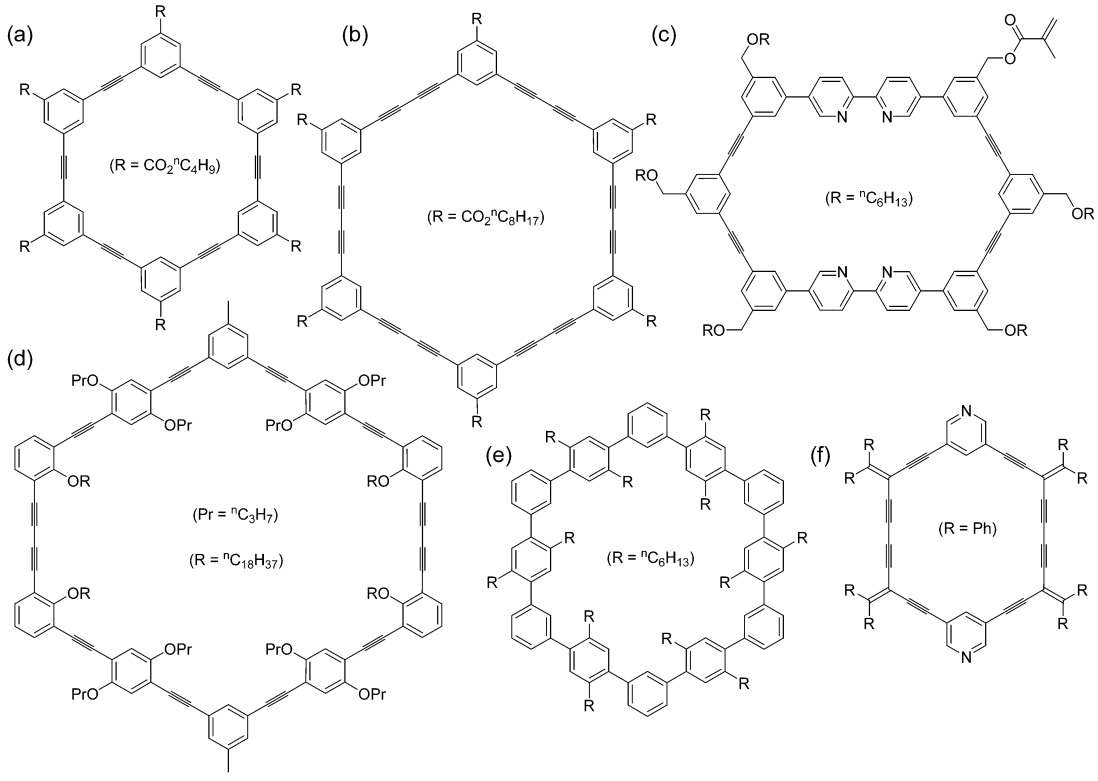
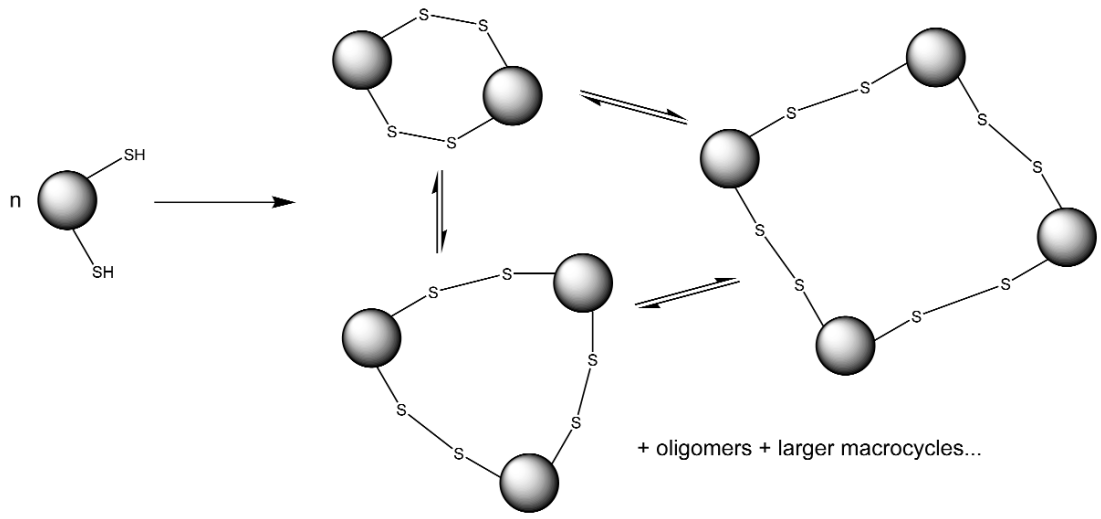


Fig. 3 Examples of shape-persistent macrocycles discussed in the text: (a) phenyleneethynylene macrocycles that are the focus of aggregation studies by Moore; (b) butadiyne macrocycles that undergo strong self-association in solution (Tobe); (c) macrocycles with intraannular coordinating groups (Schlüter); (d) macrocycles that form discotic liquid-crystalline phases (Höger); (e) phenylene macrocycles prepared by Schlüter; and (f) macrocycles with extraannular coordinating ligands (Tykwinski).

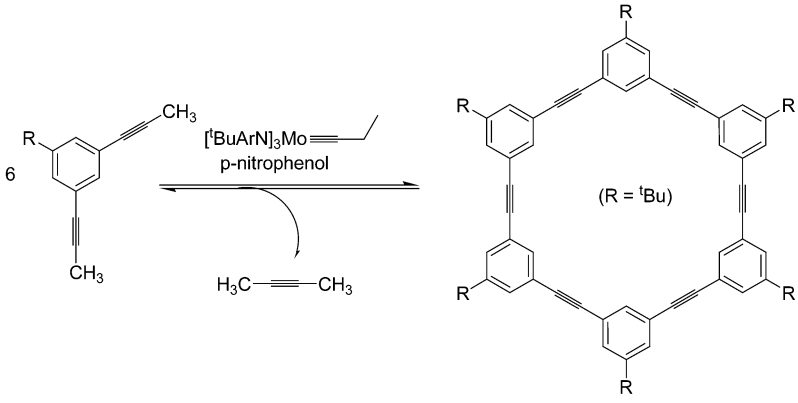
here. Figure 3 shows the macrocycles described in this paragraph, and illustrates the diverse structures available to shape-persistent macrocycles using organic chemistry.

Using a reversible reaction, which enables a reaction to reach thermodynamic equilibrium, is a useful approach to access large macrocycles [21]. Otto and Sanders have used this approach to make a large family of flexible macrocycles incorporating disulfide bonds, Scheme 4 [22]. Two chemical reactions are necessary to ensure the reaction is reversible: (1) the oxidation of thiols to disulfides; and (2) thiol-disulfide exchange. The first reaction is facilitated by any oxidant—oxygen from air is usually sufficient. The second reaction only requires the presence of a trace of thiol in solution. As long as the reactions are conducted in slightly basic (pH 7–9) aqueous solution, then the reaction can proceed reversibly until equilibrium is reached. The reaction is finally quenched by acidification of the solution. Recently, they showed that this method could be used to generate transition-state analogs for an acetal hydrolysis reaction [23].



Scheme 4 Combinatorial approach to macrocycles with disulfide linkages.

In 2000, Bunz discovered that phenyleneethynylene macrocycles could be prepared using alkyne metathesis, though the macrocycles were isolated in low yield [24]. Building on Bunz's efforts, Moore recently reported a very elegant route to shape-persistent macrocycles that have all-carbon backbones, Scheme 5 [25,26]. Using a Mo(VI) alkylidyne metathesis catalyst, phenyleneethynylene macrocycles were prepared in high yield from 1,3-dialkynylbenzene derivatives. Other related conjugated macrocycles were also prepared. In this reaction, the precipitation of the macrocyclic products from the reaction solvent is the driving force for the reaction. Moore and coworkers reported a large number of derivatives that could be prepared by this method, and have investigated the mechanism of the reaction.

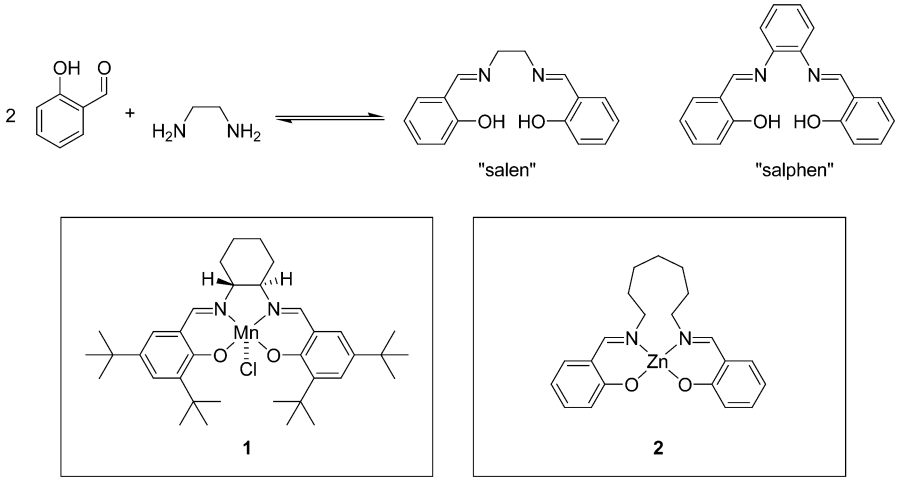


Scheme 5 The alkyne metathesis route to phenyleneethynylene macrocycles.

Our research program is directed at the synthesis and characterization of new shape-persistent molecules for supramolecular assembly. In particular, we are targeting large macrocycles that incorporate multiple metal centers that can be used to direct self-assembly and supramolecular organization. This paper highlights our work to establish a new class of macrocycles based on Schiff-base condensation chemistry.

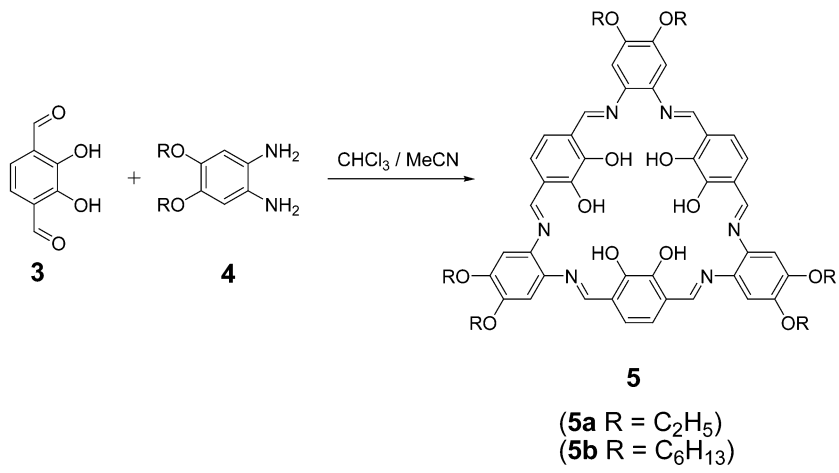
THE SCHIFF-BASE APPROACH

Our group has been exploring conjugated, shape-persistent macrocycles based on a [3+3] Schiff-base condensation reaction. The condensation of an amine and an aldehyde to give an imine is well known to be reversible; removal of water to drive this reaction to completion is often essential to obtain a good yield. This condensation has been used by many researchers to form both small and large macrocycles, usually templated with transition metals [27–34]. Indeed, this reaction is used to synthesize an important class of ligands known as salen (short for *N*,*N*'-bis(salicylidene)ethylenediamine) and salphen (*N*,*N*'-bis(salicylidene)phenylenediamine), as shown in Scheme 6. When these ligands are bound to transition metals, they form coordination complexes that can be useful for catalysis and can have very interesting optical properties. Specifically, compound **1**, known as Jacobsen's catalyst, is a potent asymmetric epoxidation catalyst [35]. The *tert*-butyl groups on the salicylaldehyde groups are essential to direct the substrate toward the chiral cyclohexanediimine moiety, where chiral discrimination is imparted. Compound **2**, a sublimable zinc salen-type complex, has been employed in prototype electroluminescent devices [36]. It showed pure blue emission with a brightness of 1460 cd m^{-2}. Incorporating salphen moieties into polymers and macrocycles is likely to give materials with interesting properties [37].



Scheme 6 Preparation of salen and salphen ligand precursors.

We planned to create conjugated, shape-persistent Schiff-base macrocycles **5** by the condensation of two bifunctional precursors, dialdehyde **3** and substituted phenylenediamines **4** (R = *n*-alkyl), Scheme 7. At the time, we were unaware that closely related macrocycle **6** (Fig. 4) was reported by Reinhoudt in 1995 [38]. To prepare triangular macrocycle **6**, Reinhoudt and coworkers required a template, Ba^{2+}, which could not be removed afterward. The chemical and structural aspects of the macrocycles were not pursued.



Scheme 7 Synthesis of macrocycles **5**.

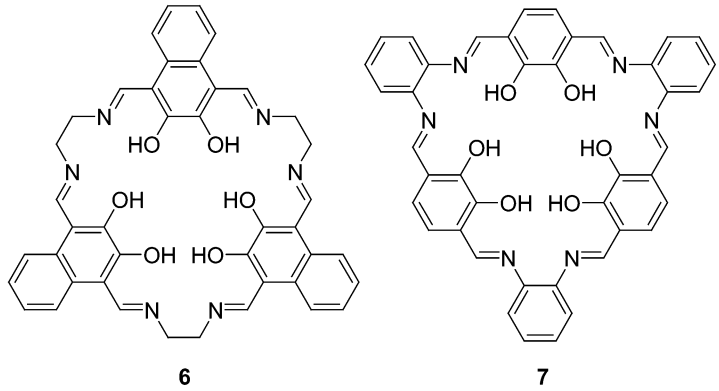


Fig. 4 Structures of [3+3] Schiff-base macrocycles reported by Reinhoudt (**6**) and Nabeshima (**7**).

About six months after initiating our work in 2001, Nabeshima and coworkers reported the structure of macrocycle **7** that has a conjugated structure identical to that of **5**, but with no peripheral substituents [39]. This macrocycle was prepared in a two-week synthesis and was insoluble in most common solvents. As a matter of fact, we had not prepared this macrocycle specifically on the assumption that it would be insoluble. Instead, we incorporated peripheral alkoxy groups by using 4,5-dialkoxy-1,2-diaminobenzene as our precursors.

Macrocycles **5** with a variety of substituents are readily prepared in ca. 50–90 % yields [40]. We have prepared macrocycles with alkoxy groups ranging from C_2H_5 to *n*-$C_{16}H_{33}$. Macrocycles with short alkoxy chains are soluble in organic solvents, but have high melting points. The macrocycles with longer alkoxy substituents, prepared in anticipation of developing porous liquid-crystalline phases, melt but exhibit no liquid crystallinity. When branched alkoxy chains (e.g., 2-ethylhexyl) are used, the macrocycles are obtained but are difficult to purify as they do not crystallize well. One of the drawbacks to these macrocycles is that they cannot be chromatographed; recrystallization is the only useful method for purification.

A single-crystal structure of macrocycle **5a** (Fig. 5) revealed a nonplanar conformation with strong hydrogen bonding between the hydroxyl groups and the imines [40]. Although the three sides of the macrocycle appear inequivalent in the solid state, the macrocycles exhibit D_{3h} symmetry by solu-

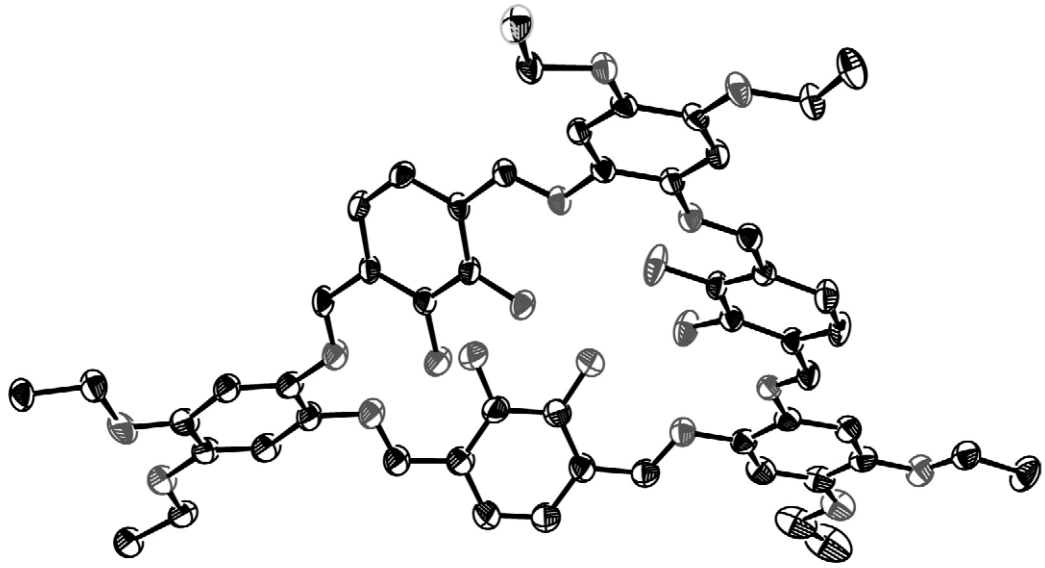
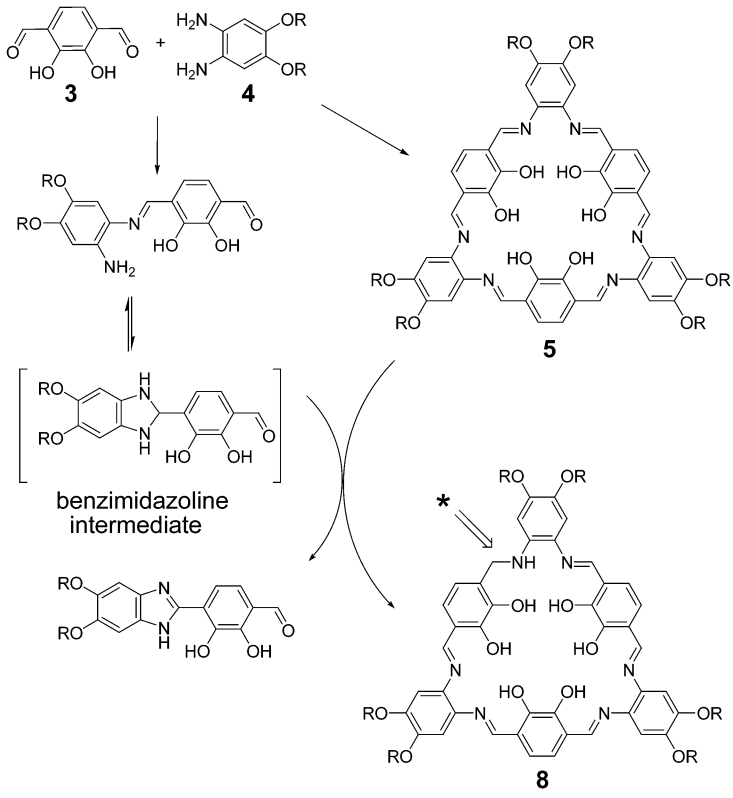


Fig. 5 Solid-state structure of macrocycle **5a** as determined by single-crystal X-ray diffraction. Thermal ellipsoids are shown at 50 % probability, with H atoms and solvent removed for clarity.

tion NMR spectroscopy. These observations have been rationalized by density functional theory (DFT) calculations that predict a relatively low energy barrier for interconversion of the nonplanar conformations. Moreover, the computational studies indicated that the lack of planarity is primarily due to twisting of the phenyl-imine bonds rather than to repulsion of the hydroxyl groups on the interior of the macrocycle. In the solid-state structure of **5a**, the macrocycles are organized in a way that reveals porous channels running through the crystal.

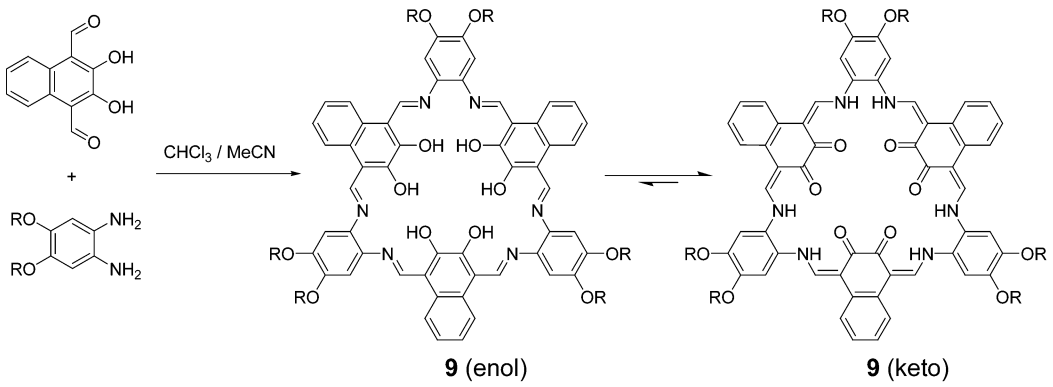
The Schiff-base condensation is a convenient route to these macrocycles as it can be done in one step and requires little or no purification of the final product. It is surprising that the [3+3] Schiff-base macrocycles are the exclusive products obtained, with no oligomers or other cycles normally observed. We believe that this macrocycle maximizes entropy by being fully condensed (i.e., no terminal amine or aldehyde groups and therefore the maximum amount of water is formed), and maximizes intramolecular hydrogen bonding relative to oligomers with end-groups. As well, this macrocycle has very little strain, which would inhibit the formation of smaller macrocycles. Thus, both entropic and enthalpic factors contribute to the stability of the [3+3] macrocyclic product. By controlling the reaction conditions or altering the ratio of the precursors, we have been able to isolate short oligomers (e.g., 1:1 and 1:2 condensation products) and demonstrated that these are intermediates of the macrocycle formation [40].

There are several side-reactions that could interfere with the clean preparation of the macrocycles. Condensation of benzaldehyde with phenylenediamine, for example, gives benzimidazole as the major product. Imine reduction is also a possibility and has been observed in the attempted preparation of metal-free [2+2] Schiff-base macrocycles. During our synthetic efforts, we occasionally obtained a product that was different from macrocycle **5**. Through a combination of NMR, crystallography, and mass spectrometry, we confirmed that the byproduct is the macrocycle with exactly one imine reduced, Scheme 8 [41]. It is remarkable that this product **8** can be prepared in 50–60 % yield with no observation of multi-imine reduction products. Mechanistic studies indicate that the reduction occurs via the reaction of a benzimidazoline intermediate with the fully conjugated macrocycle. The reduction is promoted by acid, even the residual amount present in commercial chloroform.



Scheme 8 Proposed mechanism for the formation of monoreduced macrocycle **8** from conjugated macrocycle **5** via a benzimidazoline intermediate.

We have recently prepared the naphthalene analogs to macrocycles **5**, compounds that are structurally related to the macrocycles originally investigated by Reinhoudt, but fully conjugated around the ring. These macrocycles (**9**) could also be prepared in a single-step, template-free reaction, Scheme 9 [42]. Surprisingly, macrocycles **9** exist as a mixture of tautomers—the keto/enamine tautomer is more stable than the imine/enol tautomer when benzene in macrocycle **5** is substituted for naphthalene. Calculations and X-ray crystallography of model compounds of naphthalenediimines were used to understand the tautomeric equilibrium in these compounds and to predict their structures. Expanding the macrocycles in this fashion may offer access to extended macrocycles that could be better container molecules for host-guest chemistry.



Scheme 9 Synthesis and tautomerization of macrocycle **9**.

ION-INDUCED TUBULAR ASSEMBLY

The phenol groups in the interior of macrocycle **5**, as drawn in Scheme 7, present a hexagonal arrangement of O atoms, analogous to 18-crown-6. It is well known that when 18-crown-6 binds to alkali metal ions, it wraps around the ion to coordinate all of the oxygen atoms. In the case of macrocycle **5**, the shape-persistent rigid structure of the macrocycle would prevent it from wrapping around the metal. How might these macrocycles behave when coordinated to small hard cations, such as alkali metal ions?

To investigate this, macrocycle **5b** with peripheral *n*-hexyloxy chains was treated with salts of the alkali cations and ammonium. In each case, a color change was observed that depended on the size of the cation. UV–vis titrations of the macrocycle with alkali metal cations showed a clean isosbestic point at very low concentrations of alkali metal, but this disappeared after the ion:macrocycle ratio was greater than ca. 1:4. This data indicated that an intermediate was formed at low concentration of alkali metal, but many different species are present at the higher concentrations of alkali metal cation.

^{1}H NMR experiments were very revealing. Upon titration with Na^+, the resonances assigned to the aromatic and imine protons on the macrocycles underwent large upfield shifts. The imine resonance, at ~8.5 ppm in the free macrocycle, was found at ~7 ppm when 1 equiv of $NaBPh_4$ was added. Similarly, the aromatic protons moved from ~7 to 5.5 ppm. These large upfield shifts are characteristic of stacked assemblies where the protons on the outside of the macrocycle experience of the shielding of aromatic rings from adjacent macrocycles in the stack; similar phenomena are known for stacked phenyleneethynylene macrocycles [14]. The extent of the upfield shift depends on the size of the cation employed, with Cs^+ showing much smaller changes than Na^+. This is consistent with a stacked assembly with metal ions bridging the macrocycles. In the case of Cs^+, an intermediate was observed at low concentrations of Cs^+ that corresponded to a 2:1 macrocycle:Cs^+ complex, presumably some type of sandwich compound.

Electrospray mass spectrometry also confirmed the presence of oligomeric species. In addition to $[\mathbf{5b}+H]^+$ and $[\mathbf{5b}+Na]^+$, species that are expected by this technique, $[\mathbf{5b}_2+Na]^+$ and $[\mathbf{5b}_3+Na_2]^{2+}$ were also observed. By adding sodium acetate to the sample, larger aggregates were observed that could also be explained by a linear stack of alternating macrocycle and cation. While mass spectrometry provides no information about the structure of the complexes, it does provide support for the presence of oligomers where the macrocycles are bridged by alkali metals.

Overall, based on the physical data from UV–vis, NMR, and mass spectrometry, we believe that the macrocycles are assembled into 1D structures of alternating macrocycle/ion as illustrated in Fig. 6 [43]. As the maximum ratio of cation:macrocycle that could be obtained in chloroform was 1:1, we are confident that the hard metal ions are interacting with the phenolic oxygen atoms rather than the N_2O_2 pockets of the macrocycles. Preliminary calculations also indicate that Na^+ has a stronger affinity for

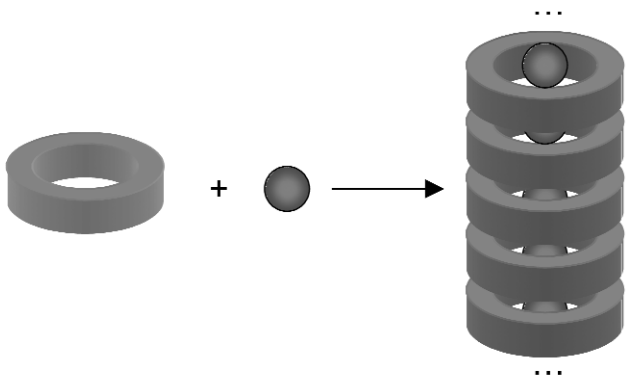


Fig. 6 Illustration of ion-induced tubular assembly of shape-persistent macrocycles **5**.

the hard hydroxyl groups over the softer imine functionalities. Further studies of this assembly mechanism are underway.

EXPANDED METALLOMACROCYCLES

In an effort to further expand the macrocycles, we have prepared extended bis(salicylaldehyde) derivatives **10**–**12**, Fig. 7, and reacted them with substituted phenylenediamines. In each case, the [3+3] Schiff-base condensation macrocycle (**13**–**15**) was the major product, further demonstrating the versatility of this reaction (Fig. 8) [44]. Notably, precursors **10**–**12** are less rigid than the dihydroxydiformylbenzene and naphthalene derivatives used to make the other macrocycles, with nearly free rotation expected about the benzene-ethynylene bond. Nevertheless, the thermodynamically stable [3+3] Schiff-base macrocycle is obtained in each case.

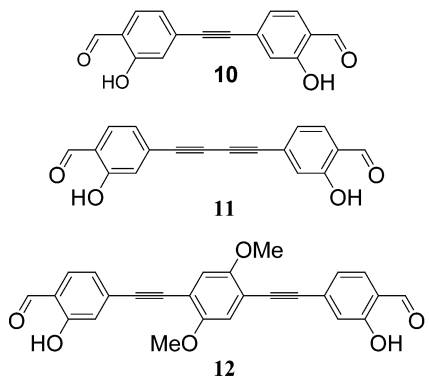


Fig. 7 Structures of bis(salicylaldehyde) derivatives **10**–**12**.

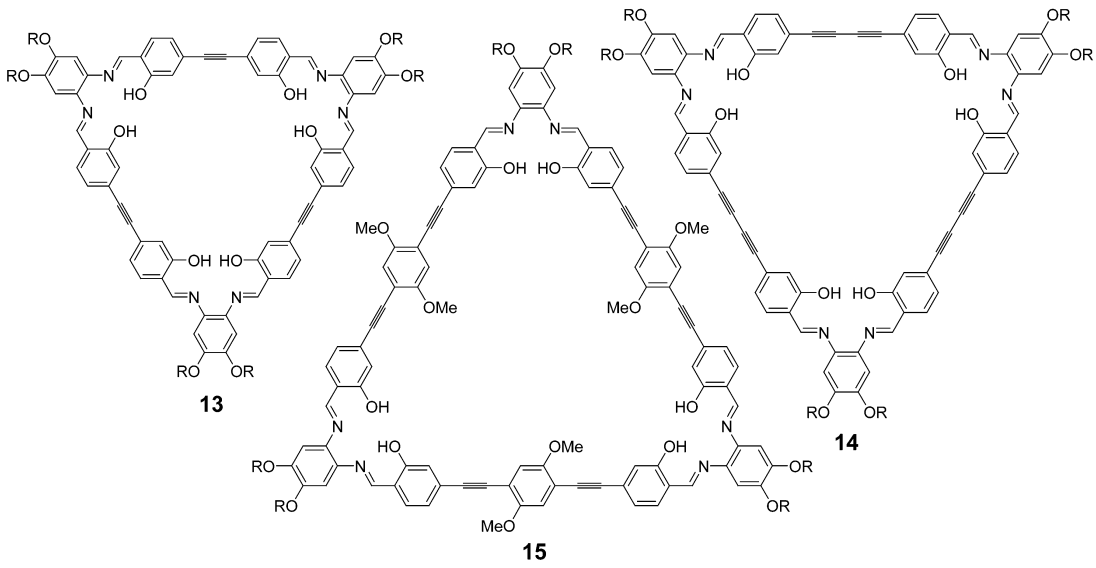


Fig. 8 Structures of conjugated [3+3] Schiff-base macrocycles **13**–**15**.

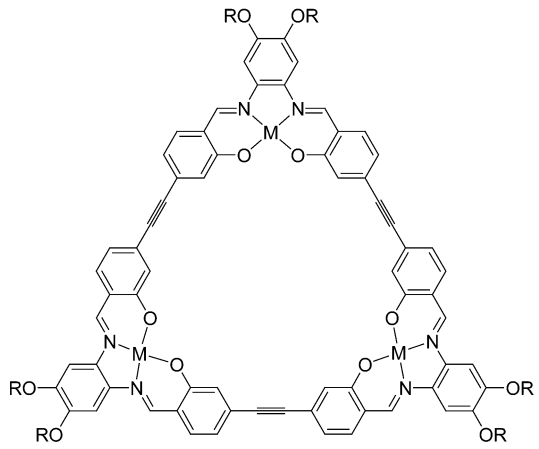
When these macrocycles are metallated with Zn^{2+}, they all form luminescent trimetallic complexes, though they have low quantum yields. It is interesting that the maximum wavelength of the luminescence from all three macrocycles (ca. 560 nm) is only slightly red-shifted relative to the monomeric zinc salphen complexes that form the corners of the macrocycle, indicating that the electronic states involved in the luminescence are localized on the metal salphen moieites. When the macrocycles were metallated with Ni^{2+}, their fluorescence is completely quenched, probably due to an overlapping ligand-to-metal charge-transfer band.

SUPRAMOLECULAR ASSEMBLY: COORDINATION-ASSISTED AGGREGATION

Macrocycle **13** could be metallated with Zn^{2+}, Ni^{2+}, or Cu^{2+} to give metallomacrocycles **16**–**18**, Fig. 9. Peripheral R groups are either *n*-C_8H_{17} or 2-ethylhexyl groups to enhance solubility of the macrocycles. NMR spectroscopy of macrocycle **16** is strongly solvent-dependent. In CD_2Cl_2, none of the resonances for the protons on the aromatic ring or the imine of the macrocycle could be observed. This is consistent with aggregation into large assemblies where the T_2 relaxation times of the protons have become so short that the resonances are extremely broad. Only upon addition of polar, coordinating solvents (e.g., THF, pyridine) could the NMR spectrum of the macrocycles be determined.

The optical properties of macrocycle **16** are strongly solvent-dependent. In CH_2Cl_2 and other noncoordinating solvents, the absorption spectrum shows only a broad, featureless peak that is characteristic of a ground-state excimer-like species. This is an indication that the macrocycles are strongly aggregated. Even at 10^{-7} M in CH_2Cl_2, the spectrum is unchanged, indicating that the macrocycles are aggregated at these very low concentrations. Upon titration with a coordinating solvent (e.g., pyridine, THF, quinuclidine), the absorption spectrum incorporates features expected for isolated molecules. Thus, coordination of the solvent to the Zn^{2+} present in the macrocycle leads to a break-up of the aggregates.

This effect could also be monitored by fluorescence spectroscopy. In noncoordinating solvents, the fluorescence of the macrocycle is nearly quenched. Upon titration with a coordinating solvent, the fluorescence of the macrocycle is significantly enhanced. This enhancement arises from the transition from a nonradiative aggregated (excimer) state to a luminescent molecular species.



16 (M = Zn)
17 (M = Ni)
18 (M = Cu)

Fig. 9 Structures of metallomacrocycles **16**–**18**.

Spectroscopic evidence suggests that the macrocycles are strongly aggregated in noncoordinating solvents, but disassemble in the presence of a coordinating ligand. The aggregation, which is very strong, could be mediated by any number of possible intermolecular interactions—π-stacking between the aromatic groups, hydrogen bonding between (hypothetical) water coordinated to Zn^{2+}, or Zn^{2+} interacting with phenolic oxygen atoms. Zinc(II) is notorious for adopting a 5-coordinate ligand environment, even in salen-type complexes, and is not likely to be in a square planar geometry [45].

To eliminate the possibility of π-stacking, the analogous macrocycles with both Ni^{2+} (**17**) and Cu^{2+} (**18**) were prepared. These macrocycles are likely to have the metal in a square planar environment, giving very flat macrocycles that should be even more amenable to π-stacking than the Zn^{2+} macrocycles. In fact, the Ni(II) and Cu(II) macrocycles both show UV–vis spectra with several discernable features. As well, the absence of any solvent-dependence in their optical spectra further indicates that these macrocycles do not aggregate in solution.

To prove that the Zn^{2+} ion is involved in the assembly, we compared the response of the macrocycles when treated with 2,6-lutidine and pyridine. Titration of macrocycle **16** in CH_2Cl_2 with 2,6-lutidine showed no change in its absorption or fluorescence spectra. In contrast, titration of macrocycle **16** in CH_2Cl_2 with pyridine showed a large change in the absorption spectrum as well as an enhancement and blue-shift in the emission spectrum. Although 2,6-lutidine is a stronger base than pyridine, it is unable to coordinate to the metal and therefore cannot break up the aggregates. As the macrocycles aggregate in methanol, it is unlikely that hydrogen bonding between axially coordinated aqua ligands is responsible for the assembly, though there may be other intermolecular interactions (e.g., π-stacking) that become important in this highly polar solvent.

Based on these results, we believe that the macrocycles aggregate strongly in noncoordinating solvents [46]. Interactions between Zn^{2+} ions and oxygen atoms from adjacent macrocycles mediate the aggregation phenomenon. This is one of the first applications of Zn···O interactions in supramolecular chemistry. Although we do not know the shape of the aggregates for certain, it is likely that they are tubular in shape since this would permit multiple intermolecular (cooperative) interactions and explain the very strong aggregation.

These macrocyclic assemblies may serve as the basis of new chemical sensors [46]. The stacking of an assembly of macrocycles in solution is disrupted by an analyte that binds to the metal center. By changing the coordination environment of the metal ion, it may be possible to enhance the selectivity

and sensitivity of the sensing action. One of the strengths of using this as a sensor is that it is a turn-on mechanism: disruption leads to an enhancement, rather than quenching, of signal. This offers improved sensitivity over most fluorescence sensing schemes that involve fluorescence quenching upon exposure to analyte.

SUMMARY

We have prepared a family of conjugated, shape-persistent macrocycles based on [3+3] Schiff-base condensation. It is surprising that these macrocycles can be readily prepared, given the number of possible byproducts and side-reactions that may occur. Among these possibilities, oligomeric intermediates of the condensation and a monoreduced macrocycle have been isolated.

The macrocycles undergo supramolecular assembly in ways that are different from other shape-persistent or flexible macrocycles. The small Schiff-base macrocycles undergo ion-induced tubular assembly with small cations to give assemblies in solution where macrocycles are bridged by alkali metal linkers. In contrast, giant Zn(II) macrocycles aggregate in nonpolar solvents without added species. Upon binding to coordinating analytes, these supramolecular assemblies dissociate, suggesting their application in new chemical sensing schemes.

It is clear that the conjugated Schiff-base macrocycles have potential for interesting supramolecular chemistry. Future studies will involve the expansion of the macrocycles and exploration of their supramolecular chemistry.

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