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Review

Metallo-supramolecular capsules

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Contents

Abstract

The formation of capsule based architectures on the molecular scale has been of interest to many researchers in recent times. The formation of these assemblies is often challenging and can produce structures on a multi nano-metre scale that can serve specific functions. Some of the approaches used to produce such assemblies are outlined in relation to various building blocks in metal-organic polyhedra, molecular boxes and molecular capsules for example. The last of these has been the focus of our recent studies since the discovery of a hydrogen-bonded nano-capsule based on *C*-methylresorcin[4]arene, although the molecule also assembles in dimeric capsule motifs. The related pyrogallol[4]arenes display similar behaviour, however a number of metal-organic analogues have recently been synthesised and characterised through a variety of techniques that suggest various assembly processes. These are highlighted in the context of related architectures in order to give a sense of potential for such assemblies that can, in some cases, be assembled instantaneously or very rapidly.

Keywords: Supramolecular chemistry; Molecular capsules; Coordination chemistry; Self-assembly; Host–guest chemistry

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1. Introduction

As the title of this manuscript suggests, the primary thrust of this review is on the synthesis and characterisation of metallo-supramolecular capsules. Supramolecular chemistry is a burgeoning field that still has much to be discovered and utilised. While this is a broad field encompassing the work of many research groups worldwide, we must limit our discussion to topics related more closely to the title, and this does unfortunately require us to make reference to a limited number of contributors to individual fields. In doing so, no particular preference has been given to the cited authors of work covered, but rather we have selected articles that display some of the key advancements in the relevant areas. In order for the reader to have a reasonable overview of the fields related closely to the title, we have selected the topics outlined in the contents page to explore approaches employed by researchers to achieve the goal of controlled self-assembly of molecular components. Although some of these approaches are applicable to important areas of research such as ‘molecular machines’, catenanes and rotaxanes, etc., we have limited our review to self-assembled systems that bear a likeness to molecular or metal-organic capsules.

As much of the work highlighted in this review is encompassed by crystal engineering, we begin with this key topic, the principles of which are succinctly discussed with some relevant references for the reader. This discussion will also focus lightly on two closely related types of material used for guest storage that have spawned partly from crystal engineering, namely metal-organic frameworks (MOFs) and the recently reported zeolite-like metal-organic frameworks (ZMOFs). Crystal engineering is also key in the other topics covered such as metal-organic polyhedra, boxes, cages and capsules, and it has indeed been influential in our own studies in many different ways. In relation to the present contribution, and in the course of our experiments, we have found that pyrogallol[4]arenes (cyclic bowl-shaped molecules) can form dimeric or hexameric metal-organic nano-capsules, thereby mimicking hydrogen-bonded analogues. Our past and recent studies in this area are described later in the review in an attempt to place them in the context of the other topics covered in the manuscript with a perspective of future prospects with these systems.

1.1. Crystal engineering

Crystal engineering is the predictable synthesis of solid-state materials that (ideally) have tailored properties or topologies to suit a particular application, a pertinent example of which is gas storage in solids [1]. Crystal engineering is becoming increasingly popular, and the design principles based on intermolecular interactions and coordination chemistry are producing a large library of coordination networks or metal-organic frameworks (MOFs) [2–9] and larger zeolite-like metal-organic frameworks (ZMOFs) [10] for example.

These topics are mentioned (among many others that use crystal engineering, some of which are covered later) as they are frequently found in the literature and serve the purpose of highlighting the effects of design principles. Indeed the fine work performed by many in this area covers many different aspects of MOF chemistry and utilisation. By carefully selecting the correct ligands prior to MOF formation, phenomena such as expanding and contracting frameworks [3], controllable network interpenetration and pore size [6] and gas sorption have all been recently reported for these materials [8,9]. The ligands employed in the formation of these different materials often contain pyridyl or carboxylato functionality [2–10]. These ligands are combined with metal centres to form different known structural building units in order to generate stable networks that are tolerant to solvent removal. Concomitant variation in the organic backbone of the ligand ultimately affords enhanced control over network formation and their resulting properties such as pore size volume.

By virtue of recent advances such as 6 wt% H_2 storage in a MOF at 78 K and pressures below 80 bar [8], controllable topology with concomitantly high hydrogen storage [9], or the use of ZMOFs as host–guest sensing materials [10], the use of crystal engineering in this area (coupled with continued innovation by many) will likely continue to result in the formation of useful and functional materials that will further serve as contributors to the already expansive library of compounds as well as to future design principles.

1.2. Metal-organic polyhedra, boxes and cages

While metal coordination in metal-organic frameworks was used above to outline the use of crystal engineering, various (and in some cases similar) approaches have been employed in the formation of metal-organic polyhedra, boxes and or cages. In many cases these three terms are interchangeable and many of the methods employed also fall under the umbrella of crystal engineering. For an example of the way transition metals can be used to assemble and template supramolecular species, the reader is directed to a chapter by Chambron *et al.* [11]. In particular, the authors show how the field of catenanes and molecular knots has moved from purely statistical approaches to template syntheses using transition metals and design principles.

In the broad topic of this section, transition metals are often used for templating, and significant advances in large superstructures or clusters have been made by Fujita and co-workers [12–18], Stang and co-workers [19,20], Raymond and co-workers [21–27] and Ward and co-workers [28–36]. Fujita has reacted pyridyl or pyrimidyl functionalised planar or near planar ligands (that are typically triangular) with *cis*-protected palladium in order to synthesise a substantial series of metal-organic cages [12–18]. By developing the principles in ligand design, clefts were introduced to hexahedral assemblies, allowing form reversible guest inclusion [14]. Most impressively, further design principles involving naked palladium centres have used V-shaped ligands to afford finite spherical coordination networks that are based on cuboctahedral geometry, that have a diameter of around 3 nm, and that have openings that are ∼1–1.5 Å wide (Fig. 1) [16]. Similarly, naked palladium centres have also been used with other pyridyl-based ligands to assemble two related solvato-controlled metal-organic coordination ‘boxes’ in which the presence of acetonitrile causes structural

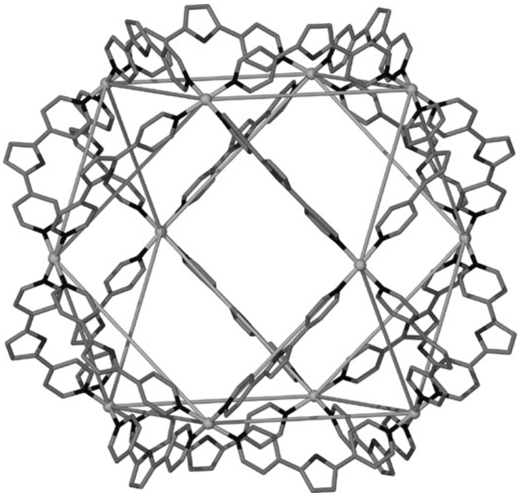


Fig. 1. The finite spherical coordination network formed by reacting naked palladium centres with directional pyridyl ligands [16]. The cuboctahedron is shown by connecting the palladium centres. Hydrogen atoms and anions are omitted for clarity.

interconversion [17]. To demonstrate the potential of some of these large metal-organic assemblies, Fujita and co-workers are currently investigating these frameworks for uses that include chirality enrichment through enantiomer recognition [18].

Stang and co-workers have also used pyridyl-based ligands with platinum metal centres to synthesise an impressive series of discrete metallo-supramolecular assemblies that are based on truncated tetrahedra for example. The authors treat *cis*-Pt(PMe_3)$_2$(OTf)$_2$ as a V-shaped building unit, and react the metal centres with triangular shaped ligands (such as 1,3,5-tris(4-pyridyl-*trans*-ethenyl)benzene) in a 3:2 ratio to build the discrete architectures in near quantitative yield (Fig. 2) [19]. The framework has openings of ∼1–1.5 nm and the assembly was co-crystallised with sodium cobalticarborane. A series of self-assembled coordination cages of D_{3h} symmetry were also assembled by similar methods using slightly varied platinum subunits and tripodal pyridyl-based ligands [20].

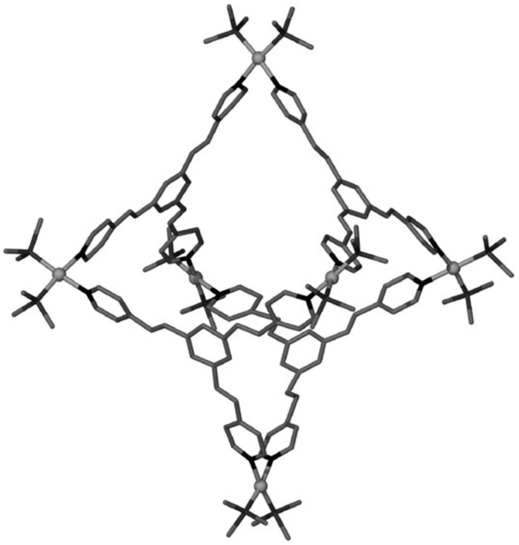


Fig. 2. The truncated tetrahedron synthesised by the reaction of *cis*-Pt(PMe_3)$_2$(OTf)$_2$ with 1,3,5-tris(4-pyridyl-*trans*-ethenyl)benzene) [19].

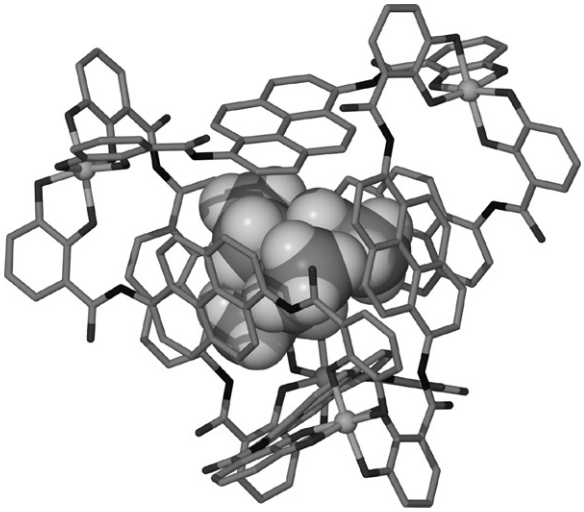


Fig. 3. The tetrahedral cluster formed by combining pyrene spaced bis-dentate catechol-based ligands with gallium centres in the presence of a cluster directing tetraethyl ammonium cation [23].

Raymond and co-workers have used ligands containing various binding groups with good effect [20–23]. By reacting catechol-based ligands with iron and gallium centres, the chelating effect and the presence of particular (naphthalene and pyrene) organic spacers between the catechols drives the formation of M_4L_6 cluster type assemblies (where M = Fe or Ga, and L = catechol-based ligand) [20–23]. The larger of these assemblies with the pyrene-based spacer has a void volume of ∼300–400 Å^3, and is thermodynamically driven by host–guest interactions with tetraalkylammonium guest species (Fig. 3). When an anthracene spacer is used, either triple helicate and tetrahedral cluster interconversion is observed, a phenomenon which is also controlled by host–guest interactions, also with tetraalkylammonium guest species [24]. In moving from transition to lanthanide metals, Raymond and co-workers also reported an octameric lanthanum pyrazolate cluster [25]. This self-assembly is more difficult to control given the high coordination numbers of the lanthanides, but the authors successfully react a rigid tris-bidentate 4-acyl-2-pyrazolin-5-one ligand with lanthanum acetylacetonate in DMSO to afford a single self-assembled ‘ring-like’ metal-organic cluster that is ∼3 nm in diameter.

Following on from these reports, Saalfrank and co-workers have also used the same tris-bidentate 4-acyl-2-pyrazolin-5-one ligand with gallium centres to assemble M_6L_6 clusters that the authors describe as a ‘cylinder’ [26]. Further modification of the trigonal ligand framework so as to generate tris-malonate-based chelator ligands, followed by combination with iron chloride, resulted in the formation of tetra- and hexa-nuclear metal clusters depending on particular functionalities (O-^{t}Bu or O-tolyl, respectively) placed on the ligand framework [27]. Control over these various cluster assemblies using the aforementioned chelators is now established and the authors are reporting metal-organic cages that rival the size of the mulit-component system of Fujita shown in Fig. 1) [16]. Furthermore, with the naphthyl-based spacer present, these authors have also recently shown that the protected environment provided by the metal-organic cage allows for acid catalysis when the assembly and guest species are present in basic solution [20b].

Ward and co-workers have used approaches similar to some of those described for the formation of catenanes and molecular knots in the book chapter mentioned at the start of this section [11,28–36]. The authors report on a series of ligands containing different numbers of *N*,*N*-bidentate chelating arms that are combined with various transition metals to form a library of metal-organic cage complexes that are based on different polyhedra. Variation in the distance between the *N*,*N*-bidentate chelating arms by means of organic modification results in changes in cage complex formation, and the voids within these assemblies are filled with the appropriate anion depending on the metal salt employed [28–36]. Recently, the authors have reported the formation of two polyhedral cage complexes that are either homoleptic or heteroleptic with respect to ligand composition [36]. By employing a *bis*-bidentate ligand, with either zinc tetrafluoroborate or cadmium perchlorate, a capped truncated tetrahedral polyhedron is formed. When this same ligand is mixed with a tris-bidentate ligand with identical functionality and copper tetrafluoroborate in a 3:1:3 ratio, the resulting assembly contains both ligands, is of cuboctahedral geometry, and is also of comparable size to those reported by Fujita and co-workers [16], Saalfrank *et al.* [27], and Stang and co-workers [19].

Somewhat related to the research mentioned above, recent work by MacGillivray and co-workers have used crystal engineering to controllably assemble materials that can undergo [2 + 2] photodimerisation [37]. By doing so, the authors have prepared an otherwise unobtainable cyclobutane functionalised with two 2-pyridyl and two 4-pyridyl groups. This ligand assembles with copper(II) ions to form a metal-organic trigonal antiprism (Fig. 4). The nature of the ligand means that the pyridyl groups dictate the formation of the polyhedron that has two trigonal openings at opposite sides of the assembly. The space within the assembly is filled by two perchlorate anions while other anions reside *exo* to the assembly framework. Most importantly, the authors have shown a beautiful example of metal-templated crystal engineering to afford a unique building block by design prior to further self-assembly.

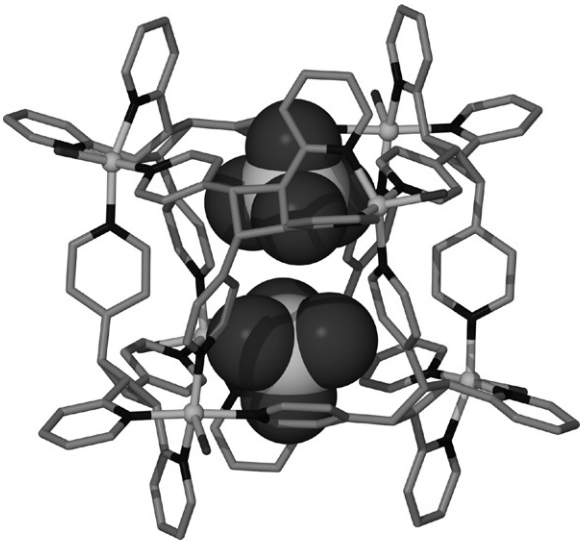


Fig. 4. The trigonal antiprsimatic structure formed by combination of novel cyclobutane tetra-pyridyl ligands with copper centres. The resulting void in the framework is filled with two perchlorate anions [37].

1.3. Covalent organic capsules/cages and capsule-like architectures

When examining the literature based on covalent organic capsules, the reader invariably becomes associated with the outstanding work of Cram. Within his extensive studies in this field, Cram first synthesised carceplexes from bowl shaped cavitands; carceplexes are carcerands (hollow closed shell compounds) that encapsulate or rather trap guest molecules [38,39]. This inspired series of studies paved the way for future works into covalent organic capsules as reaction media, or into guest exchange in such assemblies for example, while unequivocally showing the presence of such incarcerated molecules by X-ray diffraction (an example of which is shown in Fig. 5) [40–42].

In relation to the studies performed in our group with non-covalent organic and metal-organic coordination nano-capsules (see Sections 2 and 3), Sherman, Sherburn and Warmuth have all been active in the covalent synthesis of large multi-component covalent organic capsules or capsule-like architectures.

Although the Sherman group has been active in research into carceplexes similar to those reported by Chapman [43], it is their work into larger capsule or capsule like architectures that is of particular importance here [44–47]. By linking selectively functionalised cavitands together under various conditions, it

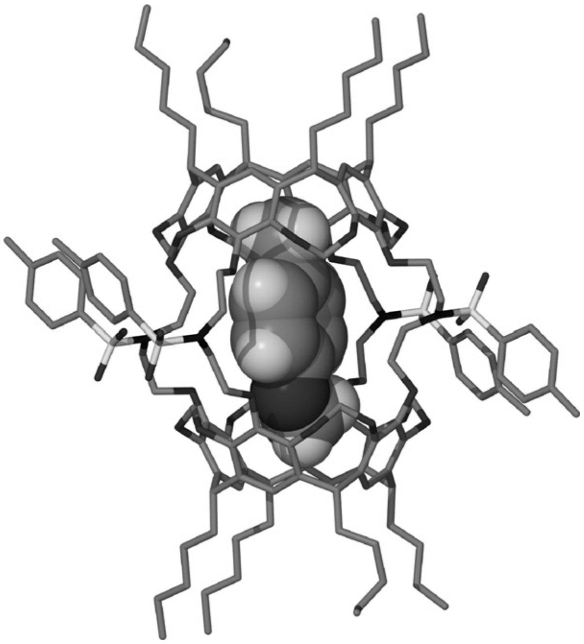


Fig. 5. View of an incarcerated guest molecule in a carcerand, thus making a carceplex [42].

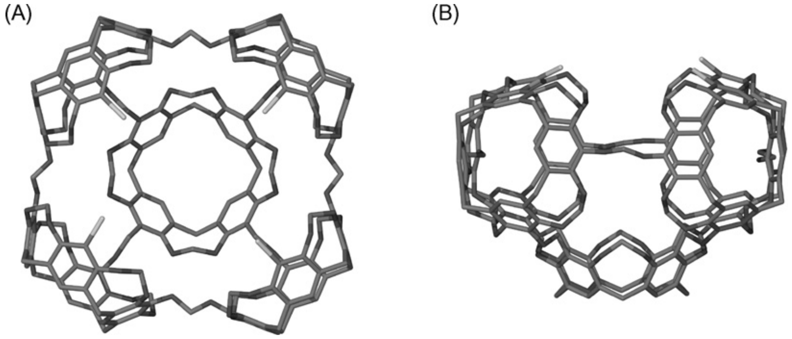


Fig. 6. (A) Top-down and (B) side-on views of the 'tetrabromosuperbowl' [48]. Hydrogen atoms, guest molecules, and 'lower rim' cavitand alkyl chains removed for clarity [48].

was shown that cyclic trimeric and tetrameric assemblies could be synthesised [44–46]. The cyclic tetramers were found to rearrange into a *bis*-carceplex type structure in the presence of different guest species. In closer relation to the latter topics of this review, Makeiff and Sherman recently reported the synthesis of a six-bowl carceplex that encapsulates seven guest molecules [47]. Although the multi-component capsule-like assembly was not characterised by X-ray crystallography (that would most likely be very interesting), the structure was confirmed by MALDI mass spectrometry and ^{1}H NMR analysis. MM2 minimised structures suggest that the assembly is of near spherical nature with small openings at the positions linking the cavitands together.

Shortly before Sherman reported the six-bowl carceplex mentioned above [47], Sherburn and co-workers reported the formation of 'superbowl' container molecules [48]. Innovative synthetic procedures allowed the group to link one 'base' cavitand to four others by selective linking at the 'upper rim'. Following this, the linked 'upper-rim' cavitands were reacted together in order to make a rigid entity composed of five cavitands, and that possesses an opening for potential guest exchange. The authors managed to crystallise the 'superbowl' and perform single crystal X-ray analysis (Fig. 6) [48], showing a near-spherical structure similar to that suggested by Sherman for the six-bowl carceplex [47].

More recently, the Warmuth group have reacted cavitands comprising 'upper rim' formyl groups with ethylene diamine to afford an octahedral capsule-like container molecule [49] similar to those synthesised by Makeiff and Sherman [47] and Sherburn and co-workers [48]. The authors report studies with an Amber force field model, and show that there are large openings in the organic superstructure [49]. The authors also examined solvent effects in these nano-cage systems to discover a larger organic cage comprising eight cavitand subunits also linked by imino groups [50]. Notably, all of these nano-cage systems are isolated from one-pot procedures with relative ease compared to the more intricate syntheses for the previously reported 'superbowl' and six-bowl carceplexes.

Although the area of large covalent organic capsules is limited at this stage, the aforementioned authors are strengthening this particular field and show potential for further development of such systems.

1.4. Non-covalent organic capsules

This section is related to a later part of this review that focuses on larger resorcin[4]arene and pyrogallol[4]arene nanocapsules. In particular, it will focus on the development of smaller self-assembled non-covalent organic capsules. Although we are primarily interested in the larger nano-scale capsules, several of the smaller documented hydrogen-bonded networks serve as key examples to the rational design of complementary building blocks. Note that while not all non-covalent organic capsules are represented here, many more exist but it is not within the scope of this article to highlight every aspect of dimeric non-covalent capsule chemistry for example.

Of the numerous researchers actively pursuing this field, Rebek and co-workers have published an outstanding series of non-covalent dimeric capsules, some of which are known as 'tennis balls' or 'softballs' [51–53]. Although these capsules are beautiful examples of predicting self-assembly, the spectrum of guests available for encapsulation is limited by the size of the capsule (~230–240 Å^3, Fig. 7).

More recent work in the Rebek group has documented a number of resorcin[4]arene molecules that are further modified at the upper rim, while employing the principles of complementarity, to generate cylindrical dimeric capsules that are capable of encapsulating a variety of larger guest species [53]. A broad series of elegant solution phase studies outline the behaviour of encapsulated species within these cylindrical capsules.

Still in the dimeric capsule order of magnitude, Gibb and co-workers have invested considerable effort into the extension of the upper rim of cavitands, thereby affording new classes of 'deep-cavity' cavitands [54,55]. The authors have shown how these molecules self-assemble into dimeric species that have hydrophobic pockets capable of controlling photophysical properties of aromatic molecules [54]. These water-soluble capsules are even capable of sequestering and separating hydrocarbon gases that are present in the headspace above the aqueous phase [55].

The complexation of small ammonium cations is a topic that has been visited by many involved in host–guest chemistry with bowl-shaped molecules, but for a pertinent example of the encapsulation of such species in dimeric resorcin[4]arene capsules, the reader is directed to recent work by Rissanen and co-workers

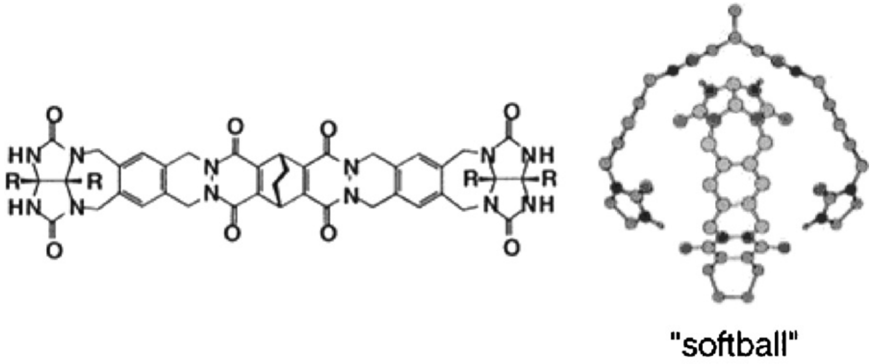


Fig. 7. The non-covalent 'tennis ball' or 'softball' formed by the tailored synthesis of complementary molecules [51–53]. Figure was reproduced from Ref. [52] with permission from the copyright holders (AAAS).

[56]. The hydrogen-bonded dimeric capsules are well suited for small molecule encapsulation, and the bound guest species can often be identified by X-ray diffraction studies.

Recent work by Ananchenko *et al.* has described a series of van der Waals capsular assemblies formed by a series of *p*-alkanoylcalix[4]arenes [57–59]. The particular novelty associated with these assemblies is the ability to exchange the encapsulated guest species within a single crystal. The phenomenon of molecular transport through non-porous materials has been documented for other calix[4]arenes [60], and these are rare cases of such a phenomenon.

Böhmer and co-workers have studied a series of 'tetra-urea' calixarenes that form dimeric capsules [61,62]. Although the authors have assembled numerous dimeric capsules, it is the further application in templation that has been the focus of recent efforts [63,64]. These capsules can be used to form monolayers on gold surfaces, and the complementarity of these molecules has been adapted to form cores for dendrimes that are based on tris-complementary type core species linked to 'tetra-urea' calixarenes [65]. These species can then be combined with other calixarenes to form dendrimer type architectures. The remarkable combination and controlled assembly of tetraurea-calix[4]arenes and tetra(tosylurea)calix[4]arene heterodimeric capsules by the same group has, with fourfold ring closure metathesis and hydrogenation, afforded a covalent fourfold [2]rotaxane of calix[4]arenes (Fig. 8) [63]. Notably, this conversion between non-covalent and covalent shows the potential that control over dimeric capsule species holds, yet much remains to be discovered and accomplished with such systems as a whole.

1.5. Metal-organic/ionic capsules and capsule-like architectures

Although the field of supramolecular chemistry has flourished as a whole in recent years, the number of voluminous metal-organic (or what may in some cases arguably be termed ionic) capsules reported in the literature is more limited than one may expect. Apart from those described later in this review, we have selected a number of examples based on the *p*-sulfonatocalix[*n*]arenes (where $n = 4$–8), cavitand molecules, and other (resorcinarene and cyclotriveratrylene based) bowl-shaped molecules that are assembled with metal ions (amongst other components) to facilitate the assembly of large metallo-supramolecular capsules or capsule-like architectures.

The *p*-sulfonatocalix[*n*]arenes have been shown to assemble with other molecular components into numerous different supramolecular arrangements including 2D or 3D coordination polymers, amino acid complexes and 'Ferris wheels' for example [66,67]. Although this is the case, it is the assembly of *p*-sulfonatocalix[4]arene (SO_3[4]) into dimeric 'Russian doll', or nanometre scale capsules (of icosahedral or cuboctahedral geometry) built from 12 calixarenes that are of special interest here [68–70].

By combining the sodium salt of *p*-sulfoantocalix[4]arene with 18-crown-6 and various metal salts, a 'Russian doll' composed of two SO_3[4] shrouding a sodium 18-crown-6 complex affords a superanion capsule complex that is capable of crystallising with various transition or lanthanide metals [66a]. Other studies using pyridine-*N*-oxide as a guest for the SO_3[4] cavity in the presence of lanthanide metal cations uncovered a series of supramolecular architectures including a C-shaped dimer that further assembles into a spherical capsule such that twelve SO_3[4] molecules are arranged at the vertices of an icosahedron (Fig. 9) [68]. It was also found that varying the pH of the crystallisation of praseodymium 'Russian dolls' resulted in the formation of a second nano-metre scaled capsule based on twelve SO_3[4] molecules(Fig. 9) [69]. In this second 'sphere', the molecules are arranged at the vertices of a cuboctahedron and the 'skin' of the overall assembly is found to contain channels which are occupied by water molecules leading to the core which contains six poly-aquo lanthanide species and disordered water molecules. When one considers the geometries of the materials formed, the two are theoretically interchangeable by a sextuple diamond square process and it is perhaps not entirely surprising that the two intimately related structural motifs are formed (Fig. 9) [70].

Other modified calix[4]arenes [71], resorcin[4]arenes and/or cavitands [72–80] have also been used to assemble (dimeric) capsule or larger capsule-like metal-organic assemblies. Of these, Harrison and co-workers have synthesised a series of resorcin[4]arene-based cavitands that possess 'upper rim' functionalities useful for metal complexation with copper, iron and cobalt for example (these molecules predominantly pos-

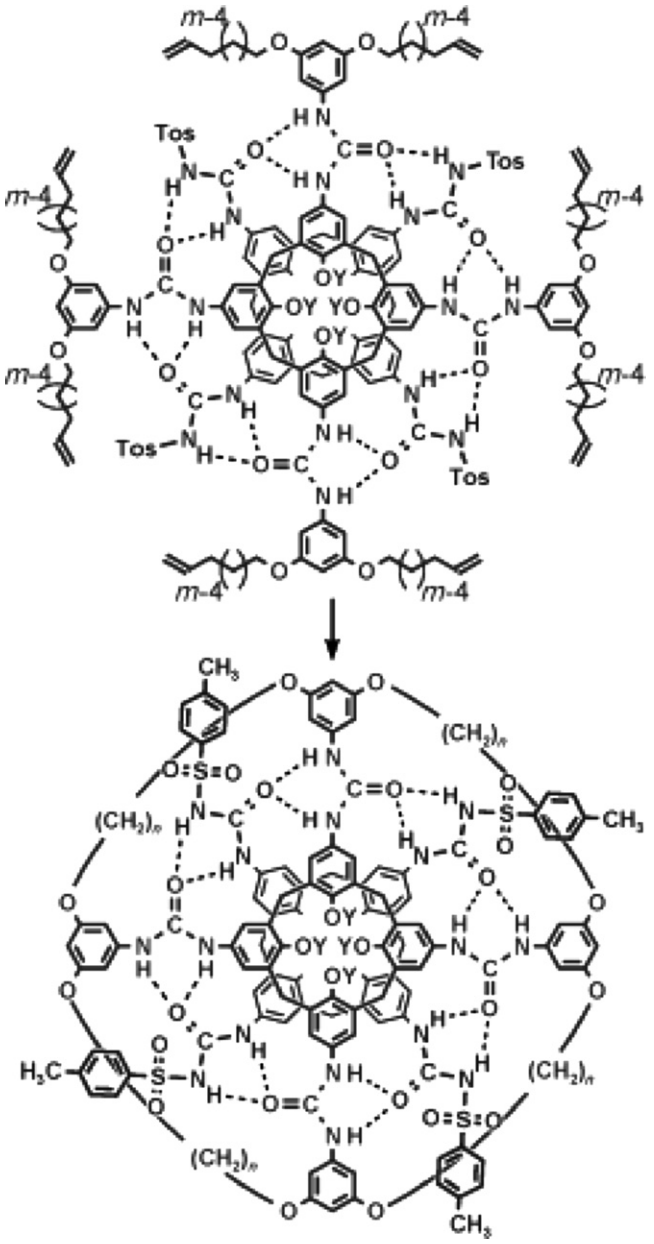


Fig. 8. Fourfold [2]rotaxanes formed by metathesis and subsequent hydrogenation [63]. Figure was reproduced from Ref. [63] with permission from the copyright holders (Wiley).

sess iminodiacetate groups but can also have dipyridylimino functionality) [72–77]. The authors show a series of elegant structures based on dimeric tetra-metallated capsules that can be pH dependent [72], and that can reversibly capture organic molecules from water [75]. Beer and co-workers synthesised resorcin[4]arene-based cavitands possessing dithiocarbamate functionality at the ‘upper rim’ [78,79]. By synthesising metal complexes with zinc, copper or cadmium, and re-crystallising from pyridine and water, the authors were able to form large loop or capsule like architectures based on three and four cavitands, respectively. The resulting assemblies have been shown to act as useful hosts for C_{60} as the loop has a suitable diameter for guest inclusion [79]. Dalcanale and co-workers have synthesised a series of coordination cages based on cavitands possessing ‘upper-rim’ nitrile functionality [81–82]. These building blocks, when combined with square planar metal centres for directed self-assembly, afford dimeric capsules that have varied anion encapsulation properties that have been studied extensively. By extending the ‘upper-rim’ functionality to ‘benzonitrile’, the authors use the same methodology to assemble a metal-organic capsule containing large equatorial portals [83]. This alteration to the system results in a large increase in the estimated internal volume (over four times greater).

Recent work in the Hardie group has focused on using selectively modified cyclotriveratrylene (CTV) to assemble capsular architectures [84,85]. The basic CTV framework is bowl-shaped, has a shallow cavity suitable for hosting guest species, and the molecule has a roughly pyramidal shape that is suitable for the formation of polyhedral shapes. Modification of the framework to afford tris(pyridylmethylamino)-cyclotriguiacyclenes (shown in Fig. 10A), followed by combination with various silver salts results in the formation of either dimeric (Fig. 10B) or tetrameric (Fig. 10C) capsular architectures with the 3-pyridyl or 4-pyridyl derivatives, respectively [84]. The tetrameric capsule has a host at each vertex of a tetrahedron, and the pyridyl moieties are bound to silver centres that in some cases also have bound acetonitrile molecules on the exterior of the capsule, resulting in a star-burst tetrahedron. The capsule contains five acetonitrile molecules (Fig. 10C), and it has also been shown that the assembly is general by exchanging simple silver salts with silver monocarbaboranes [85]. By doing so, the authors control the packing motif and alter the near close packing that is observed in the presence of smaller anions.

Many of the examples shown above are based on cup or bowl-shaped molecules, but Severin *et al.* recently demonstrated the synthesis of various metal-organic assemblies from organometallic half-sandwich complexes [86,87]. In particular, the authors have shown that a hexanuclear coordination cage, which is obtained from a reaction between $[(\text{cymene})\text{Ru}(\text{NO}_3)_2]$ with 3,5-pyridinedicarboxylic acid, can be co-crystallised with KOAc. Upon co-crystallisation, the entire assembly re-arranges into a dodecanuclear coordination cage that has icosahedral geometry [86]. These studies, coupled with those above show the flourishing area of metallo-supramolecular capsules and act as a comparison tool for the following studies that have been carried out in our research group.

2. Experimental overview

The following sub-sections are intended to firstly describe the syntheses of *C*-alkylresorcin[4]arenes and *C*-alkylpyrogallol[4]arenes that are relatively facile when compared with *p*-^{t}Bu-calix[*n*]arenes for example. Following this, the formation of hydrogen-bonded nano-capsules by means of crystallisation is addressed prior to solution phase assembly discussion. In both solution and the solid state, these types of assembly have been shown to encapsulate molecules other than solvent, a feature that is also discussed.

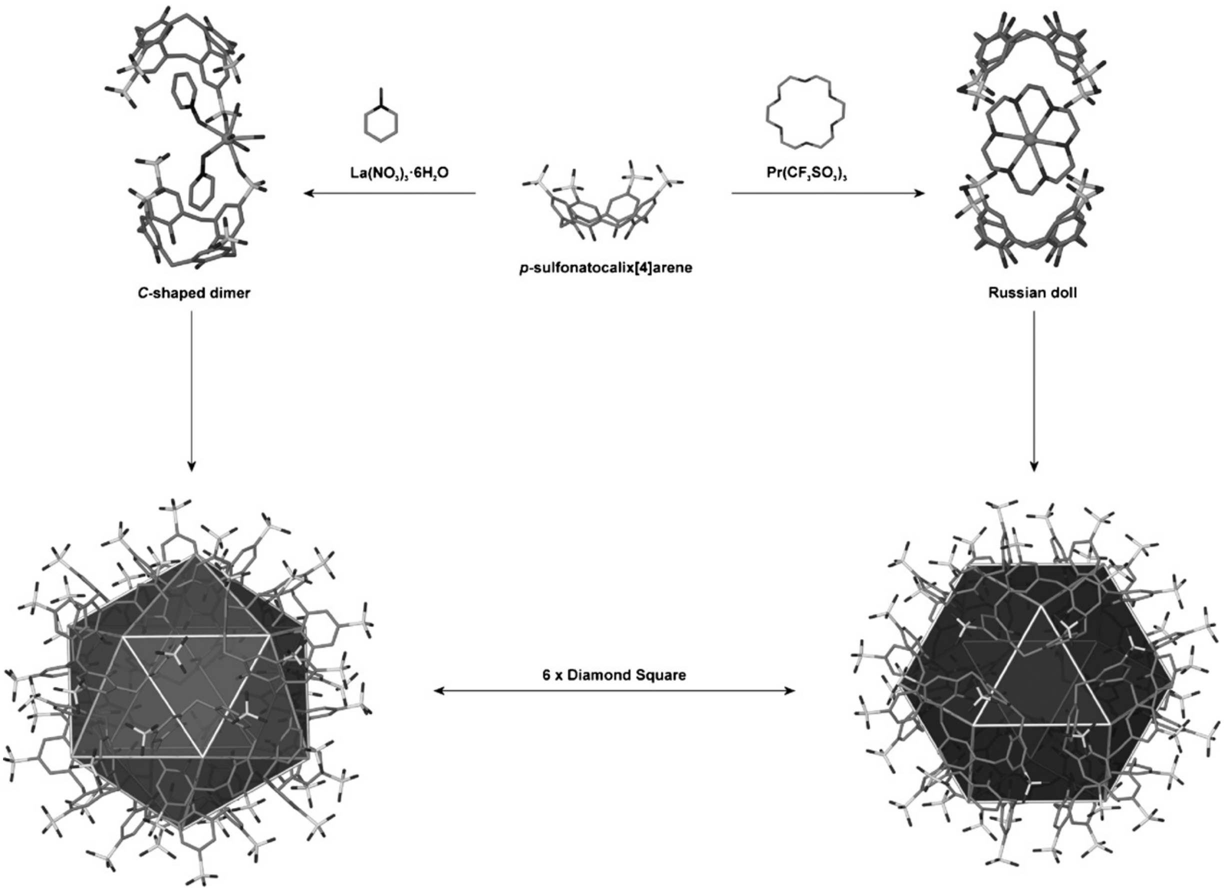
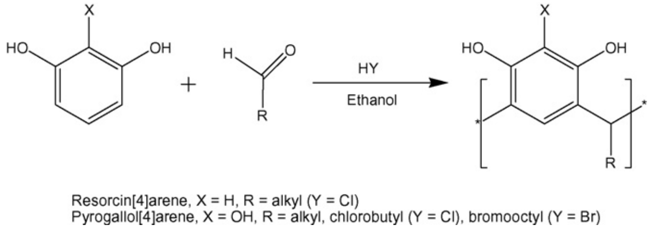


Fig. 9. Schematic formation of nanometre scale spheroids based on *p*-sulfonatocalix[4]arene. The icosahedron (Platonic) and the cuboctahedron (Archimedean) are dual solids and are related by a sextuple diamond square process. Figure was reproduced from Ref. [70] with permission from the copyright holders (RSC).

2.1. *Synthesis of the C-alkylresorcin[4]arenes and pyrogallol[4]arenes*

Since the pioneering work by Gutsche into the synthesis and (in particular the) characterisation of the *p*-^{t}Bu-calix[*n*]arenes, much effort has been invested by many to (in some cases selectively) synthesise a broad spectrum of calixarenes or calixarene-based materials [88]. If one takes the example of the synthetic procedures used to isolate the *p*-^{t}Bu-calix[*n*]arenes (where $n = 4$–8 in this instance), the cyclic tetramer, hexamer and octamer can be isolated in fair to good yield by varying reaction conditions. Variables employed include changing the base or solvent used, as well as the heating time and temperature. The cyclic pentamer, and heptamer are isolated in much lower yields (typically 5–7% for the pentamer) and involve slightly more complicated syntheses with respect to heating regimes for example, resulting in fairly labour intensive syntheses [88].

In stark contrast to the abovementioned examples, the cyclic tetrameric *C*-alkylresorcin[4]arenes and pyrogallol[4]arenes can be isolated in good to very good yields by the simple acid catalysed condensation of resorcinol or pyrogallol with an alkyl aldehyde of chosen chain length (many of which are commercially available at low cost) at reflux in ethanol over a matter of hours (Scheme 1) [89]. We have recently used two haloalkyl aldehydes, 5-chloropentanal and 9-bromononanal, to synthesise the corresponding pyrogallol[4]arenes under hydrochloric or hydrobromic conditions respectively [90]. The majority of these syntheses are facile and can be performed on a 100 g scale if so desired, although for the haloalkyl derivatives the situation is slightly different given that 9-bromononanal must be synthesised for example. Also in contrast to the *p*-^{t}Bu-calix[*n*]arenes, the workup for these compounds is far simpler, as the molecules tend to crystallise as the ethanol solvate upon cooling the reaction mixture. Hence the material is easily harvested and dried to afford a compound of sufficient purity for co-crystallisation or further reaction for example.



Scheme 1. The general acid catalysed condensation used to form *C*-alkylresorcin[4]arenes, *C*-alkylpyrogallol[4]arenes and *C*-haloalkylpyrogallol-[4]arenes [89,90].

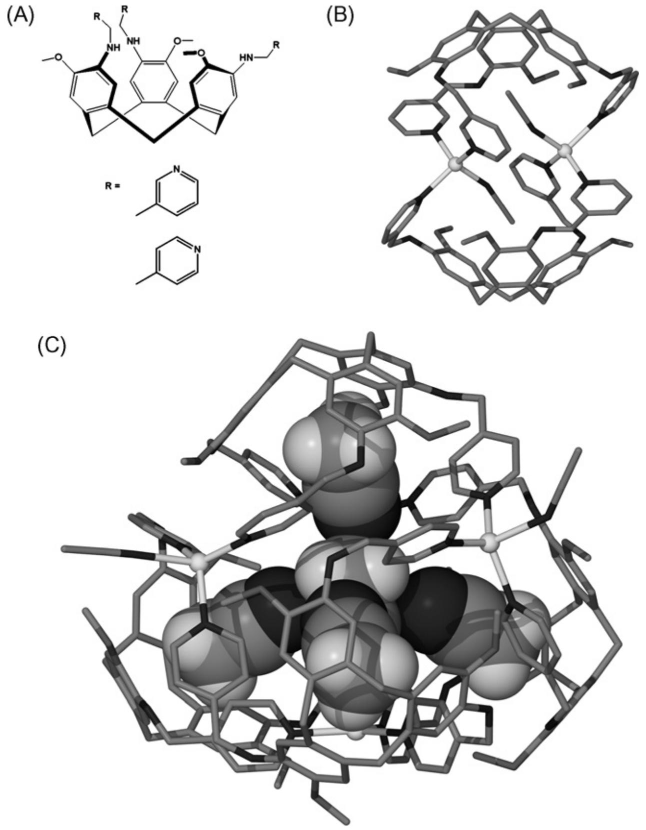
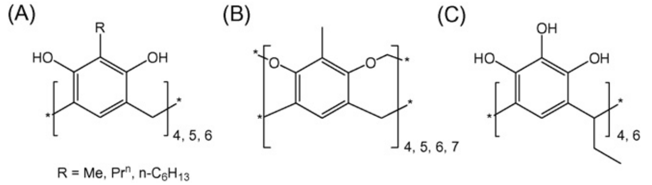


Fig. 10. Diagrams of modified CTVs and their assembly into metallo-supramolecular capsules. (A) The 3- and 4-pyridyl derivatives. (B) Dimeric capsule (formed from the 3-pyridyl derivative and silver hexafluorophosphate) shrouding two silver ligated acetonitrile molecules. (C) Starburst tetrahedron (formed from the 4-pyridyl derivative and various silver salts) shrouding five acetonitrile molecules. Anions are omitted in all figures for clarity [84,85].

Konishi *et al.* synthesised resorcin[4,5 and 6]arenes by reacting 2-alkylresorcinols with trioxane or formaldehyde diethyl acetal (Scheme 2A) [91]. Following this study, Sherman and co-workers synthesised a series of expanded [*n*]cavitands where $n \geq 4$ (Scheme 2B).[92] In addition, *C*-ethylpyrogallol[4 and 6]arene were also synthesised in a mixture, separated and structurally characterised by Nissinen and co-workers (Scheme 2C) [93]. Although this is the case, the pyrogallolarene pentamer is yet to be isolated. All of the mentioned syntheses are relatively low yielding compared to the traditional preparations for the respective tetramers, and as is the case for *p*-^{t}Bu-calix[*n*]arenes, the preferential synthesis of larger pyrogallolarenes will likely require further study and variation in reaction conditions to increase reaction efficiency.



Scheme 2. Larger resorcin[4]arenes, cavitands and pyrogallolarenes that have recently been synthesised under various reaction conditions [91–93].

2.2. *Solid-state assembly of hydrogen-bonded C-methylresorcin[4]arene and C-alkylpyrogallol[4]arene nano-capsules through crystallisation*

Although there are numerous reports on the assembly of *C*-methylresorcin[4]arene (CMRC) with various different co-crystallising species to form different solid state non-covalent networks for example [94,95], it was the discovery of a chiral self-assembled nano-capsule in 1997 that spurred recent efforts in the formation of very large and voluminous spherical non-covalent molecular capsules with these and similar molecules [96]. When crystallised from a water/nitrobenzene mixture, six CMRC molecules assemble with eight structural water molecules through 60 hydrogen-bonds and encapsulate nitrobenzene solvent molecules in the resulting capsule that has an internal volume of ~1500 Å^3 (Fig. 11A). Progress in the structural study of hexameric resorcin[4]arene nano-capsules has been limited, but Ugono and Holman recently reported an achiral variant of the capsule that was formed by replacing six of the structural water molecules with 2-ethylhexanols (Fig. 11B) [97]. The capsule was further found to encapsulate two 2-ethylhexanol molecules.

Following the 1997 discovery, Mattay and co-workers (in 1999) reported the synthesis and self-assembly of *C*-isobutylpyrogallol[4]arene from acetonitrile into a hexameric nano-capsule that has an internal volume similar to that of the CMRC analogue (~1250 Å^3, Fig. 12) [98]. The capsule is held together by 72 hydrogen bonds between ‘upper rim’ hydroxyl groups, although no order is imparted on the interior by the hydrogen-bonding groups. Furthermore, despite the capsule being successfully assembled, the authors stated difficulties in reproducing capsule formation by crystallisation. Notably, the need for structural water molecules is precluded in nano-capsule formation with this molecule as the additional complementary ‘upper-rim’ hydroxyl functionalities prevent incorporation of other species in the hydrogen-bonded seam.

By performing a mixed pyrogallol and resorcinol synthesis, Atwood *et al.* reported the formation of a statistical ‘upper rim’ mixture of the cyclic tetrameric products that would be expected [99]. From this mixture, six molecules of one particular compound (comprising three pyrogallol and one resorcinol subunit) were found to self-assemble when crystallised from diethyl ether into a distorted capsule that encapsulates six solvent molecules. The result of the distortion in the capsule, which is due to the absence of one hydroxyl group on each macrocycle, is the organisation of the interior solvent molecules, and the binding of additional diethyl ether molecules on the exterior of the assembly.

More recent studies in our group focused on the quantitative conversion of pyrogallol[4]arene monomers into corresponding hexameric nano-capsules. Examination of various solvents found ethyl acetate to be most successful for this purpose. Slow evaporation of ethyl acetate solutions of PgC$_5$, PgC$_6$, and PgC$_7$ afforded near quantitative conversion to the corresponding hexamer as confirmed by single crystal X-ray diffraction studies [100]. The structures for the PgC$_5$ and PgC$_7$ nano-capsules were essentially isostructural to that of the *C*-isobutyl analogue

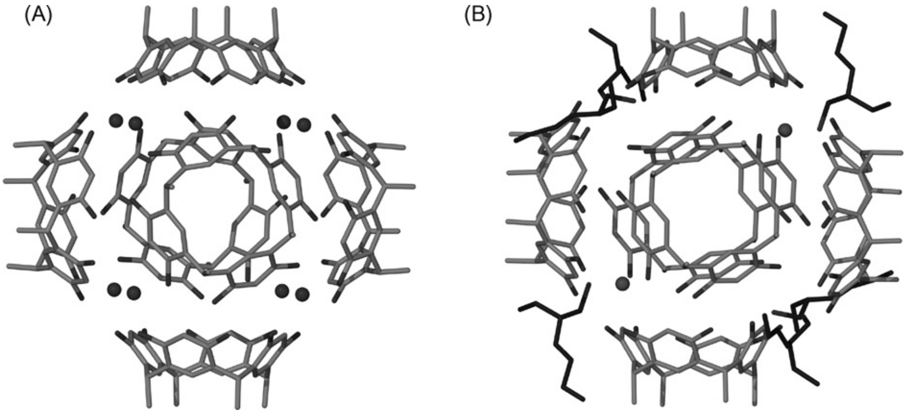


Fig. 11. Stick diagrams of the (A) chiral [96] and (B) achiral [97] CMRC hydrogen-bonded nano-capsules formed by crystallisation from nitrobenzene/water or 2-ethylhexanol/water, respectively. Note the difference in chirality of the central CMRC molecules in each capsule. Hydrogen atoms have been omitted for clarity in both (A) and (B) and structural water molecules are shown as dark spheres. Figures not to scale.

reported by Mattay and co-workers [98], but PgC_6 was found to crystallise in an unusual fashion with distortion to (and interaction between) some of the hydrogen-bonded faces between neighbouring nano-capsules. Following these studies, and in contrast to the report by Mattay and co-workers [98], we also found acetonitrile to be useful for reproducible crystallisation of hexameric nano-capsules for PgC_4–PgC_8, the majority of which have been structurally characterised by X-ray diffraction studies [101].

In relation to the latter of these results, we investigated the possibility of encapsulating probe molecules within these large assemblies with a view to reporting on the interior of these voluminous capsules [102–104]. As a starting point we picked pyrene butyric acid (PBA) as a potential guest molecule. Sonication of an acetonitrile solution of PgC_6 in the presence of PBA, followed by standing resulted in the formation of diffraction quality crystals [102]. Solid and solution phase studies showed the nano-capsule to contain more than one PBA (Fig. 13A), and the guest molecules were found to be separated by ∼8 Å and to reside on the capsule walls, effectively ‘sticking’ to the assembly through π-stacking and CH···π interactions. The nano-capsules were found to be stable in non-polar media and were studied using spectrofluorometry in a series of experiments in the presence of an appropriate quencher, dimethylaniline (DMA). When a larger probe incorporating a ‘built-in’ quencher was employed, 4-[3-(9-anthryl)propyl]-*N*,*N*-dimethylaniline (ADMA), the probe was found to crystallise on the interior of the isostructural nano-

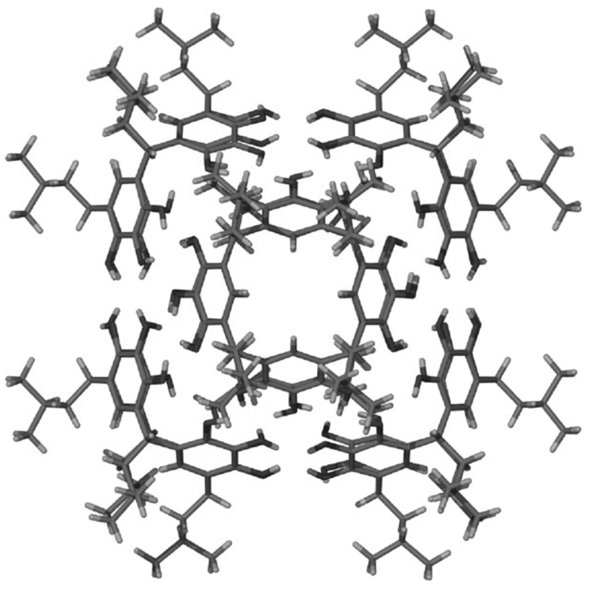


Fig. 12. The *C*-isobutylpyrogallol[4]arene hydrogen-bonded nano-capsule [98].

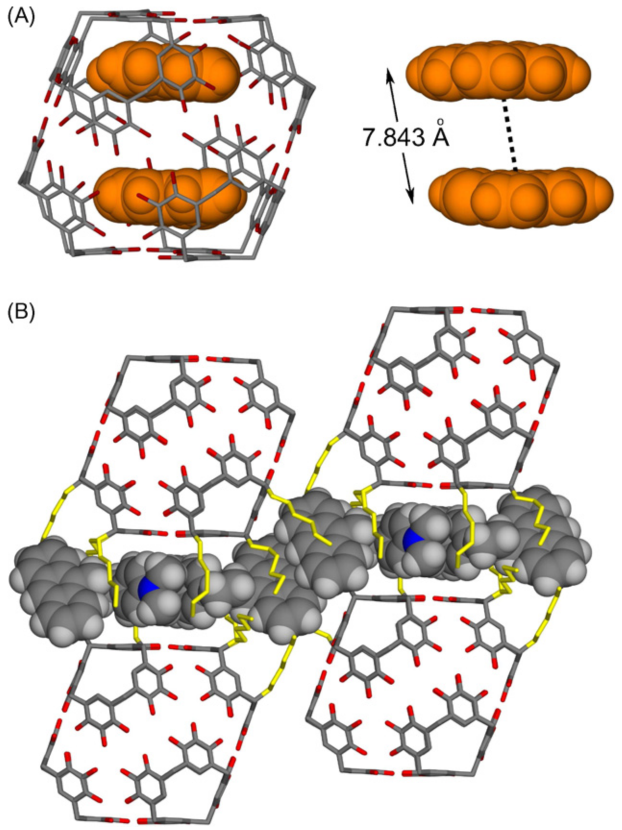


Fig. 13. Diagrams of (A) PBA encapsulated in a hexameric PgC_6 nano-capsule [102], and (B) the ADMA channels that result in the ‘pushing apart’ of neighbouring nano-capsules [103].

capsule as expected [103,104]. On occasion, however, the probe was also found to crystallise on the exterior of the capsule [103], resulting in ADMA channels in the solid state which 'push' neighbouring nano-capsules apart (Fig. 13B). Spectrofluorometric study of both materials gave markedly different spectra, indicating that when crystallised *exo*- to the capsule, the probe molecules remain sequestered for a time as part of an aggregated system once crystals are dissolved in THF. We are currently continuing these experiments with a view to encapsulating different probe molecules, determining the conformation of ADMA within hexameric PgC*n* nano-capsules, and ascertaining the guest–capsule interactions required for enhanced stability in the solution phase.

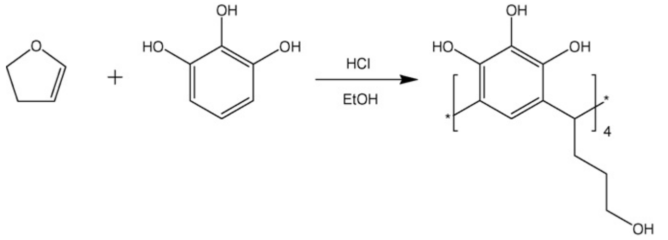
2.3. Solution based assembly of C-alkylresorcin[4]arenes and C-alkylpyrogallol[4]arenes

There has been much interest in the solution phase encapsulation behaviour of the *C*-alkylresorcin[4]arenes and *C*-alkylpyrogallol[4]arenes [105–114]. Of those (other than ourselves) who are interested in this area, the Rebek and Cohen groups have been most active in advancing the characterisation of these large non-covalent assemblies in the solution phase. There have been numerous studies on various solvents used to assemble these nano-capsules in solution, and diffusion NMR techniques have become increasingly useful for such purposes [106–108]. Cohen has shown that mixtures of pyrogallol[4]arenes have a degree of self-recognition over a period of ∼24 h, prior to them reaching an equilibrium as mixed nano-capsules [108].

With respect to much of the pyrogallol[4]arene work described within this manuscript, it is the encapsulation of other species that is especially interesting. In this regard, Rebek and co-workers have extensively studied the encapsulation of tetraalkylammonium salts, with more recent works focusing on the inclusion of glutaric acid and β-methyl D-glucopyranoside in resorcin[4]arene nano-capsules [109–113]. The same group has also recently synthesised resorcin[4]arenes that are selectively modified at the lower rim with probes, and the encapsulation of different probes can be followed using fluorescence resonance energy transfer [114]. By doing so, the authors of these papers have successfully utilised various NMR techniques to follow molecular encapsulation and self-assembly processes in these systems.

3. Metal-organic pyrogallol[4]arene nano-capsules; structural analogues to hydrogen-bonded assemblies

Driven partly by the reaction of copper with cyclodextrin [115], in addition to the potential formation of metal-organic polyhedra, copper(II) nitrate and gallium(III) nitrate were reacted with various pyrogallol[4]arenes. The results of these combinations were remarkable and led to an expansion in the size of nano-metre scale metal-organic capsules. We have also recently shown that reacting zinc(II) nitrate with *C*-propylpyrogallol[4]arene in pyridine resulted in a dimeric metallated capsule, and that combining caesium chloride with different pyrogallol[4]arenes in acetonitrile can result in the formation of dimeric ionic capsules. The following sections describe each type of metal-based capsule and place them within similar assemblies reported to date (outlined above).



Scheme 3. The synthesis of *C*-propan-3-olpyrogallol[4]arene [116].

3.1. Copper-based metal-organic pyrogallol[4]arene nano-capsules

The first of the results in this area came from the combination of *C*-propan-3-olpyogallol[4]arene and copper(II) nitrate in acetone and water [116]. Although not mentioned in Section 2.1, *C*-propan-3-olpyrogallol[4]arene was synthesised by a modified acid catalysed synthesis for a hydroxyl footed cavitand using 3,4-dihydro-2H-pyran, and resorcinol has been replaced with pyrogallol (Scheme 3) [117].

Upon allowing the mixture to stand over several days, single red crystals suitable for X-ray diffraction techniques formed [116]. Structural solution showed the metal to have reacted with the macrocycle, and a total of thirty components assembled into a metal-organic nano-capsule with elimination of 48 of the 'upper rim' pyrogallol[4]arene hydrogen atoms and the concomitant formation of 96 new Cu–O bonds (Fig. 14). Prior to this reaction, and to date, we are yet to assemble a hydrogen-bonded nano-

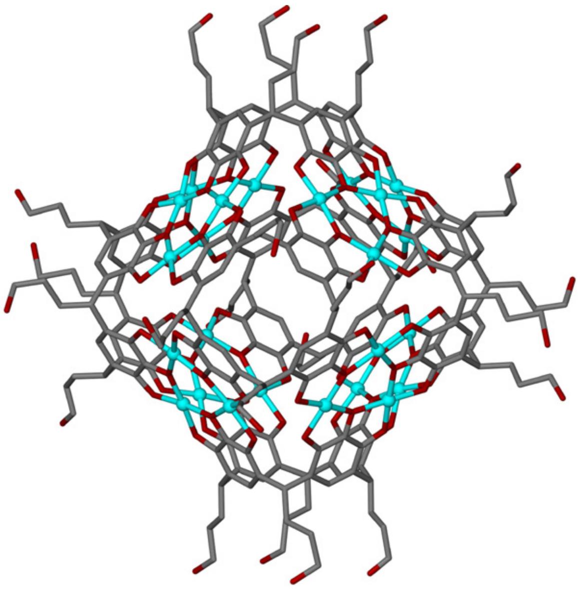


Fig. 14. The metal-organic nano-capsule formed by combining *C*-propan-3-olpyrogallol[4]arene with copper(II) nitrate [116]. Hydrogen atoms, solvent molecules and apical copper ligands are omitted for clarity.

capsule similar to those shown in Section 2.2 for PgC_3OH. When the distances between the oxygen atoms of the *C*-propan-3-olpyrogallol[4]arenes in the metal-organic capsule are compared to those in *C*-alkylpyrogallol[4]arene hydrogen-bonded nano-capsules [100], the two types of assembly are found to be very closely related, and it appeared that the non-covalent capsule was a suitable template for the insertion of metal centres into theoretical square planar binding sites. Examination of the extended structure showed that some of the 'lower rim' hydroxyl tails were coordinating to some copper centres in adjacent nano-capsules to form a coordination polymer such that each capsule links up to four neighbouring symmetry equivalents. This material was found to have limited solubility in organic solvents, but the material was characterised by MALDI-TOF mass spectrometry.

More recently we discovered that reaction of any *C*-alkylpyrogallol[4]arene (where alkyl = ethyl − undecyl) with excess copper(II) nitrate in methanol results in the instant formation of a fine brown precipitate in each case [118]. The precipitates were found to be highly soluble in various organic solvents (acetone, THF, chloroform, etc.), and were studied using MALDI-TOF mass spectrometry. The observations of the studies were unexpected, and showed a broad bi-modal distribution of masses. Within this range was a peak corresponding to the mass of an 'empty' capsule that is composed of just 6 pyrogallol[4]arenes and 24 copper centres (that have no apical ligands). The maximum peak on the right hand side of the bi-modal distribution of each metal-organic nano-capsule corresponded to the 'empty' capsule plus 633–635 mass units. This mass roughly corresponds to the encapsulation or ligation (at the copper centers) of ~20 molecules of methanol, or ~35 water molecules (which solely would be unlikely given that the only source of water is the hydrate content of the copper(II) nitrate), or any combination of both which would not be unexpected given presence of both species in the reaction mixture.

For the copper PgC_3 nano-capsule, it was possible to recrystallise the brown precipitate from acetone [118]. Although the crystals formed were very small and weakly diffracting, it was possible to obtain a partial structure that showed the expected structure (Fig. 15). This partially confirms the presence of the aforementioned 'empty' capsules and would go some way to explaining the poor diffraction of the single crystals based on varied capsule solvent occupancy for example.

Upon moving to very long alkyl chains at the lower rims of the pyrogallol[4]arene monomers (PgC_{12} and PgC_{13}), we found that crystallising these materials from ethyl acetate afforded bi-layer type structures in the solid state [118]. Indeed, we are yet to crystallise these materials in the hexameric nano-capsule motif, and as this was the case, we investigated whether it would be possible to form the corresponding copper metal-organic nano-capsules for these pyrogallol[4]arenes. Following the procedure outlined above, a brown precipitate was formed for both PgC_{12} and PgC_{13}, and MALDI-TOF analysis showed the formation of the metal-organic capsule. This therefore allows us to form such nano-capsules from materials that do not naturally form the hydrogen-bonded analogue in the solid state, even from a good 'capsule forming' solvent.

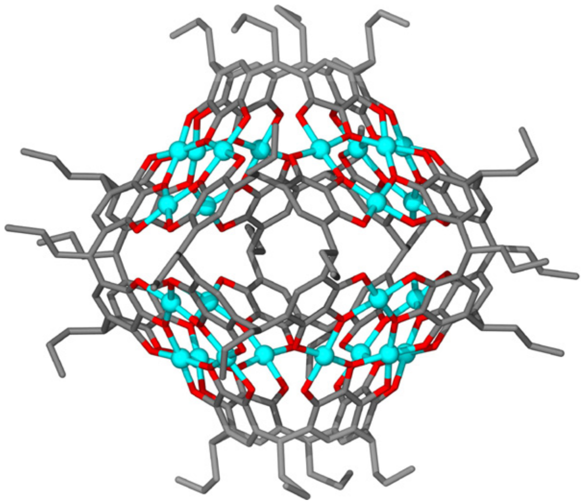


Fig. 15. Partial structure of the metal-organic nano-capsule formed by combining *C*-propylpyrogallol[4]arene with copper(II) nitrate in methanol [118].

As it was possible to instantly synthesise a series of metal-organic nano-capsules as outlined above, we investigated whether it was possible to also instantly synthesise mixed pyrogallol[4]arene analogues [118]. By reacting copper(II) nitrate in a similar way with a 1:1 mixture of PgC_6 and PgC_{11}, a fine brown precipitate also formed that was found by MALDI-TOF mass spectrometry to contain all the different permutations of the two pyrogallol[4]arenes in corresponding metal-organic capsules (Fig. 16). As discussed in Section 2.3, Avram and Cohen showed that pyrogallol[4]arenes, in mixtures, have a degree of self-association over a period of ~24 h [108], but

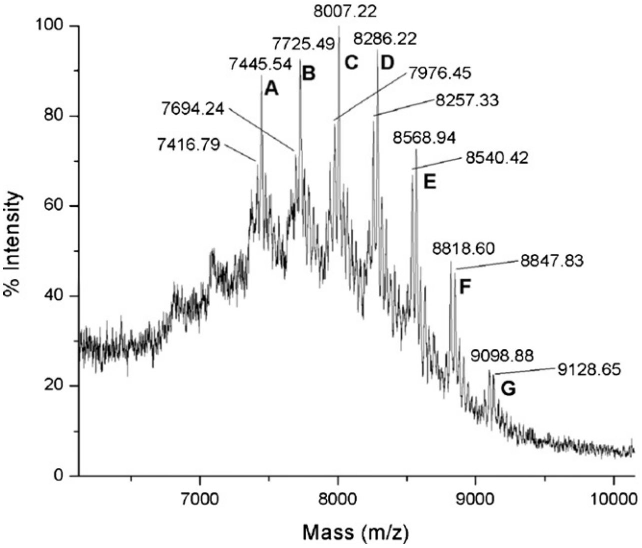


Fig. 16. MALDI-TOF mass spectrum obtained for the copper mixed pyrogallol[4]arene nano-capsules. A–G represents the 6:0, 5:1, 4:2, . . ., 0:6 ratios of *C*-hexyl:*C*-undecylpyrogallol[4]arenes present in the metal-organic nano-capsule mixture [118].

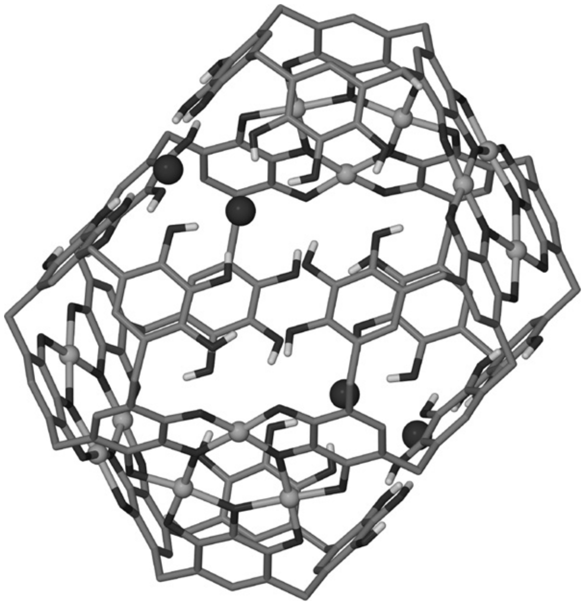


Fig. 17. The Ga PgC_3 nano-capsule showing the distorted 'rugby-ball' nature of the assembly and the water molecules occupying the surface voids (or gates) [119]. The PgC_3 propyl chains, as well as solvents of crystallisation and hydrogen atoms (except for OH) are omitted for clarity.

following this, mixed hydrogen-bonded nano-capsules result. For the metal-organic capsules formed here, it is apparent that the copper centres bind pyrogallol[4]arenes very rapidly, especially when one considers the formation of 'empty' nano-capsules, as confirmed in the MALDI-TOF analysis. Such a phenomenon lends itself to possibly indiscriminate encapsulation uses, as well as guest retention and extraction for example.

3.2. Gallium-based metal-organic pyrogallol[4]arene nano-capsules

By exchanging copper(II) nitrate for gallium(III) nitrate in an acetone/water solvent system containing PgC_3, diffraction quality colourless single crystals form over a number of hours [119]. Structural analysis of this material afforded a metal-organic capsule composed of six PgC_3 molecules and 12 gallium centres that has a distorted 'rugby-ball' like shape which is markedly different to the spherical type nano-capsules described in Section 3.1 (Fig. 17). In comparison with the copper nano-capsules, in which 24 upper rim OH groups remain, only 36 hydrogen atoms are eliminated with the concomitant formation of 48 Ga–O bonds, leaving 36 'upper rim' hydroxyl groups present. The distortion in the metal-organic capsule architecture results in the formation of 'gates' to the interior, with surface voids occupied by waters of crystallisation (Fig. 17). The interior of the assembly was found to contain acetone and waters of crystallisation, the latter of which form zig–zag chains that span the width of the assembly. Within this system, PgC_3 can be exchanged for PgC_5, and single crystals suitable for X-ray diffraction studies can be grown [120]. Structural analysis of these crystals shows the same gallium nano-capsule motif, albeit with the different chain lengths radiating from the 'lower rims' of the pyrogallol[4]arenes.

When an acetonitrile/water solvent system is used instead of acetone/water, crystals can be grown for a number of mixtures containing gallium and various *C*-alkylpyrogallol[4]arenes [120]. In some cases we have found these to be unstable toward solvent loss after removal from the mother liquor. However, for PgC_5, the crystals are stable toward solvent loss and structural analysis of these single crystals once again shows the favourable gallium nano-capsule motif similar to that shown in Fig. 17 with the assembly composed of 6 PgC_5's and 12 Ga centres, although the exact location of the encapsulated acetonitrile molecules could not be determined. Despite some of the crystals formed being susceptible to solvent loss, thus making structural study difficult, the solvent change shows the robustness of this system and generality of capsule formation. It is therefore predicted that similar metal-organic nano-capsules will form with other pyrogallol[4]arenes that are possibly functionalised at the 'lower rim'.

3.3. Mixed metal-organic pyrogallol[4]arene nano-capsules

Given that the copper addition in methanol was so effective in metal-organic nano-capsule formation, single crystals of the gallium *C*-propylpyrogallol[4]arene nano-capsule were suspended in an acetone/methanol mixture. Addition of methanolic copper(II) nitrate resulted in instant crystal dissolution and a colour change from blue/green to red/brown occurred [118]. Slow evaporation overnight afforded single red crystals that were examined using a synchrotron radiation source and showed adequate diffraction. Structural solution showed a metal-organic assembly similar to the 'Cu-only' PgC_3 nano-capsule shown in Fig. 15, although the crystals were of different symmetry and had disparate unit cell dimensions [118]. As copper and gallium are close to one another in the periodic table, the crystal structure could be solved with either metal present. Indeed it is difficult to identify which sites are occupied by copper or gallium in the resulting metal-organic nano-capsule and in order to confirm the presence of both, inductively coupled plasma (ICP) analysis was employed, and afforded a Cu:Ga ratio in the crystalline material. Given that (as described in Section 3.2), the gallium nano-capsules have 'gates' that are open for copper attack (Fig. 18A), one might expect the assembly resulting from copper addition to comprise 12 Ga and 12 Cu centres, or full expulsion of Ga from the assembly with formation of the 24 Cu species. Surprisingly, ICP analysis showed there to be 16 Cu and 8 Ga centres present (from a 2:1 ratio), indicating that remarkably only some of the Ga centres are expelled from the assembly. We postulate that the structural correction from 'rugby ball' to 'sphere' associated with copper insertion (Fig. 18B) may force some degree of strain on the gallium centres, resulting in selective expulsion and the formation of mixed copper/gallium 'faces' in the nano-capsules. It is also likely that averaging through the crystal structure would preclude exact location of particular metal sites, but this is an area we are currently investigating further, as is other mixed metal systems.

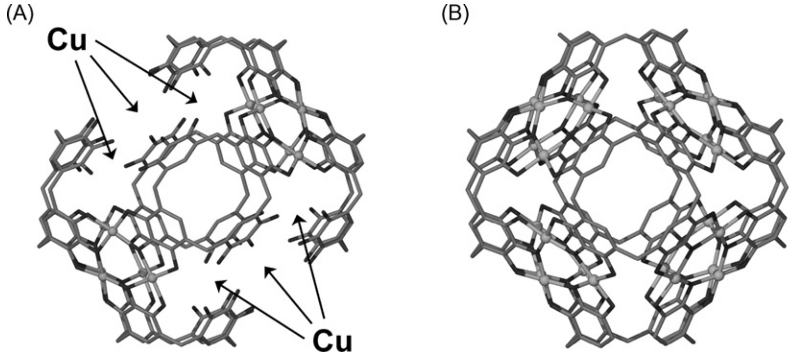


Fig. 18. (A) The 'gates' that act as potential entry points for copper in pre-formed PgC_3 Ga nano-capsules. (B) The structure of the PgC_3 Cu/Ga-MONC. In both views, *C*-propyl chains as well as hydrogen atoms, apical metal ligands and solvents of crystallisation have been omitted for clarity. In (B), mixed copper and gallium centers are shown in only one colour [118].

3.4. Metallated dimeric pyrogallol[4]arene capsules

In a distinctively different solvent system to those used for the copper, gallium and mixed copper/gallium nano-capsules described above, addition of zinc(II) nitrate to a pyridine solution of PgC_3 results in the formation (upon standing over a number of days with slow evaporation of pyridine) of single yellow crystals grow that are suitable for X-ray diffraction studies. Structural solution shows the formation of a dimeric pyrogallol[4]arene capsule that incarcerates a pyridine molecule, and that is stitched together by eight zinc centres (Fig. 19) [121]. The two PgC_3 molecules in the metal-organic capsule are arranged asymmetrically, and the pyrogallol[4]arene arrangement bears resemblance to a hydrogen-bonded analogue reported by Rebek and co-workers [122]. This metal-organic capsule can therefore be considered as another example of how hydrogen-bonded templates are useful precursors for the formation of such analogues under specific conditions.

When analysed using ^{1}H NMR, the chemical shifts of the molecule show that the relatively small capsule interior (~140 Å) is restrictive [121]. This is due to a type of 'screwing-down' of the capsule framework to allow metal coordination to the upper rim oxygen centres. Furthermore, when compared to a study of the chemical shifts of pyridine as part of a carceplex by Chapman and Sherman [123], the guest in the dimeric metallated capsule appears to be more significantly restrained, indicated by more significant Δ ppm values for protons of incarcerated pyridine. The coordination spheres of the metal centres holding the capsule together are completed by pyridine ligands, resulting in a shape reminiscent of a pelton wheel, but these ligands are exchanged in the solution phase and are therefore only weakly bound (they are also absent in the mass spectrum).

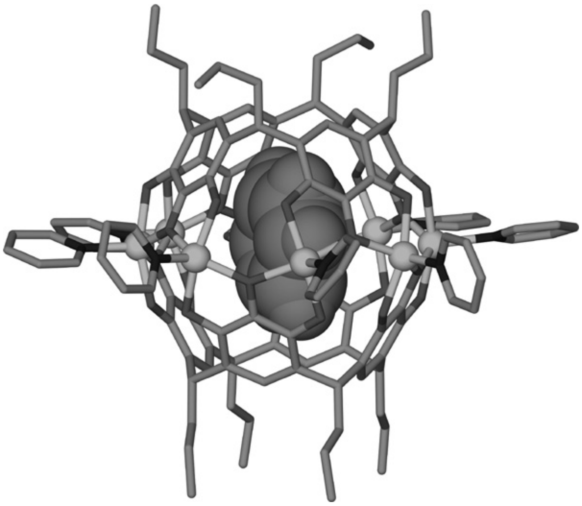


Fig. 19. The asymmetric dimeric octa-metallated Zn-PgC_3 capsule showing the incarcerated pyridine molecule (purple) and the pyridine ligands that complete the zinc coordination spheres. Hydrogen atoms, except those in the space filled encapsulated pyridine are omitted for clarity [121].

More recently we have also found that it is possible to change the guest species by simply employing a 3-methylpyridine zinc(II) nitrate complex as a starting material rather than the pyridine complex used to form the dimeric metallated capsule shown in Fig. 19. In doing so, 3-methylpyridine (3-MePy) is encapsulated in the resulting dimeric capsule and eight zinc centres are ligated by 3-MePy molecules [124]. As it was not possible to crystallise this compound from pure 3-MePy, dialysis was performed on the material in order to exchange these ligands for DMSO. Upon slow evaporation of DMSO under a flow of nitrogen, single crystals of the dimeric capsule containing 3-MePy were obtained (Fig. 20). In contrast to the pyridine analogue described above, in which the guest undergoes rapid rotation within the assembly, the methyl group of encapsulated 3-MePy is oriented in the cavity of one PgC_3 and restricts rotation, as is evident in a series of NMR studies which show the proton signals of the capsule to be split by the asymmetry of the guest. In addition, it was also possible to interchange the DMSO ligands on the zinc centres by titrating 3-MePy into a solution, the result of which is the eventual displacement of the more electron withdrawing ligands. In doing so, the upfield chemical shifts of the guest are affected dramatically, and this demonstrates a degree of electronic translation between the exterior and interior of the capsule.

Notably these metal-organic assemblies are also easily synthesised, and given their robust nature, they offer the possibility for performing chemistry on pre-formed capsules while tying up potentially complicating OH functionality without the need for difficult or time consuming 'upper rim' protection or alteration.

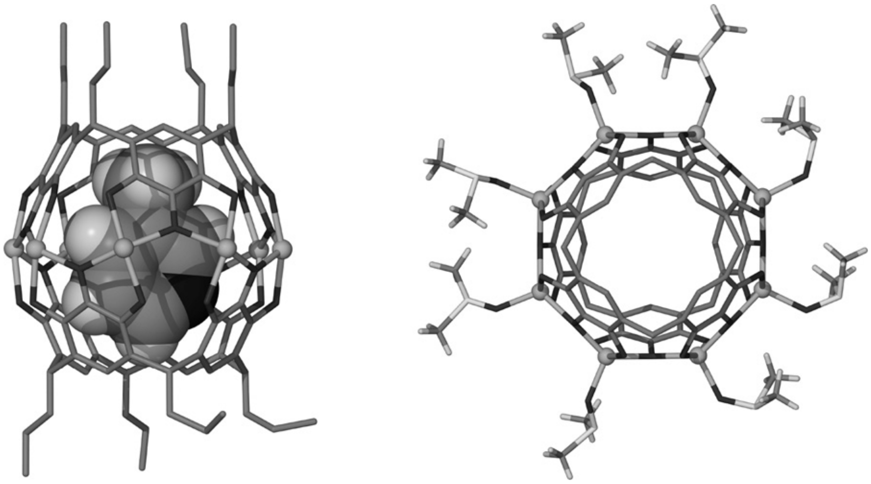


Fig. 20. Views of the dimeric metallated capsule showing encapsulation of 3-MePy in space filling representation, and DMSO ligands bound to the zinc metal centres [124].

3.5. Ionic dimeric pyrogallol[4]arene capsules

Recent times have shown an increased interest in alkali metal complexes of various types of calixarene, partly due to the fact that the typically bowl-shaped molecules offer the possibility for the study of interesting cation-π interactions in the solid state [125,126]. *p*-Sulfonatocalix[6]arene was studied for this purpose and the resulting complexes displayed polyhapto-aromatic bonding between cation and calixarene [125]. Åhman and Nissinen also recently showed that *C*-methylpyrogallol[4]arene (PgC_1) can act as an alkali metal receptor for potassium, rubidium, and caesium bromides and chlorides [126]. Their studies found the host to adopt a boat conformation as a requirement for strong cation–π interactions between the metals and the aromatic rings of PgC_1.

In our own studies in this area, we found that combining caesium chloride with either *C*-chlorobutylpyrogallol[4]arene (PgC_4Cl) or PgC_6 in aqueous acetonitrile resulted in the formation of colourless single crystals in both cases [127]. Structural solution of both caesium complexes showed that in each case, a dimeric ionic capsule containing two acetonitrile guests had formed although one capsule was in a head-to-head arrangement whilst the other was offset (Fig. 21). Within the head-to-head capsule, two caesium centres are bound to PgC_4Cl 'upper rim' oxygen centres, two aromatic rings, chloride anions and the nitriles of the guest molecules which are closely arranged within the overall assembly. The metal coordination in the offset capsule is markedly different in that four caesium centres are bound only to PgC_4Cl 'upper rim' oxygen centres and chloride anions. The non-ligated guest molecules occupy the cavities of the PgC_6 molecules in a similar way to the PgC_4Cl capsule, and both assemblies are found to be part of extended bi-layer coordination polymers of capsules.

We are currently investigating other alkali metal salts in various solvent systems to further expand on these new capsule motifs, and plan to incorporate different guest species with appropriate functionality.

4. Concluding remarks and future prospects

When considering some of the largest supramolecular container assemblies formed to date [16,19,23,47–50,68–70,84–86], hydrogen-bonded pyrogallol-[4]arene capsules (either dimeric or hexameric) are useful for the encapsulation of reasonably large non-solvent molecules, as identified by X-ray diffraction studies [96–103,116,118–120]. From the work reviewed in this article, we have also shown that they are also useful templates for metal-organic analogues [116,118–121,124,127]. The remarkable replacement of 48 hydrogen atoms in the hydrogen-bonded 'seam' with 24 copper

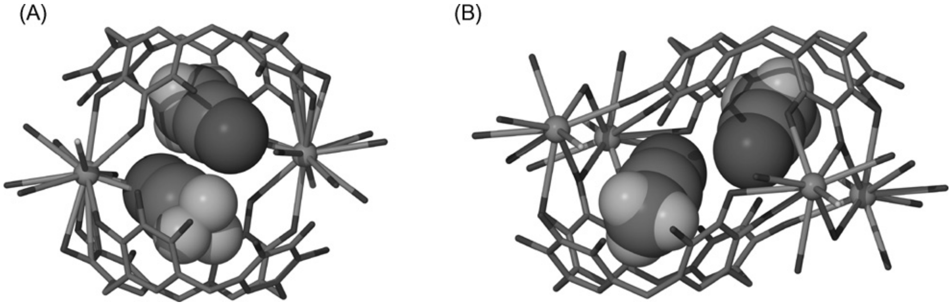


Fig. 21. The head-to-head (A) and offset (B) dimeric ionic capsules formed by combining caesium chloride with either PgC_4Cl or PgC_6 in aqueous acetonitrile [127]. Lower rim alkyl chains and hydrogen atoms omitted for clarity. The guest acetonitrile molecules are shown in space-filling representation.

centres is highly favourable and has resulted in the instantaneous formation of 'empty' or possibly kinetic metal-organic nano-capsules [118]. This feature can also be used to afford mixed metal capsules, and copper hetero-pyrogallol[4]arene nano-capsules. Although at a somewhat embryonic stage, these recent results show the potential of these instantly formed metallo-supramolecular assemblies as indiscriminate encapsulation tools or reaction platforms for example. We are currently exploring such possibilities with a view to assembling new interesting materials, along with the ultimate goal of uncovering larger metallo-supramolecular capsules. Different solvent systems and targeted hydrogen-bonded assemblies, when combined with various metal centres may also uncover new and interesting metal-organic assemblies for further examination and exploitation in host–guest chemistry.

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