Article

Metallosupramolecular Chemistry – What Now?

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About the Author

Peter Steel gained his chemistry qualifications from the University of Canterbury with a PhD under Jim Coxon's supervision. After two years postdoctoral study in France he returned to Canterbury where he is now Professor of Chemistry. His research interests are in organic chemistry, metallosupramolecular and heterocyclic Chemistry. He is currently the Chemistry Department's Director of Research.

Peter was awarded the RSNZ Hector Medal in 2009 for his research in the field of metallosupramolecular chemistry. The field is concerned with the synthesis and properties of large assemblies of organic molecules held together by metal atoms. These fascinating macromolecules can behave as nanoscale flasks within which one can isolate individual molecules. The research has potential applications in the fields of catalysis, drug delivery and nanotechnology. Currently work is directed towards the assembly of new supramolecular structures with unusual architectures, such as cages, boxes, rings, chains, necklaces and ladders, as well as the discovery of new interactions that could hold together such species. He received the UC Research Medal in 2008, an RSNZ James Cook Research Fellow for the 2006-2008 period, and the NZIC HortResearch Prize for Research Excellence in Chemical Sciences in 2006.

Peter has been successful in gaining several RSNZ Marsden grants and a number of Australian Research Council grants for collaborative projects with Profs. Richard Keene (Townsville) and Cameron Kepert (Sydney). He has published approximately 350 papers, despite being born in Gore.

It is almost ten years since I published an article in this journal entitled *Metallosupramolecular Chemistry – What Is It?*.[1] The field has evolved considerably since then and the present article is an update of the state of play in this burgeoning area of chemistry. For those readers who are not aware of this concept, *metallosupramolecular chemistry* involves the use of combinations of bridging organic ligands with metallic units to synthesise discrete or polymeric assemblies. The metal and ligand components have encoded information, both spatial and directional, that leads to the formation of a single product in high yield. The spontaneous self-organization of the components into a single aggregated structure occurs through molecular recognition, involving reversible processes that explore all the possible structures.

The simplest example of a discrete metallosupramolecular species is the *molecular square* **1**, first reported by Makoto Fujita in 1990.[2] It comprises a square-planar palladium(II) or platinum(II) centres for the corners and 4,4'-bipyridine as a linear bridging ligand for the sides. Since then numerous other examples have been reported where the size, shape and function can be varied by appropriate choice of ligand and metal. Very recently, Kitagawa[3] has shown that **1** [M = Pt(II)] undergoes oxidative polymerization with elemental iodine to generate a nanotubular assembly **2** with a uniform 6 x 6 Å internal channel. As described in my previous article,[1] the design concept used for the molecular square can be extended to other polygons (triangles, pentagons, *etc.*) by using appropriate angular components.


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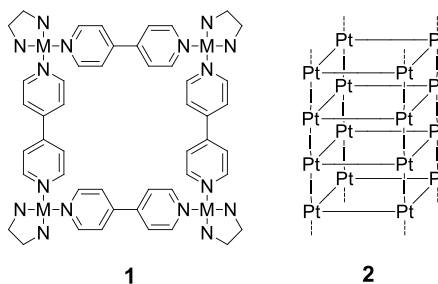
By using three-connector units this strategy can be adapted to 3D polyhedra, such as molecular cubes and dodecahedra. One of the most well-studied discrete 3D assemblies is the M_6L_4 *cage* **3**, which has an octahedral array of six palladium(II) atoms bridged by a tetrahedral array of four tridentate ligands **4**. This cage-like structure has an internal cavity, which Fujita has used as a nanoscale flask within which have been carried out many interesting chemical reactions.[4] We have prepared larger M_6L_4 cages, such as that derived from ligand **5** that increases the metal-metal separation from 19 to 24 Å.[5] However, due to the flexibility of the ligand, this cage collapses upon itself, such that the internal cavity is much smaller than we had hoped. Fujita has since reported much larger $M_{12}L_{24}$ cages derived from ligands such as **6**. These have a cuboctahedral structure with twelve Pd(II) atoms evenly distributed on an almost

spherical cage surface.[6] In another landmark paper,[7] the Fujita group has shown that subtle variations in ligand design can lead to different molecular cages, such as $M_{12}L_{24}$ cages, using ligand **7**, or giant $M_{24}L_{48}$ assemblies, using ligand **8**. It is only a matter of time before this will be extended to the enormous $M_{30}L_{60}$ and $M_{60}L_{120}$ assemblies that are theoretically possible from such component combinations. In unrelated work, other workers have prepared structurally diverse cage-like structures of varying size and shape using totally different building blocks.[8-10]
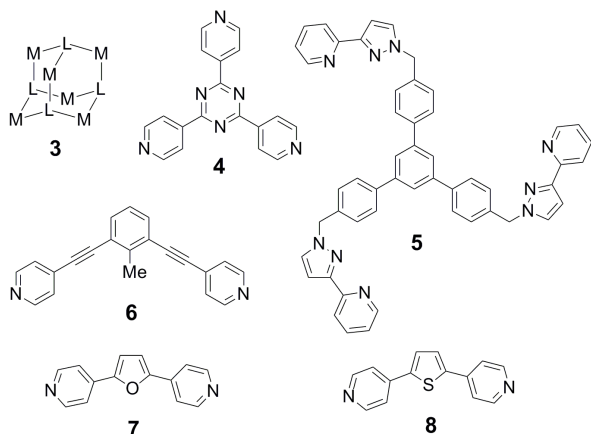
My previous report[1] contained much discussion of *helicates*. These consist of metal centres bridged by ligand strands that have sufficient flexibility to twist around the metals in a helical fashion. For example, **9** schematically represents a trinuclear double helicate, wherein three metals are bridged by two ligand strands. Many double and triple helicates have been reported over the last decade, some of which have useful properties. For example, the recently reported dinuclear iron(II) triple helicate formed from ligand **10** displays interesting spin crossover behaviour.[11] Quadruple helicates are much less common. Following our earlier report of the first of these, a number of other examples using square planar metal centres have been reported.[12] We have since prepared a quadruple helicate with square pyramidal copper(II) centres using ligand **11**.[13] Circular helicates have also been the subject of much recent interest.[14]
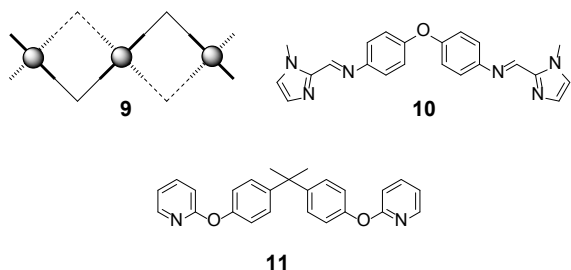
Intriguingly, helicates can serve as precursors to a range of topologically interesting species.[15,16] [2]-Catenanes represent two interlocked rings that are not covalently bonded to one another, but cannot be separated without breaking bonds. As explained in my previous article, these are most easily prepared by metal templation, whereby a mononuclear coordination complex **12** provides ligands that act as precursors to the two rings **13**. In a similar manner, a binuclear double helicate can serve as the precursor to a trefoil knot **14**. The first molecule with this topology was prepared by Sauvage using ligand **15** as the strands for the double helicate and then tying up the ends with an oligoethylene glycol chain. Extension of this design principle to a trinuclear helicate, using ligand **16**, leads, upon olefin metathesis, to a Solomon's link **17**, which is a doubly interlinked [2]-catenane. Work is currently underway to extend this even further to a tetranuclear helicate example that should lead to a pentafoil knot. There has been intense interest in this area of *chemical topology*, as has been summarised in two recent reviews.[15,16]
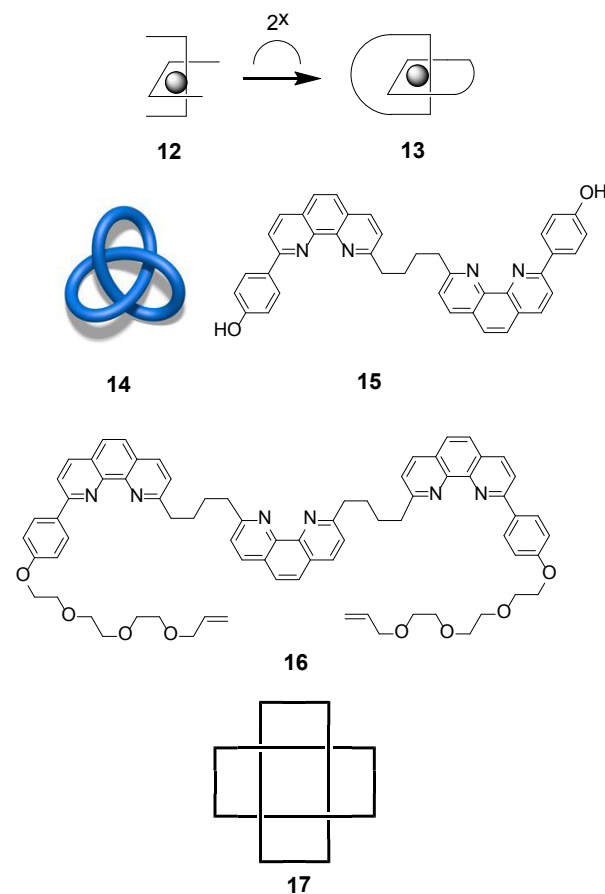
Unquestionably, the highlight of this area has been the chemical synthesis of *Borromean rings* **18**. These have an intriguing structure with three entangled rings but no two of which are interlocked. Despite this, the three rings cannot be separated from one another, although breaking one frees the other two. Synthetically this represents a significant challenge, for which there are several retrosynthetic routes. In a first approach, Siegel succeeded in using templation to prepare two such threaded rings.[17] Subsequently, Stoddart, Atwood and co-workers managed to prepare Borromean rings using self-assembly in a single one-step process.[18] The two building blocks, **19** and **20**, and the composite ring structure **21** are shown below. Simply combining the two precursors with zinc(II) ions results in a one-pot synthesis of the Borromean rings in 90% yield. The zinc atoms serve to template the synthesis by coordinating to one *endo*-tridentate binding domain of one ring and an *exo*-bidentate site of another, the final coordination site being occupied by a triflate anion. The structure was fully characterised by NMR, MS and X-ray crystallography. This remarkable reaction once again demonstrates the power of self-assembly in synthesis. Indeed, this synthesis is so straightforward that it has been developed into an undergraduate laboratory experiment.[19]

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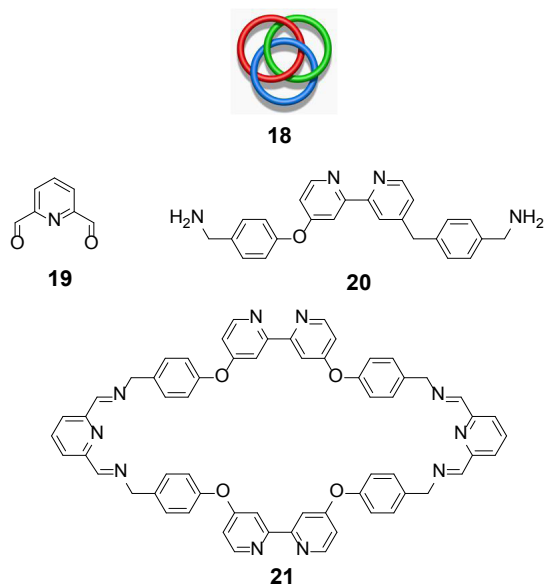
Much of the interest in catenanes and rotaxanes (rings threaded onto axles, with stoppers attached to prevent the ring from sliding off) has involved their incorporation into *molecular machines*. These are molecular scale devices that perform a function (such as translational or rotational movement) in response to an external stimulus, *e.g.* light, electropotential, pH, *etc*. Many such devices have been reported in recent years.[20] Rotaxanes within which a ring is shuttled between different sites on the axle have been particularly popular. A common stimulus for this has been the reversible oxidation of a four coordinate Cu(I) to five coordinate Cu(II), which results in migration of the Cu atom and the attached ring between two binding sites of different denticity.

The discussion thus far has centred on discrete assemblies. Probably more intensely studied over the last decade have been polymeric metallosupramolecular assemblies, which consist of 1D coordination polymers **22**, 2D grids **23** or 3D networks **24**. 1D coordination polymers come in many forms, the simplest of which consist of linear two-connecting ligand and metal components. We have prepared many of these in recent years, including chiral examples based on pyrazine bridges fused to bornane units. For example, the two C_2-symmetric isomeric ligands **25** and **26** react with silver(I) salts to assemble 1D coordination polymers that differ subtlety in terms of the directional nature of the polymers formed.[21] Other types of 1D coordination polymers include necklace- **27** and ladder-like **28** arrangements, examples of which we have also reported.[22]

2D grids have also been highly studied over the last decade, but by far the most attention has focussed on 3D networks **24**. Now known as *metal organic frameworks* (MOFs), these have been the subject of intense study over the last decade. This field dates from the pioneering work of Richard Robson[23] and underwent explosive expansion following a number of papers by Omar Yaghi.[24] The most well-studied of these is MOF-5, which is a porous 3D network constructed from zinc clusters bridged by terephthalate ligands **29**. By employing different bridging ligands, such as **30** and **31**, it is possible to control the size and shape of the resulting networks, with the result that solid
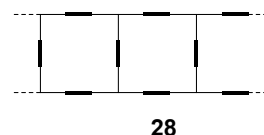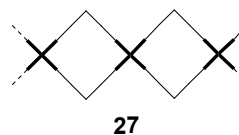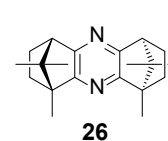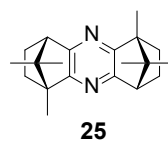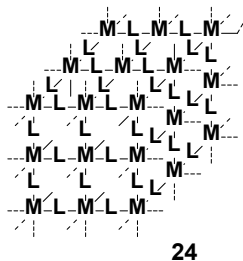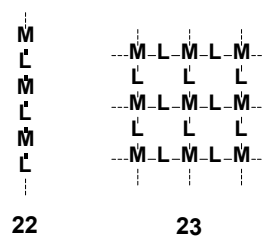
crystalline materials can be prepared with astonishingly high porosity and low density. For example, crystalline MOF-200, derived from bridging ligand **32**, has a density of 0.22 g cm^{-3} and a void volume of 90%. Interest in these compounds has centred on their ability to absorb gases within their internal cavities, with much work focussed on hydrogen absorption within MOFs as a possible method of hydrogen storage for a future *hydrogen economy*. Similarly, MOFs have been shown to be able to separate mixtures of gases.

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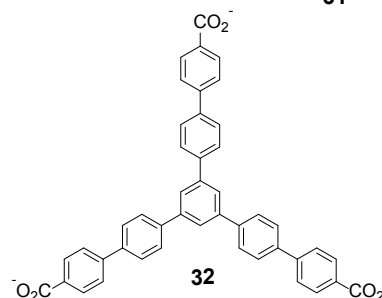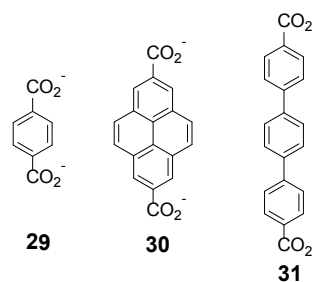
A particular feature of these materials is their ease of synthesis, typically being made in a one-pot solvothermal reaction. However, a common problem in MOF synthesis is that the large cavities involved encourage the formation of concatenated structures, in which the framework has a sec-

ond framework interpenetrated within the first. Two- and three-fold catenation have long been known to be common in 3D co-ordination polymers,[25] although examples are known of much higher levels of interpenetration, including 12-fold.[26] Although methods exist to avoid this problem, they are not general. Recently, Hupp[27] described a very simple procedure for the purification of MOFs contaminated with catenated impurities. It simply involves suspending the insoluble mixture in a solvent system of intermediate density, such that the denser catenated MOF sinks, whilst the less dense non-catenated MOF floats.

Such is the popularity of MOFs that they are now industrially prepared and commercially available. Much recent work has been carried out on so-called *post-synthetic modification* of MOFs.[28] This involves incorporating other functional groups into the structure of the bridging ligands. These can then be used as reactive sites for subsequent chemical reactions to modify the internal structures of the cavities. Such work is expected to have useful outcomes in various areas, such as catalysis. The enormous recent interest in MOFs has spawned other acronyms for related materials, such as COFs, MILs, IRMOFs, ZMOFs, PCNs and PCPs.[29]

As described above, the most commonly used M-L interaction involves the coordination of nitrogen heterocycles or aromatic carboxylates. Our own recent work in this area has focussed on a search for other useful interactions that might be employed as synthons for metallosupramolecular synthesis. The most developed of these is the *silver-alkene interaction*. Silver has long been known to bind to alkenes, a fact that has been exploited by organic chemists for the chromatographic separation of hydrocarbon mixtures,[30] and numerous silver-alkene complexes have been prepared and crystallographically characterized. Curiously however, this interaction had not been exploited as a potential building block for the assembly of new metallosupramolecular species, until our recent exploratory forays.

Our initial work in this area used the three divinylbenzenes **33**–**35** as bridging ligands that led to an intriguing array of supramolecular assemblies. These three isomeric bridging ligands furnished very different structures upon reaction with silver(I) salts. The *para*-isomer **33** led to the discrete M$_2$L$_2$ dimeric assembly **36** upon reaction with silver(I) perchlorate, whilst the *meta*-isomer **34** produced either an M$_2$L$_3$ cage or a 1D polymer, depending upon the anion involved. The *ortho*-isomer **35** proved to be more promiscuous by co-ordinating to silver through the benzene ring as well. We have since extended this to other oligovinylarenes, such as the tetravinylbenzene **37**, which upon reaction with silver tetrafluoroborate results in the formation of the interesting silver sandwich **38**, wherein two ligands gather together four silver atoms into a planar array. These results have led us to explore other alkene units appended to various central scaffolds, the results of which are yet to be reported. They have led us to believe that there may be many other potentially useful combinations of organic functional groups that could be combined with metal units as useful synthons for the construction of interesting metallosupramolecular assemblies. We are currently exploring these possibilities, which will form the basis of the third

chapter in this series: *Metallosupramolecular Chemistry – What Next?*
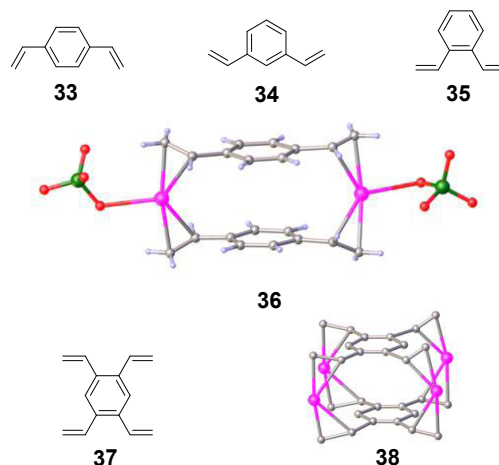
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