

Supramolecular coordination chemistry

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This Chapter reviews the literature reported during 2006 in the field of Supramolecular Chemistry. The review focuses on the design, synthesis and self-assembly of metal-based units leading to the construction of metallo-supramolecular architectures.

Highlights

Highlights include the synthesis and structural characterisation of Chiral Borromeanes, knots that are characterized by the Brunnian link,⁴ the formation of 1D luminescent inorganic micro- and nano-wires directed by Pt^{II}...Pt^{II} interactions,¹⁵ and the self assembly and crystallization of giant polyoxometalates, comprising both wheel shaped and hollow, spherical structures. These are combined together leading to a single mesoscopic molecule.⁶⁴ The direct crystallographic observation of the *in situ* generated Cp'Mn(CO)₂ (Cp' = methylcyclopentadienyl) 16 electron unsaturated complex by photodissociation of Cp'Mn(CO)₃ in a self assembled coordination cage has been achieved and shows that the geometry of an unsaturated 16 electron transition metal centre adopts a pyramidal geometry.⁶⁸

1. Introduction and scope

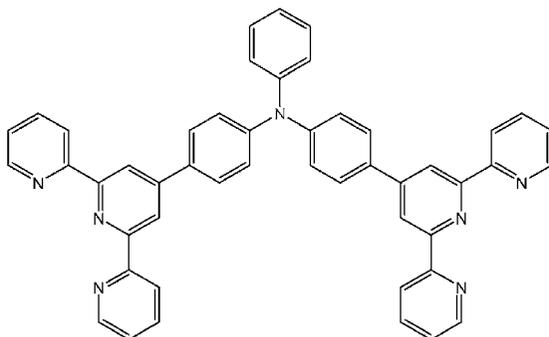
This report focuses on the development in design, synthesis and self-assembly of metal-based architectures and ligands designed to aid the construction of metallo-supramolecular architectures. As was the case last year, the degree of selectivity applied when compiling this account is, therefore, very high although we have attempted to summarise some of the most important developments. Several crystal structures have been included in this report to aid visualisation and conceptualisation of the many interesting architectures that have been characterised. For ease of representation and understanding a common colour scheme/size scheme is used in all the structural figures unless otherwise stated; the carbon atoms are light grey, nitrogen atoms white, metal ions large black spheres, sulfur atoms large grey spheres, oxygen or phosphorus atoms are small black spheres.

2. Metallomacrocycles

A new ditopic triphenylamine-based bis(terpyridine) ligand 4,4'-bis(2,2':6',2''-terpyridinyl)triphenylamine (**L1**) possessing the disubstituted triphenylamine unit as an angle-control element, which can form hexagonal metallomacrocycles, has been synthesized. This ligand system is found to form a unique hexagonal metallomacrocyclic family [Fe₆(**L1**)₆(PF₆)₁₂] and [Zn₆(**L1**)₆(BF₄)₁₂], utilizing terpyridine–metal(II)–terpyridine connectivity. The structures of the ligand and the corresponding

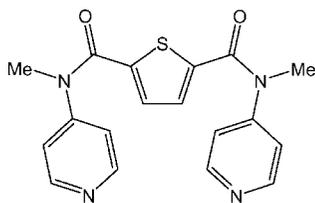
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metallomacrocycles were confirmed by means of ^1H and ^{13}C NMR, UV-Vis spectroscopy and mass spectrometry. Crystal structure analysis of the ligand **L1** shows that the angle between the two terpyridinyl moieties is 119.69° , which enables the formation of the hexagonal-shaped metallomacrocycles.¹

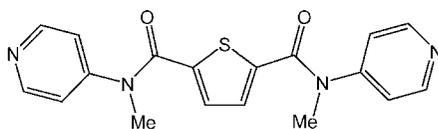


L1

The thiophene-based bis(*N*-methylamidopyridine) ligand $\text{SC}_4\text{H}_2\text{-2,5-(C(=O)-N(Me)-4-C}_5\text{H}_4\text{N)}_2$ (**L2**) has been found to react with silver(I) salts (AgX) to form 1:1 macrocyclic complexes $[\text{Ag}_2\{\text{L2-A}\}_2][\text{X}]_2$ in the solid state, which have the *cis* conformation of the C(=O)N(Me) groups when $\text{X}=\text{CF}_3\text{CO}_2$, NO_3 , or CF_3SO_3 (see Fig. 1 for one example) but as the polymeric complex $[\text{Ag}_n\{\text{L2-B}\}_n][\text{X}]_n$, with the unusual *trans* conformation of the C(=O)N(Me) groups, when $\text{X} = \text{PF}_6$. The macrocyclic complexes reported with this ligand are found to contain transannular argentophilic secondary bonds.²



L2-A cis, cis, syn



L2-B trans, trans, syn

The arene-linked bis(pyrazolyl)methane ligands *m*-bis[bis(1-pyrazolyl)methyl]benzene, (*m*-[CH(pz)₂]₂C₆H₄, **L3**), *p*-bis[bis(1-pyrazolyl)methyl]benzene, (*p*-[CH(pz)₂]₂C₆H₄, **L4**), and 1,3,5-tris[bis(1-pyrazolyl)methyl]benzene (1,3,5-[CH(pz)₂]₃C₆H₃, **L5**) are found to react with AgX salts ($\text{pz} = 1\text{-pyrazolyl}$; $\text{X} = \text{BF}_4^-$ or PF_6^-) to form silver(I) complexes. Two types of molecular motifs are formed depending on the arrangement of the ligating sites about the central arene ring. Reactions of the *m*-phenylene linked **L3** with AgBF_4 and AgPF_6 afford complexes consisting of discrete, metallacyclic dications: $[\text{Ag}_2(\mu\text{-L3})_2](\text{BF}_4)_2$ and $[\text{Ag}_2(\mu\text{-L3})_2](\text{PF}_6)_2$, but when the *p*-phenylene-linked **L4** is treated with AgBF_4 and AgPF_6 , acyclic, cationic coordination polymers are obtained: $\{[\text{Ag}(\mu\text{-L4})]\text{BF}_4\}_\infty$ and $\{[\text{Ag}(\mu\text{-L4})]\text{PF}_6\}_\infty$. However, reaction of **L5**, containing three bis(pyrazolyl)methane units in a meta arrangement, with an equimolar amount of AgBF_4 again yields discrete metallacyclic dications in

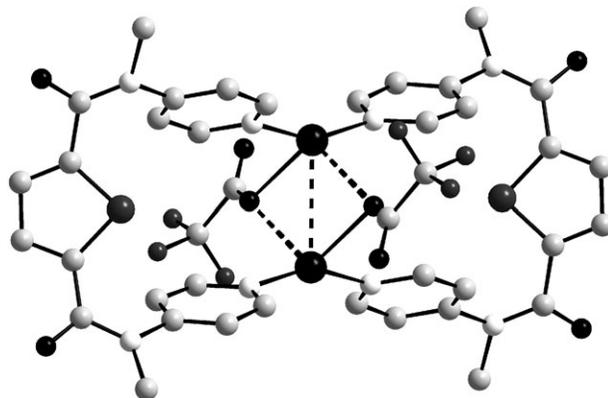
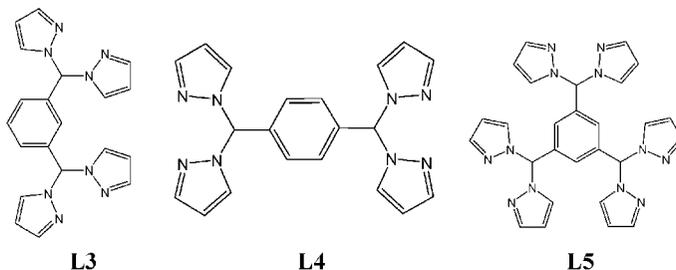


Fig. 1 A view of the structure of the macrocyclic trifluoroacetate complex $[\text{Ag}_2(\text{CF}_3\text{CO}_2)_2 \cdot \{\text{L2-A}\}_2]_2$

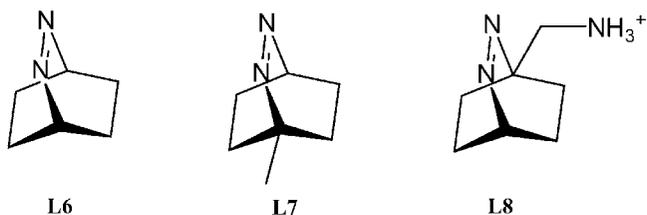
which one bis(pyrazolyl)methane unit on each ligand remains uncomplexed: $[\text{Ag}_2(\mu\text{-L5})_2](\text{BF}_4)_2$. Treatment of **L5** with an excess of AgBF_4 affords a polymer of metallacycles, $\{[\text{Ag}_3(\mu\text{-L5})_2](\text{BF}_4)_3\}_\infty$. On the whole the supramolecular structures of the silver(i) complexes are organized by noncovalent interactions, including weak hydrogen bonding, π - π , and anion- π interactions.³



Two pairs of enantiomerically related Borrromeates were synthesized stereospecifically from enantiomeric phenylglycine derivatives using Zn^{2+} ions to template their formation. All four optically active compounds have three macrocycles each containing four stereogenic centres. The one example whose crystal structure has been determined adopts an asymmetric conformation. Furthermore, the Zn^{2+} octahedra, found in the X-ray crystal structure, deviate substantially from ideal geometry, suggesting that chirality is being transferred efficiently from the 12 stereogenic centres to the six Zn^{2+} centres. Also in the chiral Borrromean rings, the expected C_3 axis was not present, the symmetry is reduced to C_1 on account of one of the three macrocycles adopting a flipped chair-like conformation.⁴

A supramolecular approach to metalloenzyme models in aqueous solution based on the dynamic self-assembly between macrocyclic hosts with cation receptor properties, organic guests, and metal ions is reported. In this study calixarenes were employed as hosts, bicyclic azoalkanes (**L6**, **L7**, **L8**) in particular 2,3-diazabicyclo[2.2.2]oct-2-ene (**L6**), as ideal guest molecules. Upon addition of transition metals (*e.g.*, Zn^{2+} , Co^{2+} , Mn^{2+}), a hypsochromic shift was observed, which signals

the formation of a ternary complex in which the azo group functions as a monodentate ligand.



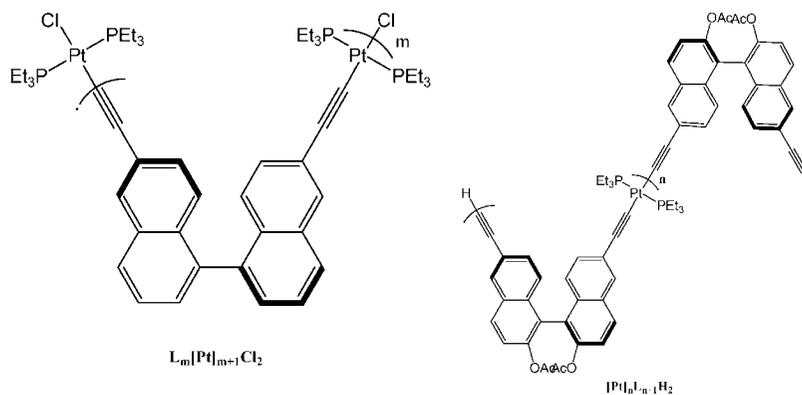
In the resulting *ternary complex*, the guest is held in place by hydrophobic interactions with the host, while the metal ion experiences attractive Coulombic interactions with the negative charges positioned at the portal of the macrocycle. It was found that only in the presence of the macrocyclic host will the guest and metal form the desired complex, that is, the host assists or “templates” the formation of the metal–ligand bond. The host brings two species together to form a metal–ligand complex which, in the absence of host, is not present in significant amounts because of low bimolecular affinity. Conceptually, the phenomenon of host-assisted metal–ligand bond formation stands out, as well as the high selectivity for the formation of a ternary complex. This strategy results in an interesting interplay between co-operative and competitive binding arising from a triple supramolecular recognition motif.⁵

Kinetically-locked, metallomacrocycles incorporating adenine based ligands have been synthesised through self-assembly using a $[\text{Ru}^{\text{II}}(\text{[9]aneS}_3)]$ templating moiety and the formation of macrocyclic trimers has been evidenced from NMR and FAB-MS spectrometry studies. Also it was found that, for suitably hindered adenine derivatives the synthetic procedure appears to be general.⁶

A general strategy for the construction of nanoscopic and mesoscopic functional supramolecular architectures of controllable size, chirality, and functionality has been reported. Described include the expeditious stepwise directed assembly of large homochiral metalocycles with up to 38 6,6'-bis(alkynyl)-1,1'-binaphthalene bridging ligands (**L**) and 38 *trans*-Pt(PEt₃)₂ (**[Pt]**) centres and with cavities as large as 22 nm in diameter. These unprecedented mesoscopic metalocycles are synthesized by cyclization of different lengths of oligomeric building blocks, $\text{L}_m[\text{Pt}]_{m+1}\text{Cl}_2$ ($m = 1, 2, 3, 5, 7, 11, 19, \text{ and } 31$) and $[\text{Pt}]_n\text{L}_{n+1}\text{H}_2$ ($n = 1, 2, 3, 4, 5, 6, 10, 18, \text{ and } 30$), (see Scheme 1) and have been characterized by a variety of techniques. The extension of this methodology to the synthesis of non-homochiral metalocycles of diverse topologies and macrocyclic structures is also possible.⁷

3. Grids

A compartmentalized $\{4 \times [2 \times 2]\}$ Mn(II)₁₆ antiferromagnetically coupled square grid $[\text{Mn}_{16}(\text{L9})_8(\text{OH})_8(\text{NO}_3)_8]$ has been reported from the self-assembly reaction of a tetratopic pyridazine bis(hydrazone) ligand (**L9**) and Mn(II). Fig. 2 shows the core structure of this molecule.



Scheme 1

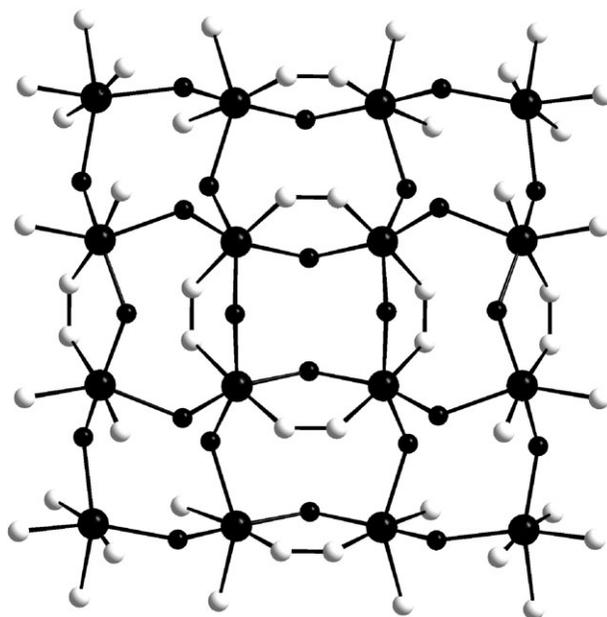
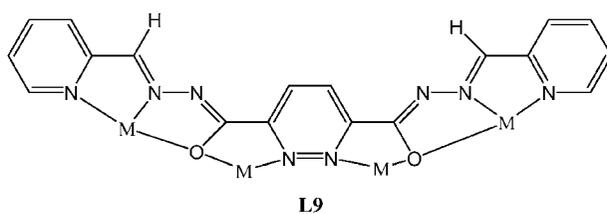
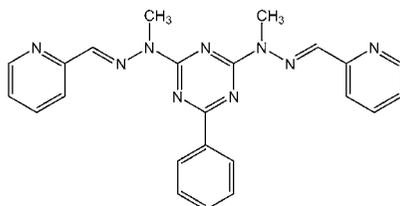
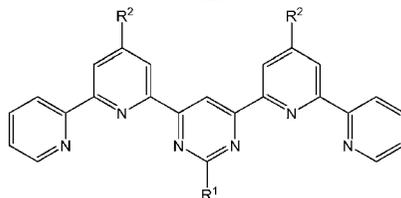


Fig. 2 Core structure of the square grid molecule $[Mn_{16}(L9)_8(OH)_8](NO_3)_8$.

The tetratopic bis(hydrazone) ligand **L9** has two pairs of coordination pockets, arranged on either side of a central pyridazine group, which can bind to four metal ions. However, the bend in the ligand structure was considered to be a possible impediment for self-assembly to form a $[4 \times 4] M_{16}$ grid.⁸ Reversible conversion of a grid-like into a pincer-like complex modulated by the nature of the solvent has been reported. The triazine derived ligand **L10** reacts with one equivalent of Co^{2+} salts to give complexes whose architecture were found to depend on the solvent employed: the $[2 \times 2]$ -grid like tetranuclear complex and the pincer-like mononuclear complex, obtained respectively by crystallization from nitromethane and from acetonitrile, may be inter-converted reversibly, the grid-pincer conversion being markedly accelerated by adding an amine.⁹



L10



L11 $R^1 = Me, R^2 = H$

L12 $R^1 = Br, R^2 = H$

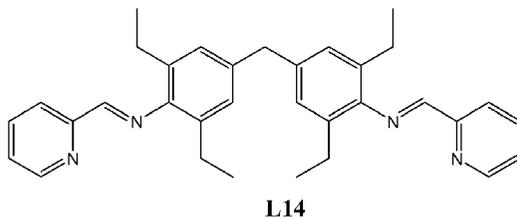
L13 $R^1 = H, R^2 = S^oPr$

From single crystal measurements, a metamagnetic-like behaviour in supramolecular $[2 \times 2]$ grid molecules of general formula $[Co^{II}_4(L11-L13)_4]^{8+}$, with bis(bipyridyl)pyrimidine-based ligands **L11-L13**, was demonstrated. The magnetization curves exhibit metamagnetic-like behaviour and are explained by the weak-exchange limit of a minimal spin Hamiltonian including Heisenberg exchange, easy-axis ligand fields, and the Zeeman term. It is also shown that the magnetic coupling strength can be varied by the substituent R_1 in the two-position on the central pyrimidine group of the ligand **L**.¹⁰

The interaction of appropriate metal ions (Pb^{2+} , Zn^{2+}) with helical ligand strands, obtained by hydrazone polycondensation, generates polymetallic supramolecular architectures of rack and grid types, by uncoiling of the ligand. The interconversion between the helical free ligand and the linearly extended ligand in the complexes produces reversible ion-induced, nanomechanical molecular motions of large amplitude. It has been integrated in an acid-base neutralisation fuelled process, which links the extension/contraction of the ligand strands to alternating changes in pH.¹¹

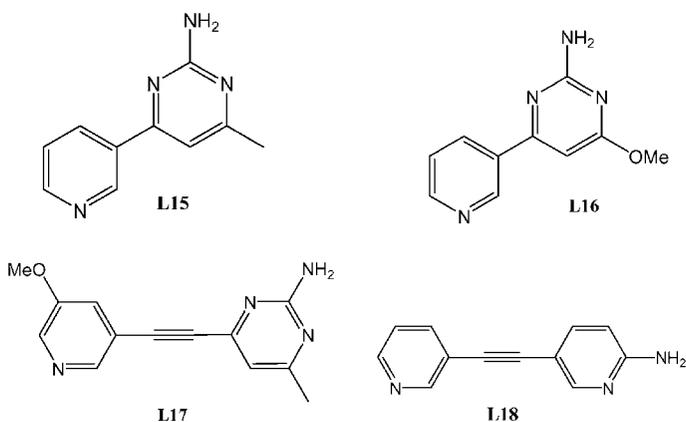
4. Cylinders, rings and squares

A di-cationic dicopper(II) metallosupramolecular cylinder is prepared from pyridyl-imine-based ligand **L14**. DNA binding studies showed that this cylinder binds more strongly to DNA than the spherical dication $[\text{Ru}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) showing potential for the design of supramolecular arrays with size and shape similar to DNA recognition motifs over small molecular units.



This copper cylinder also exhibits interesting DNA-cleavage activity in the presence of peroxide. The cylinder exhibits an unusual tendency to perform a double-strand cleavage at the same site. The cleavage ability extends the potential applications of these metallosupramolecular cylinders, opening up the possibility of using copper-based cylinders as artificial nucleases.¹²

The construction of Cu^{2+} -containing 1D supramolecular chains is achieved by the reaction of bifunctional organic ligands **L15**, **L16**, **L17** and **L18** with dinuclear Cu^{2+} acetate or $\text{Cu}(\text{II})$ 2-fluorobenzoate complex ions. **L15–L18** contain a metal-coordinating pyridyl site and a self-complementary hydrogen-bonding moiety. The structures of the complexes formed with copper(II) display a “paddlewheel” arrangement, with four carboxylate ligands occupying the equatorial sites, leaving room for the bifunctional ligand to coordinate in the axial positions and the structure of one such complex is shown in Fig. 3. The self assembly process, which organizes the coordination-complexes into the desired infinite 1-D chains, is driven by a combination of $\text{N-H}\cdots\text{N}$ and $\text{N-H}\cdots\text{O}$ hydrogen-bonds in five of the seven structures.¹³



The reaction of chelating conjugated Schiff-base macrocyclic ligands **L19–L21** with $\text{Zn}(\text{OAc})_2$ gives bowl-shaped heptanuclear Zn complexes featuring Zn in

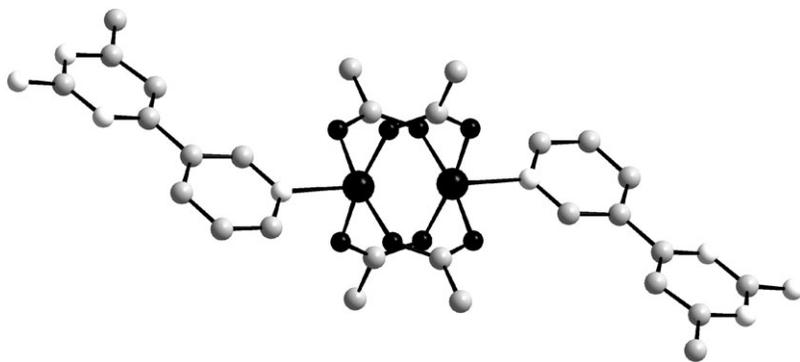
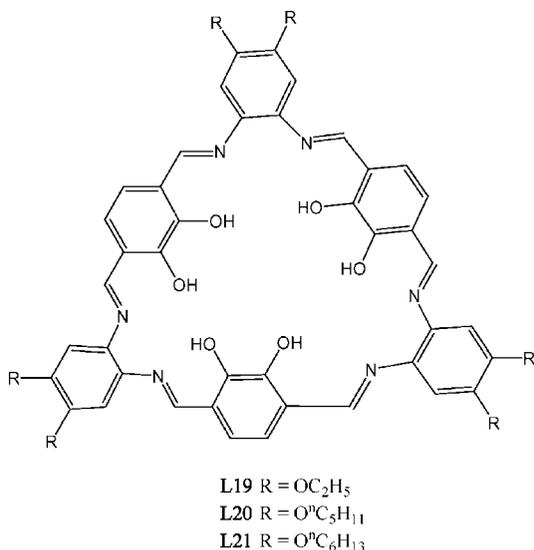


Fig. 3 Basic structure of the copper complex containing the ligand L15.

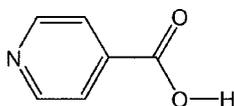
tetrahedral, octahedral, and square-pyramidal geometries. Structural and solution studies indicate that vacant Zn coordination sites within the bowl may be accessed, suggesting that these coordination complexes may be used as mimics for Zn fingers and hydrolytic Zn^{II}-containing enzymes.¹⁴



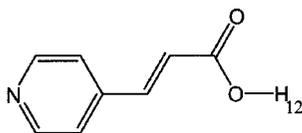
1D luminescent inorganic micro and nanowires from [Pt(CN*t*Bu)₂(CN)₂] that are aggregated and directed by Pt^{II}...Pt^{II} interactions has been reported. The precursor [Pt(CN*t*Bu)₂(CN)₂] was synthesized in high yield by stirring K₂PtCl₄ and excess *tert*-butyl isocyanide in water at room temperature. This is interesting since weak Pt^{II}...Pt^{II} interactions provide a bonding influence for the construction of 1D chains. More importantly, Pt^{II}...Pt^{II} interactions not only induce the formation of 1D nanostructures but are also responsible for the intense green ³[5d_σ*,6p_σ] emission of the self assembled [Pt(CN*t*Bu)₂(CN)₂]wires.¹⁵

5. Frameworks

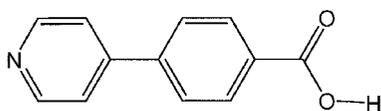
The expansion of the rectangular cavities (RCs) is achieved by replacing bridging isonicotinic acids **L23** with longer 4-pyridyl-substituted carboxylic acids (PCA). For this purpose, the following PCAs have been employed: *trans*-3-(4-pyridyl)propenoic acid (acrylH) **L24**, 4-(4-pyridyl)benzoic acid (pybenH) **L25**, and *trans*-3-(4-(4-pyridyl)phenyl)propenoic acid (pppeH) **L26**. Self-assembly of Ni^{2+} , SCN^- , and each of four PCAs involving isoH, acrylH, pybenH, and pppeH in the presence of an aromatic guest gives rise to inclusion compounds of the form: $[\text{Ni}(\text{SCN})_2(\text{isoH})_2] \cdot 1/2(\text{benz}[a]\text{anthracene})$, $[\text{Ni}(\text{SCN})_2(\text{acrylH})_2] \cdot 1/2(\text{benz}[a]\text{anthracene})$, $[\text{Ni}(\text{SCN})_2(\text{pybenH})_2] \cdot (\text{pyrene})$, and $[\text{Ni}(\text{SCN})_2(\text{pppeH})_2]_{3/2} \cdot (\text{benz}[a]\text{anthracene})$. The crystal structures show layered 2D grid-type coordination frameworks (2D host layers) framed with bridging ligands of the corresponding PCA dimers and 1D chains consisting of Ni^{2+} ions and $\mu_{1,3}\text{-SCN}^-$ ions. The lengths of the PCA dimers are 12.269(5) Å (isoH dimer), 16.890(4) Å (acrylH dimer), 20.89(2) Å (pybenH dimer), 25.387(3) Å (pppeH dimer A), and 25.527(4) Å (pppeH dimer B). Each 2D host layer has RCs defined by the two corresponding PCA dimers and the two SCN bridges. The dimensions of the RCs are expanded in proportion to the increase in the lengths of the PCA dimers and reflect the number of aromatic guests that can be included in the RCs.¹⁷



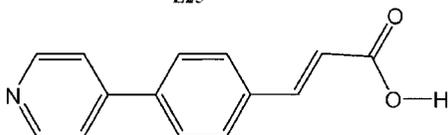
L23



L24



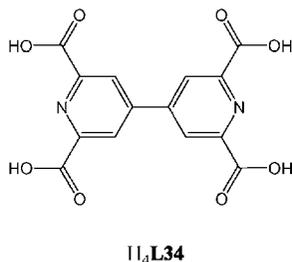
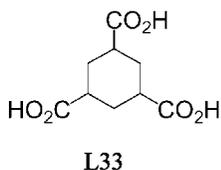
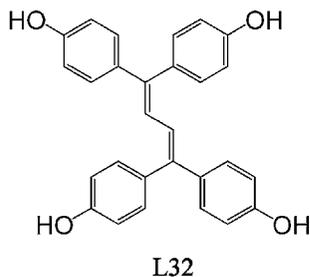
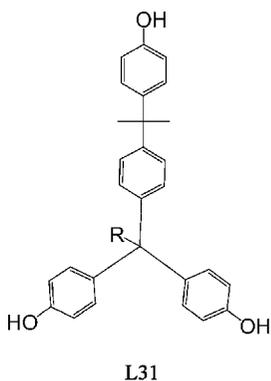
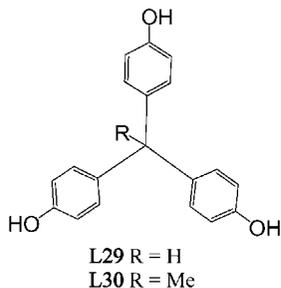
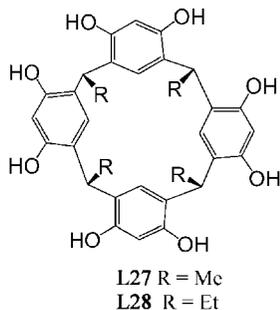
L25



L26

The trapping and dilution of the photosensitizer-dye cation $[\text{Cu}(\text{dmp})_2]^+$ ($\text{dmp} = 2,9\text{-dimethyl-1,10-phenanthroline}$) in eight different anionic frameworks formed by resorcinerenes, poly(hydroxyphenyl) compounds, and fully saturated cyclohexanetricarboxylic acid (**L27–L33**) has been reported.¹⁸ The photophysical properties of the new phases are strongly affected by the electronic structure of the framework components. The use of saturated frameworks leads to optimization of excited-state

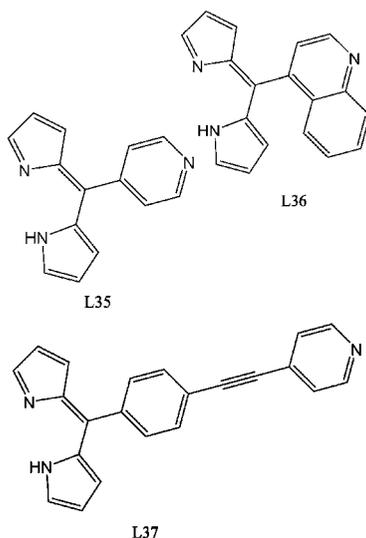
lifetimes of the guest molecules which means that host–guest solids can be designed so as to optimize the desired photophysical properties.



The synthesis and properties of a robust metal organic framework compound $\{[\text{Zn}_2(\text{L34})] \cdot 4\text{H}_2\text{O}\}_\infty$, prepared by hydrothermal reaction of ZnCl_2 and 4,4'-bipyridine-2,6,2',6'-tetracarboxylic acid ($\text{H}_4\text{L34}$) is described and the structure of framework has an unusual 5-connected network with a 4^46^6 topology comprising Zn^{2+} bound to $(\text{L34})^{4-}$. The water molecules in the newly-prepared material can be dehydrated simply by heating the sample in vacuum to yield $[\text{Zn}_2(\text{L34})]_\infty$ and this resulting porous material is found to be of high thermal stability, robust and chemically inert.¹⁹

New heterometallic metal-organic frameworks (MOFs) based on tris(dipyrinato) metalloligands $\text{M}(\text{L35})_3$, $\text{M}(\text{L36})_3$, $\text{M}(\text{L37})_3$, where $\text{M} = \text{Fe}, \text{Co}$ and Ag salts, are reported. These were prepared systematically to examine the effects of the core metal ion, counteranion, and ligand structure on the topology of the resultant network.

The effect of the metal ion (Fe^{3+} vs. Co^{3+}) on MOF structure was generally found to be negligible, thereby permitting the facile synthesis of trimetallic Fe/Co/Ag networks. However, the choice of anion was found to have a pronounced effect on the MOF topology. Networks prepared with salts of AgO_3SCF_3 and AgBF_4 reliably formed three-dimensional (10,3) nets, whereas use of AgPF_6 and AgSbF_6 produced two-dimensional (6,3) honeycomb nets. The topology generated upon formation of the MOF was found to be robust in certain cases, as demonstrated by anion-exchange experiments, and anion exchange was confirmed by X-ray crystallography in a set of single-crystal-to-single-crystal transformations. This implies that the coordinative ability of the anion does not play a significant role in the observed templating effect but changes in the length of the tris(dipyrinato) metalloligand were found to override the anion templating effect, resulting exclusively in two-dimensional (6,3) nets.²⁰



Hydrothermal reactions of lanthanide(III) salts with *m*-sulfonatophenylphosphonic acid (spa) (H_3spa) and 1,10-phenanthroline (phen) or *N,N'*-piperazinebis(methylenephosphonic acid) (ppza) yields six novel lanthanide(III) sulfonate-phosphonates based on tetranuclear clusters, namely, $[\text{La}_2(\text{spa})_2(\text{phen})_4(\text{H}_2\text{O})]$, $[\text{Ln}_2(\text{spa})_2(\text{phen})_2(\text{H}_2\text{O})_3]$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{Er}$), and $[\text{Ln}_2(\text{Hspa})(\text{H}_2\text{ppza})_2(\text{H}_2\text{O})_4]$ ($\text{Ln} = \text{La}$ and Nd). These compounds represent the first examples of lanthanide(III) complexes of sulfonate-phosphonate ligands. More interestingly, they display isolated, 1D and 3D structures based on two types of tetranuclear lanthanide units. The dimension of the structure is controlled by mainly the lanthanide ionic size, the binding modes of the sulfonatophosphonate ligand, and the second metal linker.²¹

A new synthetic route to cyclic nickel thiolate complexes using stepwise introduction of two kinds of thiolate ligands to Ni^{2+} center has been reported. In this approach, two different thiolate bridges, namely an alkylthiolate ligand (*SiPr* or *SiBu*) and 2-methylthioethanethiolate (mtet) have been used and the use of these ligands resulted in the selective formation of *cyclo*- $[\{\text{Ni}(\mu\text{-SiPr})(\text{mtet})\}_6]$ and *cyclo*- $[\{\text{Ni}(\mu\text{-SiBu})(\mu\text{-mtet})\}_{10}]$. Structure of a benzene included complex $[\text{C}_6\text{H}_6 \subset$

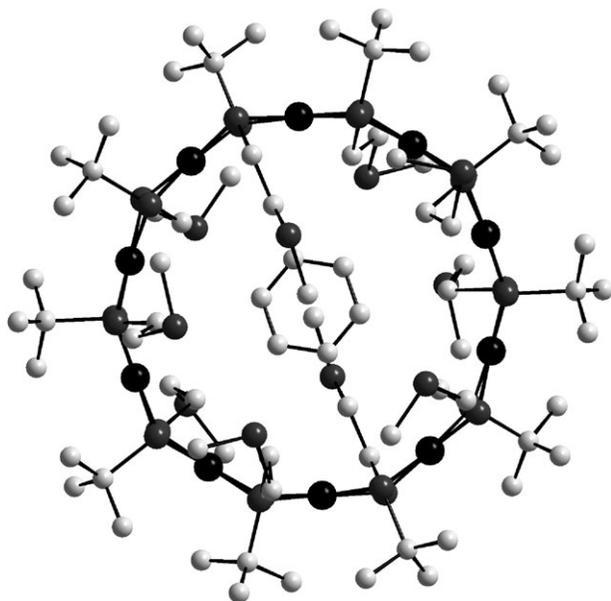


Fig. 4 Molecular structure of the inclusion complex $[C_6H_6 \subset \{Ni(\mu-SrBu)(\mu-mtet)\}_{10}] \cdot 2C_6H_6$.

$\{Ni(\mu-SrBu)(\mu-mtet)\}_{10} \cdot 2C_6H_6$ derived from (*SrBu*) is given in Fig. 4. It was found that the ring configuration of the decanuclear nickel cluster is flexible and exhibits either a circular or ellipsoidal form which is dependent on the presence or absence of an encapsulated guest molecule.²²

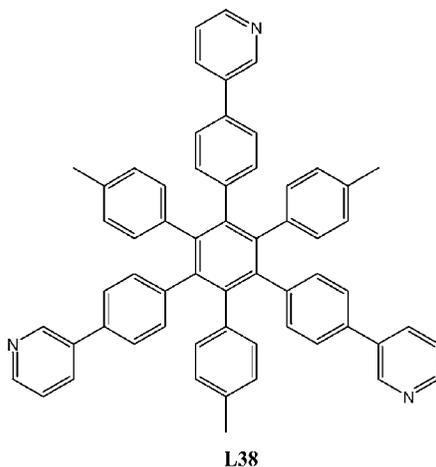
A multifunctional large-pore metal organic open-framework complex $[Cd_{11}(\mu_4-HCOO)_6(bpdc)_9] \cdot 9DMF \cdot 6H_2O$ ($H_2bpdc = 4,4'$ -biphenyldicarboxylic acid), which contains the largest known Cd^{II} -carboxylate cluster SBUs (secondary building units) and has a rare bcu topology has been synthesized by utilizing a flexible organic acid (HCOOH) as a strong bridging ligand. The Cd^{II} -centered octahedra are linked together by 18 carboxylate groups from bpdc anions, which bind in a bidentate or a chelating/bridging bidentate fashion, and six μ_4-HCOO^- moieties to build up a nanosized undecanuclear $\{Cd_{11}(\mu_4-HCOO)_6(CO_2)_{18}\}$ cluster with C_3 symmetry. These undecametall clusters, which behave as SBUs, are interconnected through the biphenyl groups of bpdc molecules to generate an extended 3D framework.²³ The transformation of a low dimensional framework to a high dimensional architecture based on different metal ions have been demonstrated by five novel metal pamidronates (3-ammonium-1-hydroxypropylidene-1,1-bisphosphonate, APD) formulated as $Ni_2(C_3NH_{10}P_2O_7)_4 \cdot 4H_2O$, $M(C_3NH_9P_2O_7) \cdot H_2O$ ($M = Co, Mn, Zn$) and $Cu_3(C_3NH_8P_2O_7)_2 \cdot 2H_2O$. Their structures span zero, one, two, and three dimensions, on the basis of the different binuclear SBUs and different coordination modes of APD. The Ni-based cluster is a molecular binuclear nickel cluster. Different dinuclear SBUs are observed in compounds which depend on the different coordination modes of APD. They also exhibit different photoluminescence properties.²⁴ Self-assembly of 4-hydroxypyridine-2,6-dicarboxylic acid (H_3CAM) and pyridine-2,6-dicarboxylic acid (H_2PDA) with Zn^{2+} salts under hydrothermal conditions yields the coordination polymers $\{[Zn(HCAM)] \cdot H_2O\}_n$

and $\{[\text{Zn}(\text{PDA})(\text{H}_2\text{O})_{1.5}]_n\}$. These comprise a 2D (4,4) net and a 1D zigzag chain, respectively. The reactions of H_3CAM and H_2PDA with Nd_2O_3 in the M/L ratio 2:3 gave $\{[\text{Nd}_2(\text{HCAM})_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$ and $\{[\text{Nd}_2(\text{PDA})_3(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O}\}_n$. In the former, a square motif as a building block constructed by four Nd(III) ions was further assembled into a highly ordered 2D (4,4) grid whereas the latter is a 3D microporous coordination polymer.²⁵

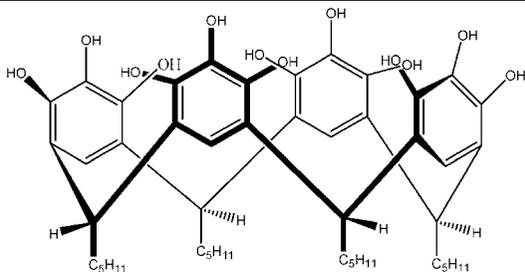
Two microporous cobalt(II) polymers, $[\text{Co}(\text{HAIP})_2]_n \cdot 3n\text{H}_2\text{O}$ and $[\text{Co}(\text{AIP})(\text{H}_2\text{O})]_n$ (AIP = 5-aminoisophthalate) have been hydrothermally synthesized and are constructed from the same $\text{Co}_2(\text{CO}_2)_2$ secondary building units, which are extended into a 1D chain in former and a 2D layer in the latter complex.²⁶

6. Capsules and cages

A novel disk-shaped tris-monodentate ligand **L38** has been described which forms 10 structurally equivalent coordination capsules, $[\text{M}_6(\text{L38})_8]^{12+}$, with a series of divalent d^5 - d^{10} transition-metal ions, where M = Mn, Fe, Co, Ni, Pd, Pt, Cu, Zn, Cd, and Hg. The resulting complexes have an octahedral structure whereby the six metal ions lie on the apices and the eight sides are occupied with eight ligands. X-ray structural analysis of a single crystal of $[\text{Hg}_6(\text{L38})_8(\text{CF}_3\text{SO}_3)_{12}]$ revealed a 3-nm-sized octahedron-shaped capsule structure, with sides of 1.8 nm in length.²⁷



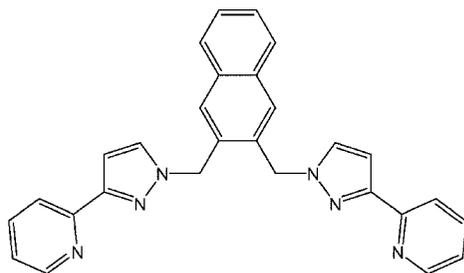
The one-step formation of a 22 component molecular nanospheroid assembly consisting of six C-pentylpyrogallol[4]arene molecules **L39** and 12 Ga^{3+} metal-ions which in turn enclose 1150 \AA^3 of space has been reported. This multicomponent assembly is stabilized by metal-ion coordination and hydrogen bonding interactions. The nanospheroid array, formed by the reaction of **L39** with $\text{Ga}(\text{NO}_3)_3$ consists of six molecules of C-pentylpyrogallol[4]arene, 12 Ga^{3+} metal-ions, and 4 water molecules located within the nanospheroid. The calixarenes are arranged at the vertices of a squeezed octahedron which defines the cavity.²⁸



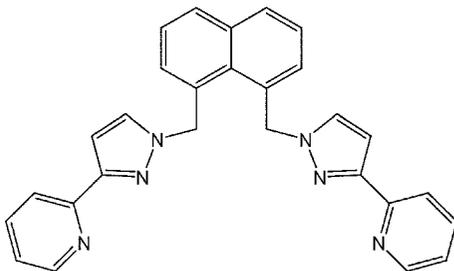
L39

The unprecedented selective encapsulation of $trans\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ from the mixture of *trans* and *cis* isomers into the cavity of macrocyclic cavitand cucurbit[8]uril (CB[8]) has been achieved which leads to the inclusion compound $\{trans\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]@\text{CB}[8]\}\text{Cl}$, Fig. 5. It was found that the encapsulation within the CB[8] cavity significantly alters the properties of guest cation $trans\text{-}[\text{Co}(\text{en})_2\text{Cl}]^+$ in both the solid state and solution. Inclusion increases the thermal stability of the metal complex and blocks its tendency to isomerize into the *cis* form. Furthermore, single-crystal X-ray analysis, ^1H NMR, and ESI-MS spectra confirm the formation of the host–guest complex in both solid state and solution, and the geometry of the complex cation alters significantly upon inclusion, which causes appreciable hypsochromic shifts of the absorption bands of the guest complex.²⁹

Red-shifted luminescence from naphthalene-containing ligands due to π -stacking in self-assembled coordination cages has been observed with ligands **L40** and **L41** after complexation and self assembly into cage structures with Zn^{2+} . In these cages the presence of extensive aromatic π -stacking between adjacent ligands results in a redshifted ‘excimer-like’ luminescence which is diagnostic of cage formation.³⁰



L40



L41

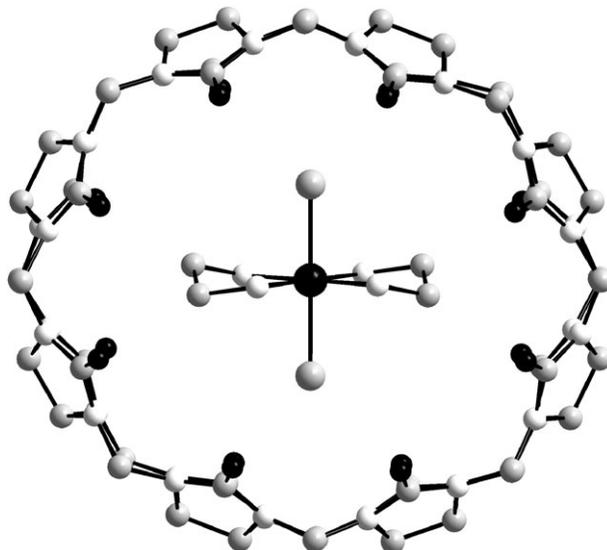
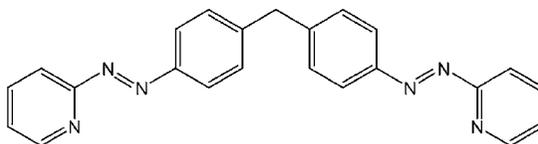


Fig. 5 Top view of the structure of the inclusion complex $\{trans-[Co(en)_2Cl_2]@CB[8]\}Cl$.

The reaction of 4-ethynylpyridine with *tert*-butyl lithium followed by its addition to $(Me_3tacn)RhCl_3$ ($Me_3tacn = N,N',N''$ -trimethyl-1,4,7-triazacyclononane) affords the facial octahedral complex $(Me_3tacn)Rh(CCPy)_3$, condensation of which with the square planar complex *cis*-(DCPE)Pt(NO₃)₂ results in a self-assembled trigonal bipyramidal cage with Rh(III) and Pt(II) atoms occupying the vertices (Fig. 6).³¹

7. Helices

Three isomeric dinuclear unsaturated ruthenium(II) complexes each with a different double-stranded supramolecular architecture have been synthesized by the reaction between a dinucleating bisazopyridine ligand with a di(4-phenyl)methane spacer (**L42**), which is the azo analogue of the bispyridylimine ligand systems, and $[RuCl_2(dmsO)_4]$.



L42

The three isomers comprise an arc-shaped nonhelical metallocyclophane (Fig. 7), an unsaturated conventional double helicate, and a new type of double helicate, in which just one of the two metal centres is responsible for imparting helicity to the ligand strands. Moreover, these compounds are the first compounds to bridge the fields of metallocyclophane architecture and anticancer drug design. The initial cell-line experiments showed that the compounds show very good activity. The isomeric dinuclear $[Ru_2Cl_4L_2]$ complexes reported herein are among the first, and to date the most promising, dinuclear ruthenium anticancer agents.³²

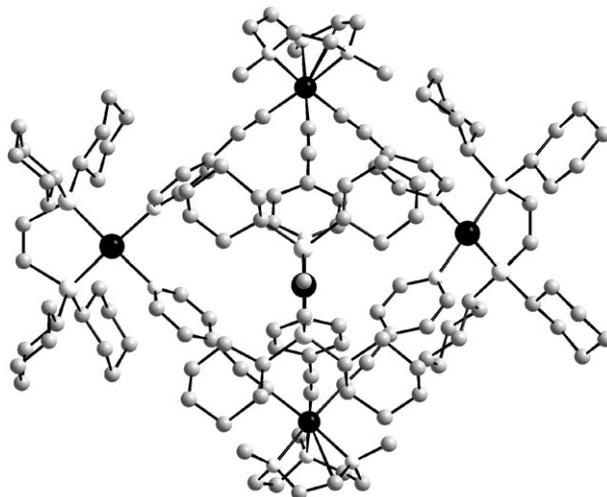
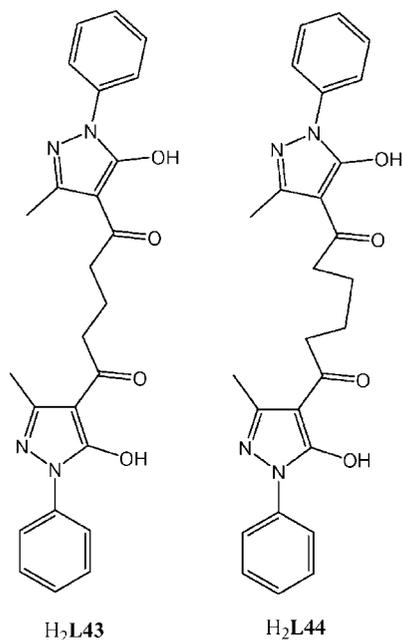


Fig. 6 Crystal structure of trigonal bipyramidal cage portion of the Rh(III)/Pt(II) complex.

Actinide quadruple-stranded helical supramolecular architectures have been synthesized in which two capped square-antiprismatic Th^{IV} centres are coordinated by four bisbidentate 4-acylpyrazolone chelating strands. The Th^{IV} quadruple-stranded helicate complexes were prepared by treatment of Th^{IV} tetrakisacetylacetonate with two equivalents of bisbidentate pyrazolone ligands H₂L43 or H₂L44 in a solution of MeOH/CHCl₃ (1:1). These Th^{IV} complexes are found to have the M₂L₄ stoichiometry. Fig. 8 shows the crystal structures of complexes [Th₂(L43)₄(dmf)₂] and [Th₂(L44)₄(dmf)₂]. These complexes are the first structurally characterized examples of bisbidentate quadruple-stranded helical complexes and



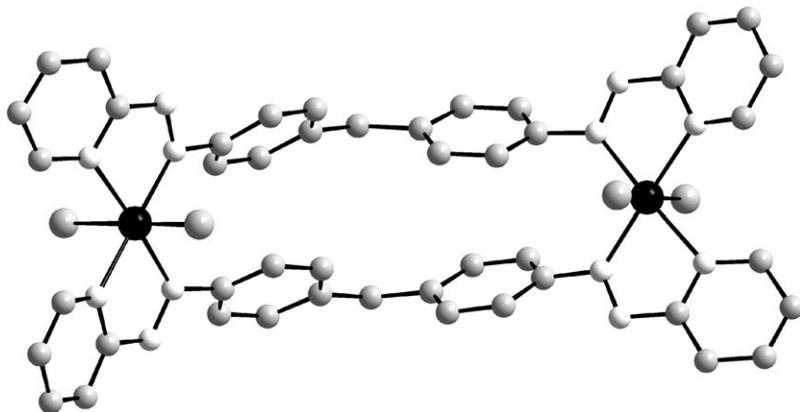
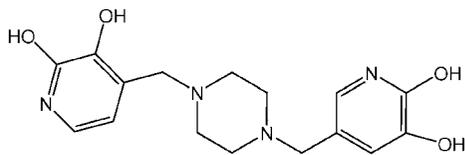


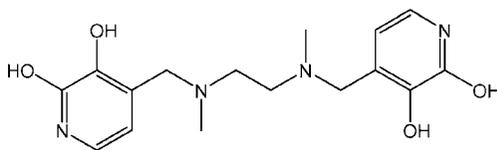
Fig. 7 Structure of the metallocyclophane ruthenium complex derived from **L42**.

are another remarkable example of cluster formation by incommensurate coordination number.³³

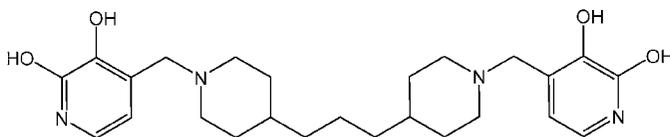
The syntheses and the structures of three (two ruthenium and one rhodium) hexanuclear complexes, which were obtained by base induced assembly of organometallic half-sandwich complexes $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}_2]_2$ and $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{RhCl}_2]_2$, with bis(dihydroxypyridine) ligands **L45–L47** of piperazine, *N,N'*-dimethylethylenediamine, or 1,3-di(4-piperidyl)propane have been reported.³⁴ The complexes display a unique structural motif: two chiral $[(\pi\text{-ligand})\text{M}]_3\text{L}_3$ fragments are connected by three flexible linkers. They can thus be described as expanded triple-stranded helicates. The synthetic concept appears to be quite flexible because the bridging ligand as well as the metal fragment can be varied. Complexes of this kind are expected to display an interesting host–guest chemistry because they contain 12-



L45



L46



L47

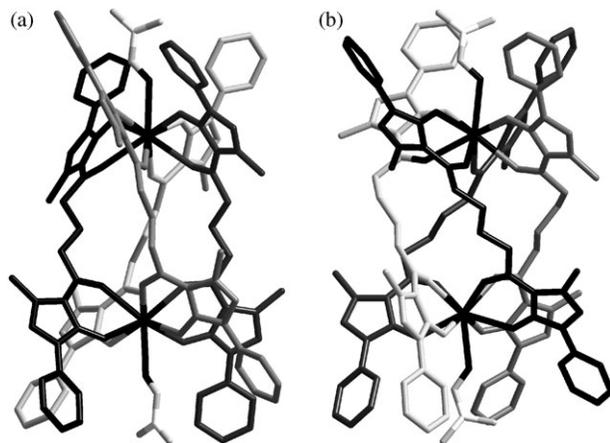
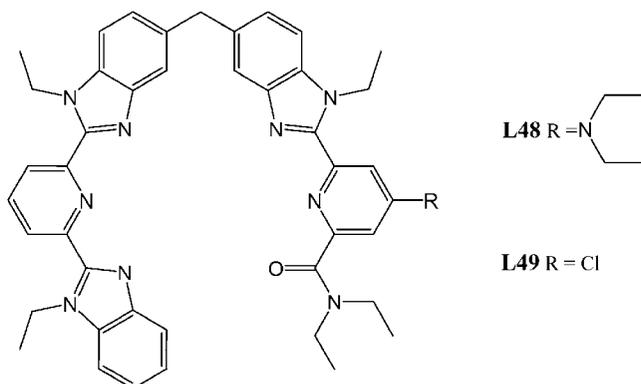


Fig. 8 Wire representations of the crystal structure of (a) $[\text{Th}_2(\text{L43})_4(\text{dmf})_2]$ and (b) $[\text{Th}_2(\text{L44})_4(\text{dmf})_2]$ as viewed perpendicular to the twofold axis of the quadruple-stranded helicate. For clarity, each ligand strand is represented in a different colour.

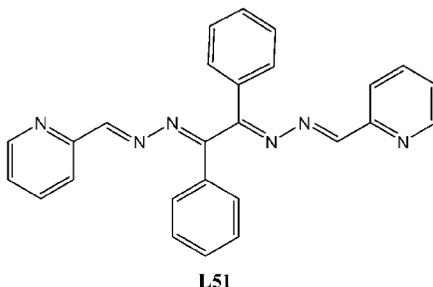
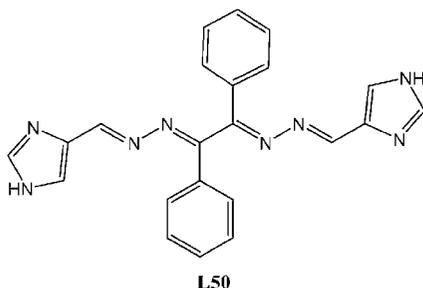
metallacrown-3 sites, which should be suited for the complexation of small metal ions, as well as a flexible cavity decorated by amine groups.³⁴

Two unsymmetrical ditopic hexadentate ligands (**L48**, **L49**) designed for the simultaneous recognition of two different trivalent lanthanide ions have been synthesized.



Under stoichiometric 2:3 (Ln/L) conditions, these ligands self-assemble with lanthanide ions to yield triple-stranded bimetallic helicates. The crystal structures of four helicates with **L49** of composition $[\text{LnLn}'(\text{L49})_3](\text{ClO}_4)_6$ (CeCe, PrPr, PrLu, NdLu) show the metal ions embedded into a helical structure with a pitch of about 13.2–13.4 Å. The metal ions lie at a distance of 9.1–9.2 Å and are nine-coordinated by the three ligand strands, which are oriented in a head–head–head fashion, where all ligand strands are oriented in the same direction. In the presence of a pair of different lanthanide ions in acetonitrile solution, the ligand **L49** shows selectivity and gives high yields of heterobimetallic complexes. **L48** displays less selectivity, and this is shown to be directly related to the tendency of this ligand to form high yields of head–head–tail isomer. A fine-tuning of the head–head–head–head–head–tail equilibrium and of the selectivity for heteropairs of Ln^{III} ions is possible.³⁵

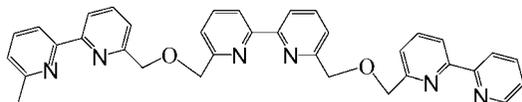
Chiral spontaneous resolution of silver double helicates $\text{Ag}_2\text{L}_2^{2+}$ is realized from achiral ligands, **L50** N',N' -bis[1-(imidazol-4-yl)methylidene]benzil dihydrazone and **L51** N',N' -bis[1-(pyridin-2-yl)methylidene]benzil dihydrazone.



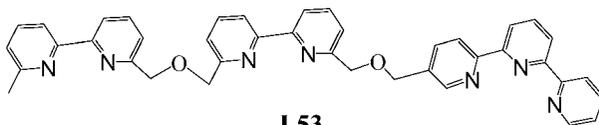
It was observed that the atropisomer chiral bridging mode of the ligands translates the chirality of the first metal center to the second one, resulting in the formation of the chiral helicate, and the intermolecular $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ stacking interactions are expected to be homochiral and strong enough to control the chiral aggregation, from which conglomerates are formed and spontaneous resolution on crystallization is achieved.³⁶ A study involving four tritopic polypyridine ligands, **L52–L55**, in solutions containing different mixtures of Zn^{II} , Cu^{II} and Cu^{I} cations has been undertaken. These represent dynamic combinatorial libraries distributed in accord with thermodynamic preferences, resulting from the nature of the coordination environments. By establishing a complex system of constitutionally dynamic metallosupramolecular species, in this case double helicates, the possibility of information-directed self-assembly by self selection of the correct double strand/metal cation partners from an equilibrating set of polytopic strands and metal cations could be observed using electrospray mass spectrometry.³⁷

Reaction of a bent py-hyz-pym-hyz-pym **L56** and of a linear py-hyz-py-hyz-pym **L57** (py = pyridine; pym = pyrimidine; hyz = hydrazone) ligand strands with silver(I) tetrafluoroborate in CH_3NO_2 generates double-helical dinuclear and trinuclear complexes. These complexes form polymeric, highly ordered solid-state structures, with wire-like, linear continuous or discontinuous polycationic Ag_n^+ arrays with Ag–Ag distances of 2.78 to 4.42 Å. Ligand **L58**, an isomer of **L56**, is found to yield a $[2 \times 2]$ grid-type complex. Titration experiments reveal the formation of linear rack-type dinuclear species. Acid–base modulated, reversible interconversion between strands and double helicates may be achieved by using tren as a competing complexing agent (tren = $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$).

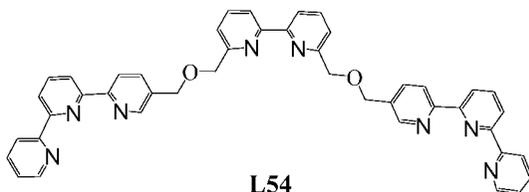
The present results show that the easily accessible hydrazone-connected ligands **L56** and **L57** react with $\text{Ag}(\text{I})$ ions to produce the double-helical complexes by



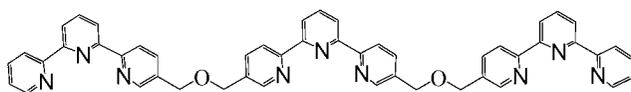
L52



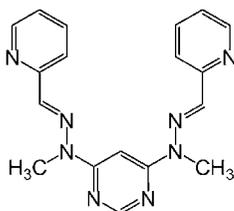
L53



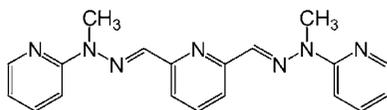
L54



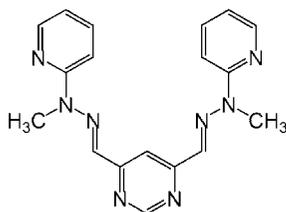
L55



L56



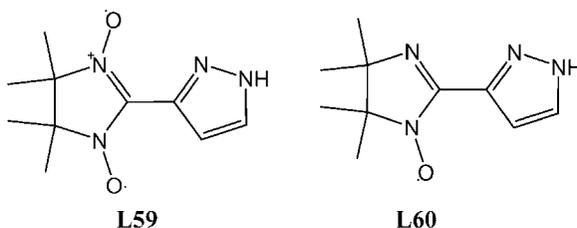
L57



L58

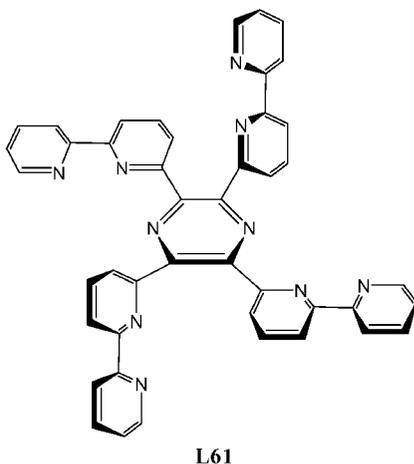
coordination of the metal ions to the terminal py-hyz units of the two ligand strands. These complexes undergo poly association in the solid state to generate self-assembled highly ordered polymeric architectures containing linear arrays of silver ions with, depending on the ligand structure, two types of polynuclear Ag^+ ionic sequences; a discontinuous one with ligand **L56** and a continuous one with ligand **L57**. Such architectures are models for linear wire-like polymetallic nanostructures and represent building blocks for the design of solid state $\text{Ag}(\text{I})$ -based metallo supramolecular assemblies.³⁸

Two self-assembled *meso*-helicates of linear trinuclear nickel(II)-radical complexes with triple pyrazolate bridges are reported whereby complexation of 3-nitronyl-nitroxide-substituted pyrazolate (pzNNH) **L59** and 3-imino-nitroxide-substituted pyrazolate (pzINH) **L60** with nickel(II) gave $[\text{Ni}_3(\text{pzNN})_6]$ and $[\text{Ni}_3(\text{pzIN})_6]$, respectively.



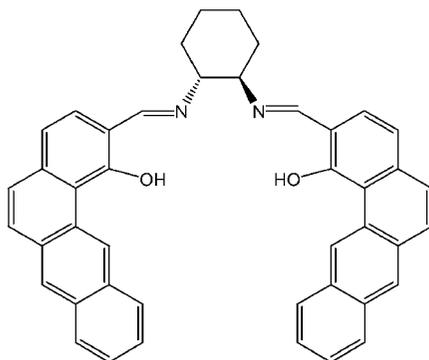
These linear trinuclear complexes were practically isomorphous with neighboring nickel ions triply bridged by pyrazolate moieties. The space groups were $P2_1/n$ but the molecules have a pseudo three-fold axis and the opposite chirality around the inversion centre at the central nickel(II) ion leads to a *meso*-helical symmetry in the whole molecule. See Fig. 9 for the structure of one such complex. The radical oxygen atoms participate in the 6-membered chelation at the terminal nickel(II) ions.³⁹

A double helical cobalt complex $[(\text{L61})\text{Co}_2(\text{CH}_3\text{CN})_4][\text{ClO}_4]_4$ with two heptadentate Co(II) sites has been isolated from the oligomers formed by the self assembly of the multidentate ligand 2,3,5,6-tetrakis(2,2'-bipyridyl)pyrazine (**L61**) and divalent cobalt.



The X-ray structure of this complex confirmed the double-helical structure with two heptadentate Co(II) sites, and a helical pitch of *ca.* 28.1 Å. Coupled Co(I/II) redox processes are also observed between the two metal centres.⁴⁰

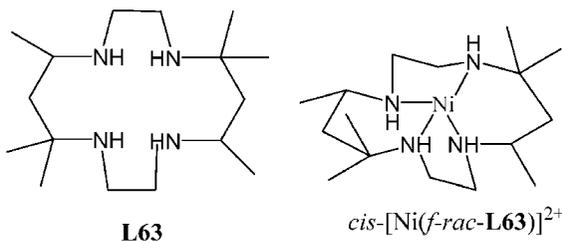
An enantiomerically pure C_2 -symmetric salen ligand **L62** with benz[*a*]anthracene side arms produces *M* helical complexes with Fe^{II} and Zn^{II} in solution which show varying degrees of attractive π - π stacking for the overlapped benz[*a*]anthryl side arms.



L62

It is observed that in THF, the *M* conformer predominates for both the Zn^{II} and Fe^{II} complexes. The Zn^{II} complex maintains this structure in the solid state, but the Fe^{II} complex crystallizes as a 1:1 mixture of diastereomeric helices from pyridine.⁴¹

Three helical supramolecular stereoisomers of *meso*-**2**, Δ -**2**, and Δ -**3** with the formula of *cis*-[Ni(*f-rac*-L)][Ni(CN)₄] were successfully constructed based on the [Ni(*f-rac*-**L63**)²⁺ and [Ni(CN)₄]²⁻ building blocks (**L63** = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).



L63

cis-[Ni(*f-rac*-**L63**)]²⁺

In all three supramolecular stereoisomers, *cis*-[Ni(*f-rac*-**L63**)²⁺ cations are alternately bridged by [Ni(CN)₄]²⁻ anions through two *cis* (in *meso*-**2** and Δ -**2**) or *trans* (in Δ -**3**) cyano groups to form one-dimensional (1D) helical chains of *cis*-[Ni(*f-rac*-L)][Ni(CN)₄]. In *meso*-**2**, the right/left-handed chirality of the originally formed chain is transferred oppositely to adjacent chains through the interchain hydrogen-bonding interactions of hexameric water clusters, leading to the formation of *meso*-**2** with a central symmetrical space group, $P2_1/n$, in which the 1D helical chains are packed in an alternating right- and left-handed chirality. In Δ -**2** and Δ -**3**, the right/left-handed chirality of the original chain is transferred uniformly to adjacent chains through the zipper-like interchain hydrophobic interactions, resulting in the formation of Δ -**2** and Δ -**3** with chiral space groups of $P2_12_12_1$ and $P3_12_1$, respectively, in which all of the 1D helical chains are arranged in the same right/left-handed chirality. A detailed structural investigation indicates that the interchain hydrogen-bonding and hydrophobic interactions play a key role in the transfer of chirality

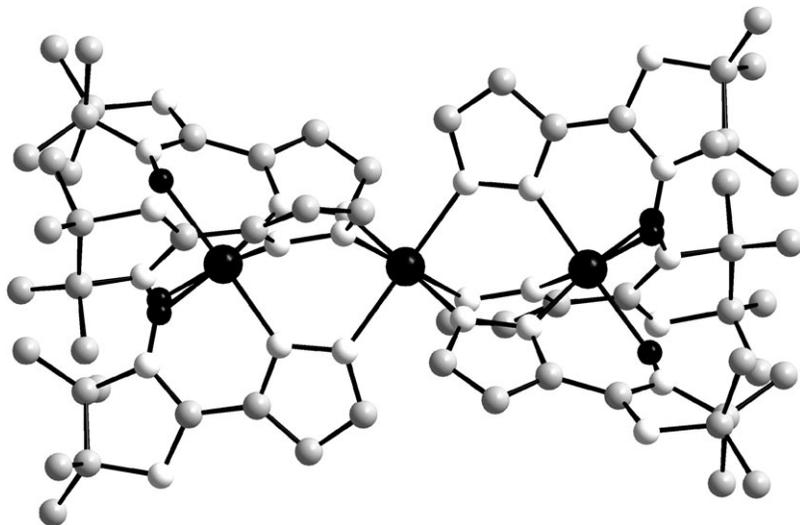
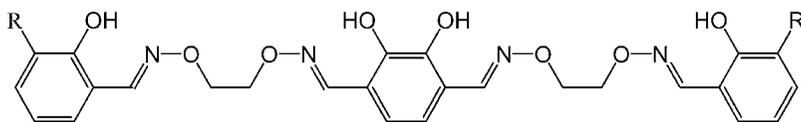


Fig. 9 Representation of the structure of the $[\text{Ni}_3(\text{pzIN})_6]$, a meso helicate complex.

between neighbouring helical chains, leading to the 1D helical chains being packed in an achiral or homochiral manner.⁴²

Helical metallo-host-guest complexes *via* site selective transmetallation of homo-trinuclear complexes has been achieved using an interesting bis(N_2O_2) chelate ligand $\text{H}_4\text{L64}$ that affords a C-shaped O_6 site on the metallation of the N_2O_2 sites.



$\text{H}_4\text{L64}$

UV-Vis and ^1H NMR titration showed that the complexation between $\text{H}_4\text{L64}$ and zinc(II) acetate affords the 1:3 complex $[(\text{L64})\text{Zn}_3]^{2+}$ *via* a highly cooperative process. Although the O_6 recognition site of the dinuclear metallohost $[\text{LZn}_2]$ is filled with an additional Zn^{2+} , the O_6 site can bind a guest ion with concomitant release of the initially bound Zn^{2+} . The novel recognition process “guest exchange” takes place quantitatively when rare earth metals are used as a guest. In the case of alkaline earth metals, selectivity of $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} \gg \text{Mg}^{2+}$ was observed. However, transmetallation did not take place when alkali metals were used for the guest. The trinuclear complex $[\text{LZn}_3]^{2+}$ is excellent in discriminating charge of the guest ions. The metallo host-guest complexes thus obtained have a helical structure, and the radius d and winding angle θ of the helix depend on the size of the guest. The La^{3+} complex has the smallest θ (288°), and the Sc^{3+} complex has the largest θ (345°). Because the radius and winding angles of helices are tunable by changing the guest ion, the helical metallohost-guest complexes can be seen as a type of molecular spring or coil. Therefore, the site-specific metal exchange of the trinuclear complex $[\text{LZn}_3]^{2+}$ described here is utilized for selective ion recognition, site-selective synthesis of $(3\text{d})_2(4\text{f})$ trimetallic complexes, and construction of “tunable” metallo-helicenes.⁴³

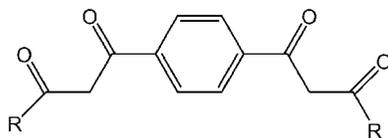
A simple and straightforward synthesis of arene ruthenium metallo-prisms is reported. Self-assembly of 2,4,6-tripyridyl-1,3,5-triazine (tpt) subunits with arene ruthenium building blocks and oxalato bridges affords cationic triangular metallo-prisms of the type $[\text{Ru}_6(\text{arene})_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ (arene = C_6Me_6 and $p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me}$); the unexpected double helical chirality of the metalloprisms observed in the solid state persists in solution giving rise to two different stereodynamic processes as demonstrated by NMR.⁴⁴

Four homochiral porous lanthanide phosphonates, $[\text{Ln}(\text{H}_2\text{L})_3] \cdot 2\text{H}_2\text{O}$, ($\text{H}_3\text{L} = (\text{S})\text{-HO}_3\text{PCH}_2\text{-NHC}_4\text{H}_7\text{-CO}_2\text{H}$, Ln = Tb, Dy, Eu, Gd), have been synthesized under hydrothermal conditions. These compounds are isostructural and they possess a 3D supramolecular framework built up from 1D triple-strand helical chains. Each of the helical chains consists of phosphonate groups bridging adjacent Ln(III) ions. The helical chains are stacked through hydrogen bonds to form 1D tubular channels along the *c* axis. Moreover, helical water chains are located in the 1D channels and, after removal of these water chains, the compounds exhibit selective adsorption capacities for N_2 , H_2O and CH_3OH molecules. Such chiral porous materials hold promise in applications such as enantioselective separation and heterogeneous asymmetric catalysis.⁴⁵

A new route for the synthesis of coordination compounds with dimethyl sulfide (DMS) ligands has been reported in which the DMS is formed during reaction by the reduction of dimethyl sulfoxide (DMSO). A luminescent 2-D double-layered polymer, $[(\text{CuI})_4(\text{CH}_3\text{SCH}_3)_3]_\infty$, containing helical chains has been constructed by flower-basket-shaped Cu_4I_4 clusters. This new cluster is an open cubane-like Cu_4I_4 cluster and is further assembled to form a 2-D polymer with unique helical structure. The results are interesting not only for the preparation of a new luminescent polymeric compound with Cu_xI_y blocks but also for a new route for synthesis of coordination compounds with DMS by using DMSO as a starting material instead of the disfavoured DMS.⁴⁶

8. Networks

Neutral trinuclear (triangular) copper(II) complexes of type $[\text{Cu}_3\text{L}_3]$ incorporating the 1,4-aryl linked bis- β -diketonato bridging ligands, 1,1-(1,4-phenylene)-bis(butane-1,3-dione) ($\text{H}_2\text{L65}$), 1,1-(1,4-phenylene)-bis(pentane-1,3-dione) ($\text{H}_2\text{L66}$) and 1,1-(1,4-phenylene)-bis(4,4-dimethylpentane-1,3-dione) ($\text{H}_2\text{L67}$) have been synthesized.



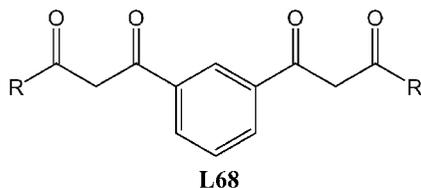
$\text{H}_2\text{L65}$, R = Et

$\text{H}_2\text{L66}$, R = Pr

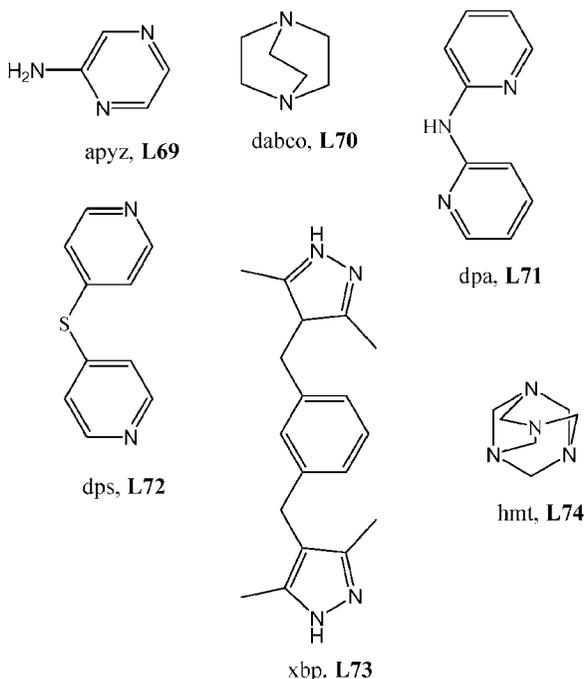
$\text{H}_2\text{L67}$, R = ^tBu

These complexes were found to act as 'platform-like' precursors which on reaction with selected heterocyclic nitrogen donor bases generate extended supramolecular architectures. On reaction with 4,4'-bipyridine (bipy), $[\text{Cu}_3(\text{L65})_3]$ yields polymeric structures of type $\{[\text{Cu}_3(\text{L65})_3(\text{bipy})(\text{THF})]\}_n$ and $\{[\text{Cu}_3(\text{L65})_3(\text{bipy})(\text{THF})] \cdot \text{bipy}\}_n$ while with pyrazine (pyz), $\{[\text{Cu}_3(\text{L65})_3(\text{pyz})]\}_n$ was obtained. Each of these extended structures contain alternating triangle/linker units in a one-dimensional polymeric

chain arrangement in which two of the three copper sites in each triangular ‘platform’ are formally five-coordinate through binding to a heterocyclic nitrogen atom. Interaction of the multifunctional linker unit hexamethylenetetramine (hmt) with $[\text{Cu}_3(\text{L66})_3]$ afforded an unusual, chiral, three-dimensional molecular framework of stoichiometry $[\text{Cu}_3(\text{L66})_3(\text{hmt})]_n$. The latter incorporates the trinuclear units coordinated to three triply bridging hmt units. In marked contrast to the formation of the above structures incorporating bifunctional linker units and five-coordinate metal centres, the trinuclear platform $[\text{Cu}_3(\text{L65})_3]$ reacts with the stronger difunctional base 1,4-diazabicyclo[2.2.2]octane (dabco) to yield a highly symmetric trigonal columnar species of type $\{[\text{Cu}_3(\text{L67})_3(\text{dabco})_3] \cdot 3\text{H}_2\text{O}\}_n$ in which each copper centre is octahedrally coordinated.⁴⁷ New examples of adducts between di- (and, in one instance, tetra-) functional nitrogen ligands and planar ‘platform-like’ dinuclear copper(II) complexes, $[\text{Cu}_2(\text{L68})_2]$, incorporating the 1,3-aryl linked bis- β -diketonato bridging ligand 1,1’-(1,3-phenylene)-bis(4,4-dimethylpentane-1,3-dione) ($\text{H}_2\text{L68}$) have also been explored.



The ditopic bridging units employed in the present studies were aminopyrazine (apyz, **L69**), 1,4-diazabicyclo[2.2.2]octane (dabco, **L70**), 4,4’-dipyridyl sulfide (dps, **L71**), dipyridylamine (dpa, **L72**) as well as bis-pyrazole system, 4,4’-(1,3-xylylene)-bis(3,5-dimethylpyrazole) (xbp, **L73**). The nature of the product obtained on using the potentially tetradentate linker hexamethylenetetramine was also elucidated.



The interaction of $[\text{Cu}_2(\text{L68})_2]$ with the ditopic ligand apyz yielded the sandwich-like tetranuclear species $[(\text{Cu}_2\text{L68}_2(\text{apyz}))_2]$. A variable-temperature magnetochemical investigation of this product indicated weak antiferromagnetic coupling between the (five-coordinate) copper centres, mediated by the 2-aminopyrazine linkers. An analogous structure, $[(\text{Cu}_2\text{L68}_2(\text{dabco}))_2]$, was generated when dabco was substituted for aminopyrazine while use of dps and xbp as the ditopic 'spacer' ligands resulted in polymeric species of type $[\text{Cu}_2\text{L68}_2(\text{dps})]_n$ and $[\text{Cu}_2\text{L68}_2(\text{xbp})]_n$, respectively. These latter species exist as one-dimensional chain structures in which copper(II) centres on different dinuclear platforms are linked in a 'zigzag' fashion. In contrast, with 2,2'-dipyridylamine (dpa) a discrete complex of type $[\text{Cu}_2\text{L68}_2(\text{dpa})_2]$ was formed in which one potential pyridyl donor from each 2,2'-dipyridylamine ligand remains uncoordinated. The use of the potentially quadruply-bridging hexamethylenetetramine (hmt, **L74**) ligand as the linker unit was found to give rise to an unusual two-dimensional polymeric motif of type $[(\text{Cu}_2(\text{L68}_2)_2)_3(\text{hmt})_2]_n$. The product takes the form of a (6,3) network, incorporating triply bridging hexamethylenetetramine units.⁴⁸

The synthesis and characterization of the first examples of organic-soluble transition-metal phosphates with cores that resemble the double-four-ring secondary building units (SBU)s of zeolites have been reported. These zinc phosphate cubes are prepared by reacting $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 2,6-di(isopropyl)phenylphosphoric acid in methanol in the presence of properly substituted pyridine ligands in the reaction mixture. The additional functional groups, namely NH_2 , OH and CH_2OH were placed in appropriate positions on the pyridine ring to enhance hydrogen bonding between the D4R cubes, thus resulting in noncovalently linked 1D, 2D and 3D structures. These studies suggest that it is very important to have a hydrogen-bond donor on the pyridine ligand at an appropriate position. The presence of NH , NH_2 or OH groups on the surfaces of these clusters opens up new possibilities for further reactions with metal alkyl reagents to build dendritic heterometallic superstructures.⁴⁹

A new two dimensional compound $\{[\text{KCu}^{\text{II}}_6(\text{bdap})_6(\mu_{1,3}\text{-SCN})_3\text{Cu}^{\text{I}}(\text{NCS})-(\text{SCN})_4]\}_n$, has been prepared and its magnetic properties analysed. The structure is made up of a potassium cation sandwiched between two triangular tricopper(II) units, connected to six similar adjacent sandwiches by $[(\mu_{1,3}\text{-SCN})_3\text{Cu}^{\text{I}}(\text{NCS})]^{3-}$ groups to form an infinite 2D network structure. The positive charge of the $\{\text{K}[\text{Cu}^{\text{II}}_3\text{O}_3]_2[\text{Cu}^{\text{I}}(\text{SCN})_4]\}^{4+}$ unit is compensated by four free thiocyanate anions. The system does not behave as a 2D magnet, and the intramolecular magnetic interactions between the copper(II) ions, mediated by the alkoxo bridge of the bdap ligand, were found to be antiferromagnetic. One another important aspect about this structure is that it reveals a new environment of the potassium cation, being in a tricapped trigonal prism $[\text{O}_6\text{N}_3]$.⁵⁰

The synthesis and characterization of a Pt(II) molecular square with capping [9]aneS₃ ligands, formed *via* self-assembly mediated by Pt(II) has been reported. The four corners of this complex are comprised of Pt(II) ions, each one coordinated by one [9]aneS₃ ligand and bridged by four (4,4'-bipy) ligands. All four corners of this complex show the axial Pt–S interactions that account for the unusual Pt(II) coordination chemistry of [9]aneS₃. As expected, each one of the four [9]aneS₃ ligands is fluxional on the rigid Pt(II) square metal–organic framework, "turning like four wheels on a wagon".⁵¹

Tetrametallic rectangular box complexes are prepared by the reaction of a heteroligated Rh(I) bimetallic macrocycle with rigid ditopic ligands (1,4-di-

cyanobenzene, 4,4'-dicyanobiphenyl, or dipyriddy terminated salen ligand). Formation of this macrocycle demonstrates the applicability of heteroligated complexes as novel building blocks where a single coordination site at each Rh centre can be used to template the assembly of higher ordered multimetallic architectures.⁵²

9. Porphyrins

A new concept of the use of twinning polymers that act as helical hosts to include a conjugate polymer has been introduced. In order to achieve this, oligomeric porphyrins are designed such that in their energy minimized state, these oligomers form helical structures in which a coordinative open face of the Zn porphyrin unit is always turned inwards so that the central metal ion can interact with the included conjugated polymer. Based on studies using conjugated polymers bearing coordinative amino groups and porphyrin oligomers bearing R groups to control the spacing between the porphyrin oligomer/conjugated polymer composites and also to increase the solubility in organic solvent, it is proposed that the porphyrin oligomers twine around the conjugated polymer strands and the resulting composite aggregate into relatively large 2D structures in the solid state.⁵³

Monomeric and dimeric iron N-confused porphyrin (NCP) complexes with a bi-related phenolate as the axial ligand have been synthesized and characterized. The dimeric NCP complex exhibits a novel NCP architecture with sodium ions bridging in between the axial phenolate oxygen and peripheral nitrogen on the paired NCP complexes to give a rectangular type shape. See Fig. 10 for the structure of one such complex. Importantly, the dimer assembles into a channel-like geometry in the crystal lattice to form a rare well-organized architecture in the NCP complexes. The data of the monomeric complex are in agreement with a high spin iron(II) centre. The dimeric iron(III) complex obtained from the oxidation of the monomer demonstrates a new method to create a central core within a hydrophobic porphyrinic environment taking advantage of the peripheral nitrogen and axial ligand.⁵⁴

A systematic study of axially bound benzoates to aluminium(III) porphyrins and their potential use as supramolecular building blocks has been presented. The synthesis of aluminium(III) porphyrin is achieved by the addition of benzoic acid to a solution of the reactive intermediate generated by the addition of

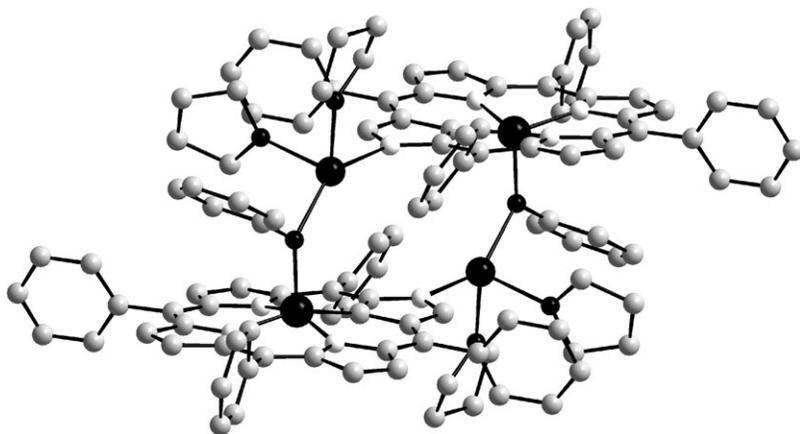


Fig. 10 A dimeric NCP complex exhibiting a rectangular type NCP architecture.

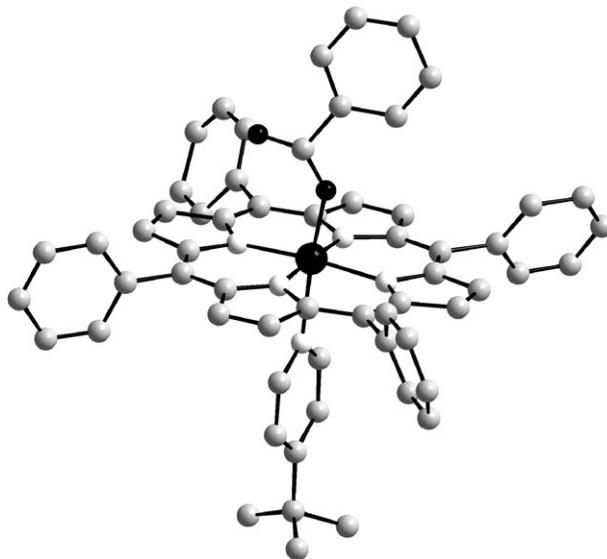


Fig. 11 Ball and stick representation of 4-*tert*-butylpyridine coordinated aluminium porphyrin complex.

trimethylaluminium to tetraphenylporphyrin. The axially-bound benzoate ligand is not displaced by water but exchange does occur with excess competitive carboxylic acids. The vacant sixth coordination site of the aluminium(III) porphyrin can be filled by neutral nitrogen donor ligands. The binding of 4-*tert*-butylpyridine or *N*-methylimidazole was confirmed by UV-Vis spectroscopy. Single crystal X-ray analysis (Fig. 11) confirms the coordination of 4-*tert*-butylpyridine to the vacant site of the aluminium(III) porphyrin. These aluminium(III) porphyrins effectively have two independent faces capable of binding both an oxygen donor and nitrogen donor, simultaneously, in the axial positions. This robustness and ability to coordinatively differentiate the two sides of the porphyrin make them an attractive alternative to tin(IV) porphyrins.⁵⁵

Reversible switching between intra- to inter-molecular electron transfer pathways has been accomplished by adding and extracting potassium ions to the supramolecular porphyrin–fullerene conjugates made by complexing porphyrin functionalized with a benzo-18-crown-6 entity and fullerene functionalized with an alkylammonium cation entity. The intra- to inter-molecular switching was achieved by the addition of potassium cations which dissociated the crown ether–alkylammonium complex, while inter- to intra-molecular switching was achieved by the addition of 18-crown-6 to extract the potassium ions of the porphyrin–crown entity.⁵⁶ The preparation of supramolecular porphyrin prisms *via* coordinative self-assembly has been reported. These prism-shaped assemblies featuring three, six or nine porphyrins and comprising, respectively, triplicate sets of porphyrin monomers, dimers or trimers are found to be highly chromophoric and the largest of the prisms resists break up in the presence of excess linker ligand.⁵⁷

The photophysical, electrochemical and self-assembly properties of a new triply fused Zn^{II}–porphyrin trimer were investigated and compared to the properties of a triply fused porphyrin dimer and the analogous monomer. In the presence of trifluoroacetic acid, the trimer forms extremely strong and nearly irreversible

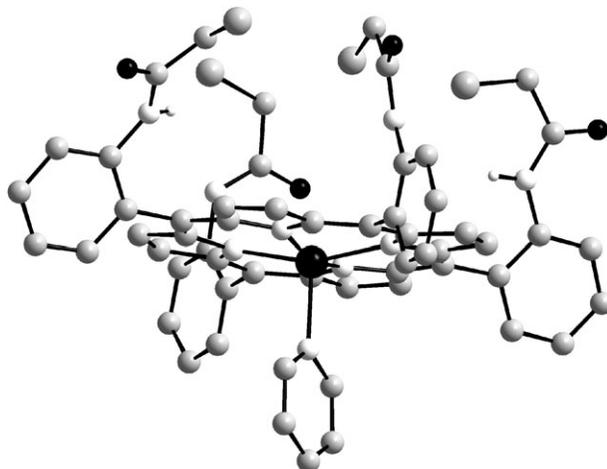


Fig. 12 Crystal structure of one pyridine coordinated Zn porphyrin receptor.

supramolecular interactions with single-walled carbon nanotubes (SWNTs), resulting in stable solutions of porphyrin–nanotube complexes in THF. Atomic force microscopy (AFM) was used to observe the supramolecular porphyrin–nanotube complexes and revealed that the porphyrin trimer formed a uniform coating on the SWNTs.⁵⁸

A supramolecular, three-component $A_nB_mC_l$ bis(zinc porphyrin) tweezer has been prepared using the heteroleptic bisphenanthroline. Upon addition of spacers of different length, *e.g.* 4,4'-bipyridine and 1,4-diazabicyclo[2.2.2]octane, to set up an additional orthogonal binding motif ($Zn_{Por}-N_{spacer}$), three structurally different, four-component $A_nB_mC_lD_k$ assemblies were formed. The structures of these assemblies were named as a bridged monotweezer A_2BC_2D , a doubly bridged double tweezer $A_4B_2C_4D_2$, and a triply bridged double tweezer $A_4B_2C_4D_3$, the latter resembling a porphyrin stack. It was observed that the same structures were equally formed directly from a mixture of the constituents A, B, C, and D put together in any sequence if the correct stoichiometry was applied.⁵⁹ Structural studies of a new set of zinc porphyrin receptors appended with amide and amide-imidazolium groups show that the zinc is five coordinate, with pyridine as the fifth coordinating ligand (see Fig. 12). Anion titration studies reveal the positively charged tetra-imidazolium zincmetalloporphyrin receptor strongly binds anions in a cooperative 1:1 manner. Further, the charged receptor is found to be a superior anion binding reagent to the neutral amide zinc porphyrin, being capable of strong and selective complexation of sulfate in aqueous–DMSO solvent mixtures.⁶⁰

A 2-D infinite 22.2 Å square-grid coordination network was prepared from a dicopper(II) tetraacetate $[Cu_2(AcO)_4]$ as a linear linker motif and 5,10,15,20-tetra-4-pyridyl-21*H*,23*H*-porphine (H_2TPyP) as a four-connected vertex, forming a regular high-porous structure. The characterization by N_2 adsorption indicated that this coordination network has uniform micropores and gas adsorption cavities.⁶¹ A general and high yielding synthetic protocol for the preparation of flexible metal-directed supramolecular co-facial porphyrin complexes through the use of new hemilabile porphyrin ligands with bifunctional ether-phosphine or thioether-phosphine substituents at the 5 and 15 positions on the porphyrin ring has been reported. The resulting architectures contain two hemilabile ligand-metal domains (Rh^I or Cu^I

sites) and two co-facially aligned porphyrins (Zn^{II} sites), offering orthogonal functionalities and allowing these multimetallic complexes to exist in two states, “condensed” or “open”. The change in cavity size allows these structures to function as allosteric catalysts for the acyl transfer reaction between X-pyridylcarbinol (where X = 2, 3, or 4) and 1-acetylimidazole.⁶² Finally, the synthesis of pentameric and hexameric macrocyclic porphyrin arrays by complementary coordination of *m*-bis(ethynylene)phenylene-linked imidazolylporphyrin has been reported and the proton NMR spectra of these arrays indicate fast rotation of the porphyrin moieties along the ethyne axis.⁶³

10. Polyoxometallates

A carefully controlled polymerization reduction process has been reported by which two predominant structural types of giant polyoxometallates- cyclic, or ring shaped structures and hollow, spherical structures- are combined together leading to a single mesoscopic molecule. The synthesis of this novel molecule is achieved by the acidification of a mixture of vanadate and molybdate followed by controlled reduction with hydrazine sulfate and subsequent addition of KCl leading to a vanadium(IV)-containing nanoring-nanosphere assembly, $K_{43}Na_{11}(VO)_4\{[Mo^{VI}_{72}V^{IV}_{30}O_{282}(H_2O)_{66}(SO_4)_{12}]\{Mo^{VI}_{114}Mo^V_{28}O_{432}(OH)_{14}(H_2O)_{58}\}} ca. 500 H_2O \{Mo_{214}V_{30}\}$. Structural investigation of this giant molecule reveals an open “clam-like” nanoscopic assembly (*ca.* 6 nm in length) comprising a spherical $\{Mo^{VI}_{72}V^{IV}_{30}\}$ anion and a ring-shaped $\{Mo_{142}\}$ anion linked by two K centres acting as a hinge. Interestingly, the spherical subunit present in this molecule exhibits a regular icosahedral structure (virtual I_h symmetry) in contrast to the previously reported more distorted D_{5d} $\{Mo_{72}V_{30}\}$ cluster, with potential implications for the magnetic properties.⁶⁴

A luminescent logic gate with dual output based on surfactant encapsulated polyoxometallate complexes (SEC) has been realized by utilizing synergetic interaction between each component and taking advantage of the supramolecular self assembly. The two components of the present SEC, the luminescent polyoxometallopeuropate ($Na_9EuW_{10}O_{36}$) and a multifunctional surfactant *trans*-10-(4-(4'-pyridylvinylene)phenyl)oxydecyldodecyldimethylammonium bromide ($PyC_{10}C_{12}N$), are connected together through electrostatic interactions. The dual output logic function (INHIBIT and NOR) of the reported organic/inorganic hybrid material consisting of SEC is realized by the supramolecular synergy between the two components. Also, the present methodology indicates that, besides organic molecules, the inorganic nanosized materials can be introduced into the logic gate as well.⁶⁵

A range of complexes based on the high-nuclearity $\{W_{36}\}$ isopolyoxotungstate cluster, $[H_{12}W_{36}O_{120}]^{12-}$, with a triangular topology have been isolated by using the organic cation, protonated triethanolamine. It was found that the cluster can form alkali and alkaline earth metal complexes $\{M \subset W_{36}\}$ ($M = K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}$ and Ba^{2+}) analogous to 18-crown-6 crown ether. These complexes demonstrate that the $\{W_{36}\}$ can act like a kind of inorganic “crown ether” with similar preferences to 18-crown-6, but with much greater rigidity and, therefore, potential to distinguish between different cations.⁶⁶

A detailed investigation of the voltammetric, photophysical and photo-electrochemical properties of the Dawson polyoxometalate anions $\alpha-[S_2M_{18}O_{62}]^{4-}$ ($M = Mo, W$), in the absence and presence of a series of $[Ru^{II}L_n]^{+/2+}$ cations [$L_n = (bpy)_3, (bpy)_2(Im)_2, (bpy)_2(dpq), (bpy)_2(box)$ and $(biq)_2(box)$] has been presented.

A series of salts $[\text{RuL}_n]_2[\text{S}_2\text{M}_{18}\text{O}_{62}]$ were isolated in substance and their voltammetry studied in both the solution and solid states; reversible reduction of anions were observed at similar potentials in the presence or absence of cations $[\text{RuL}_n]^{2+}$. Photolysis experiments were performed on solutions of the salts $[\text{R}_4\text{N}]_4[\text{S}_2\text{M}_{18}\text{O}_{62}]$ ($\text{R} = n$ -butyl or n -hexyl) and $[\text{Ru}^{\text{II}}\text{L}_n]_2[\text{S}_2\text{M}_{18}\text{O}_{62}]$ at 355 and 420 nm in dimethylformamide and acetonitrile in the presence and absence of benzyl alcohol (10% v/v). When associated with $[\text{Ru}(\text{bpy})_3]^{2+}$, the molybdate anion exhibited a large increase in the quantum yield for photo-reduction at 420 nm. The quantum yield for the tungstate analogue was lower but the experiments again provided clear evidence for sensitization of the photo-reduction reaction in the visible spectral region. The origin of this sensitization is ascribed to the new optical transition observed around 480 nm in static ion clusters $\{[\text{Ru}(\text{bpy})_3][\text{S}_2\text{M}_{18}\text{O}_{62}]\}^{2-}$ and $\{[\text{Ru}(\text{bpy})_3]_2[\text{S}_2\text{M}_{18}\text{O}_{62}]\}$ present in solution. Measurable photocurrents resulted from irradiation of solutions of the anions with white light in the presence of the electron donor dimethylformamide. Evidence is also presented for possible quencher-fluorophore interactions in the presence of certain $[\text{Ru}^{\text{II}}\text{L}_n]^+$ cations.⁶⁷

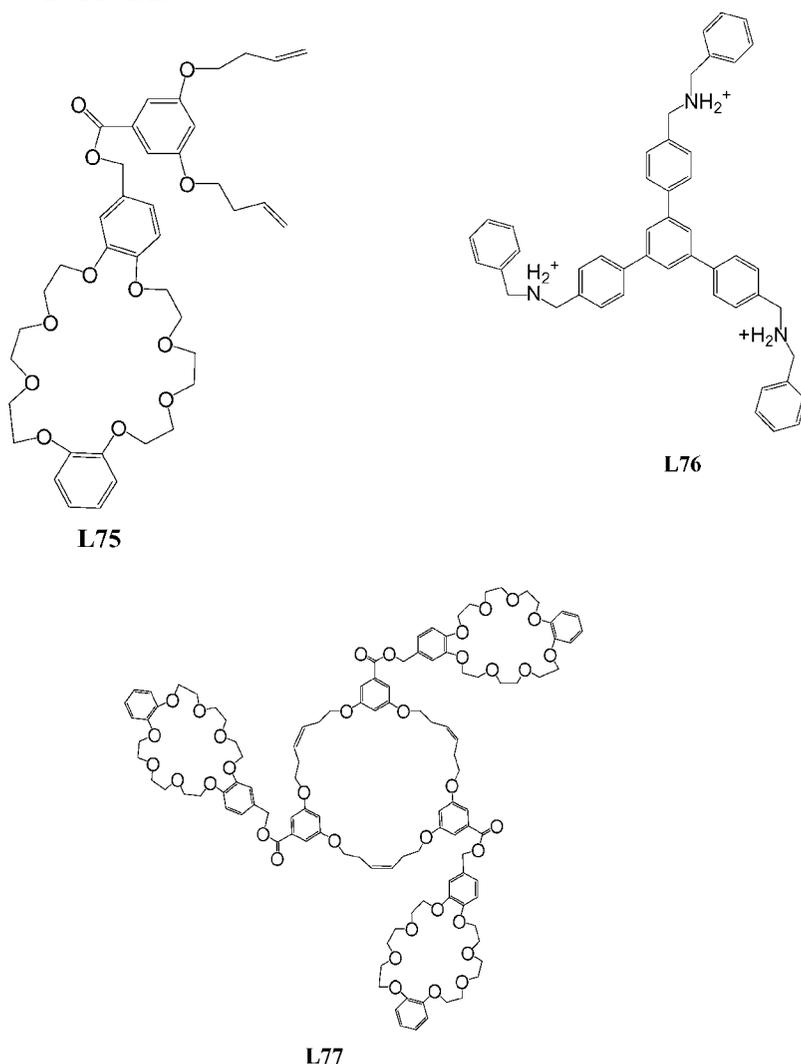
11. Miscellaneous

An efficient method for stabilizing highly labile coordinatively unsaturated transition metal complexes has been reported by Fujita *et al.* In this work, the direct crystallographic observation of *in situ* generated $\text{Cp}'\text{Mn}(\text{CO})_2$ ($\text{Cp}' =$ methylcyclopentadienyl) by photodissociation of $\text{Cp}'\text{Mn}(\text{CO})_3$ in a self assembled coordination cage has been achieved. This represents the much awaited crystallographic evidence for the geometry of an unsaturated transition metal centre and showed that the 16 electron unsaturated Mn complex adopts a pyramidal geometry. Further, the structure determination of such a short lived highly reactive species is made possible mainly due to the highly crystalline nature and high binding ability of the cage used to entrap the species.⁶⁸

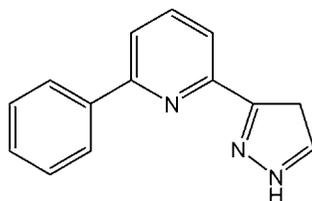
Self-assembly of hydrogen-bonded aggregates of pyrogallol[4]arene hexamers and their metal (Ga) coordinated capsules into spherical and tubular superstructures on the sub-micron scale has been reported. By using various electron or force microscopy techniques these superstructures are shown to link and/or bud from one another. The tecton here is a near spheroidal hexameric nanocapsule based on pyrogallol[4]arene, held together by 72 hydrogen bonds, and has lipophilic alkyl chains of varying length that radiate from the spheroid shell to different extents depending on the precursor selected. For particular carbon-chain lengths, the hydrogen-bonded “seams” or “faces” of the spheroid can become exposed (in the solid state at least) and it is proposed that these combined factors may play a crucial role in superstructure stabilization on the submicron level. These supramolecular systems are unique in that the self-assembly of the hexamer takes place prior to the formation of larger aggregates. Solvent properties are very important in the formation of these large structures, and an abundance of water appears to hinder aggregate formation, thereby suggesting that hexamer-to-hexamer interactions may be disturbed under such conditions. Although the specific inter-hexamer interactions are unknown to date, the aggregation phenomenon is general for a number of pyrogallol[4]arenes. The large aggregates may either be stabilized by a large number of van der Waals interactions between neighbouring alkyl chains, or by face-to-face hexamer interactions between hydrophilic regions of the discrete supramolecular assemblies, as is observed in the solid state. The ability to attach a range of

functionalities to the alkyl chains of the nanospheroids, coupled with the ability to modify the interior of the hexamers with a range of guest molecules will undoubtedly prove useful in the future study and application of these spherical and tubular sub-micron assemblies.⁶⁹

Template directed one step synthesis of cyclic trimers by acyclic diene metathesis (ADMET) has been achieved. A cyclic trimer **L77**, based on a DB24C8 acyclic diene **L75**, was produced by ADMET at low concentrations in the presence of the trifurcated template **L76-H₃³⁺** containing three $\text{RCH}_2\text{NH}_2^+\text{CH}_2\text{R}$ recognition sites. The threading of the monomers onto the template is demonstrated to be vital for cyclic trimer formation. The reaction scheme involves (i) the complex formation in a 3:1 molar ratio of the DB24C8 derivative **L75** bearing two olefinic sidearms and the trifurcated trisammonium template **L76-H₃³⁺** (as its 3BArF^- salt) and (ii) the formation of the macrocyclic tris-DB24C8 derivative **L77** in one pot as a result of triple ADMET reactions, catalyzed by ruthenium-alkylidene complexes at relatively low concentrations.⁷⁰



A tridentate π -conjugated C,N,N_{pyrazolyl} cyclometallating ligand, 2-phenyl-6-(1H-pyrazol-3-yl)pyridine (**HL78**), that contains a C_{phenyl}, a N_{pyridyl}, and a N_{pyrazolyl} donor moiety as well as a 1-pyrazolyl-NH that can still be available for further chemical interactions, such as protonation/deprotonation, after cyclometallation has been designed. Reaction of **HL78** with K₂PtCl₄ affords the cyclometalated complex [Pt(**L78**)Cl] which further reacts with bis(diphenylphosphino)methane (dppm) to give the binuclear {[Pt(**L78**)₂(μ -dppm)}(ClO₄)₂. This complex represents a molecular “pivot hinge” where the two [Pt(**L78**)] moieties are held by the diphenylphosphino functionalities of the μ -dppm with the bridging methylene as the pivot. Opening and closing of the pivot-hinge is regulated by the deprotonation/protonation of the 1-pyrazolyl-NH of the C,N,N-pyrazolyl ligands.⁷¹



HL78

Syntheses, spectroscopic and some structural properties of a series of complexes [Ru(CN)₄(HAT)]²⁻, [{Ru(CN)₄}₂(μ ₂-HAT)]⁴⁻ and [{Ru(CN)₄}₃(μ ₃-HAT)]⁶⁻, in which one, two or three {Ru(CN)₄}²⁻ units are connected to the bidentate sites of the tri-topic ligand hexaaza-triphenylene (HAT) have been reported. These new polynuclear cyanoruthenate chromophores are of interest for both their structural properties (in cyanide-bridged coordination networks with high connectivities), and for their photophysical properties (with the ability to act as panchromatic light absorbers and energy donors whose properties can be tuned by the nature of the solvent). The extended aromatic bridging ligand and the presence of up to three chromophoric centres results in a remarkably intense, low energy, highly solvatochromic absorption of light. The complexes [Ru(CN)₄(HAT)]²⁻, [{Ru(CN)₄}₂(μ ₂-HAT)]⁴⁻ and [{Ru(CN)₄}₃(μ ₃-HAT)]⁶⁻ contain four, eight and twelve externally-directed cyanide ligands, respectively; they show strongly solvatochromic and intense MLCT absorptions, and [{Ru(CN)₄}₃(μ ₃-HAT)]⁶⁻ forms a high-dimensionality cyanide-bridged coordination network with Nd(III), in which Ru \rightarrow Nd energy transfer results in sensitised near-IR luminescence. The crystal structure of the Nd(III) salt of Nd₂{[Ru(CN)₄}₃(μ ₃-HAT)} \cdot 23H₂O, illustrates the potential of these high connectivity complex anions as components of coordination networks. The structure consists of two dimensional sheets (Fig. 13).⁷²

The synthesis of the cage [Eu₂Zn₄L₄(OAc)₆(NO₃)₂(OH)₂] \cdot 2Et₂O (HL = 5-bromo-3-methoxycyclicaldehyde) has been reported. Molecules of this complex have an unusual central cage-like cavity, and, in the solid state a combination of short intermolecular Br \cdots O interactions and π - π stacking give rise to a 3-dimensional framework which contains open channels. Guest molecules of diethyl ether or methanol are reversibly encapsulated in cavities formed by the 3-dimensional supramolecular framework of heteropolynuclear, luminescent [Eu₂Zn₄L₄(OAc)₆(NO₃)₂(OH)₂] \cdot 2Et₂O.⁷³

Solid state preparation of hybrid organometallic-organic macrocyclic adducts with long chain dicarboxylic acids has been achieved. The supramolecular

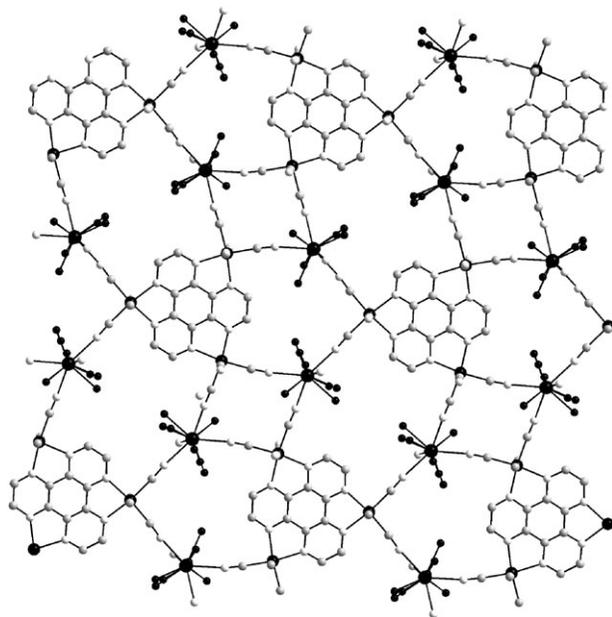


Fig. 13 View of the structure of $\text{Nd}_2\{\text{Ru}(\text{CN})_4\}_3(\mu_3\text{-HAT}) \cdot 23\text{H}_2\text{O}$ showing one of the two dimensional layers present in the molecular structure.

macrocyclic adducts of general formula $\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{H}_4\text{N})_2 [\text{HOOC}(\text{CH}_2)_n\text{-COOH}]\}_2$ with $n = 4, 6, 7, 8$ have been obtained quantitatively by kneading powdered samples of the crystalline organometallic and organic reactants with drops of MeOH. More specifically, manual grinding of the solid organometallic complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{H}_4\text{N})_2]$ with the solid dicarboxylic acids of formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ [where $n = 4$ (adipic), 5 (pimelic), 6 (suberic), 7 (azelaic) and 8 (sebacic)] in the presence of traces of MeOH (by kneading) yields macrocyclic compounds (for $n = 4, 6$ and 7) and by direct crystallization from MeOH for $n = 8$, while the adduct with $n = 5$ represents an isomeric open chain alternative to the macrocycle. In all cases, the organic and organometallic moieties are held together by hydrogen bonds between the carboxylic $-\text{OH}$ groups and the pyridine nitrogen atoms. Reactions between crystalline solids of the type used to prepare these macrocycles can be regarded as supramolecular reactions between solid, periodic supermolecules. In reactions between molecular solid reactants to form a new molecular solid product, the covalent bonding is not affected, while non-covalent van der Waals or hydrogen bonding interactions are broken and formed.⁷⁴ The coordinative properties of a calix[6]arene presenting nitrogenous binding sites at each rim has been investigated. The coordination of a first $\text{Zn}(\text{II})$ ion to the calix[6]arene presenting three imidazolyl arms at the small rim and three aniline moieties at the large rim allows the binding of a second $\text{Zn}(\text{II})$ ion while hosting a $(\text{H}_3\text{O}_2)^-$ unit in the aromatic cavity.⁷⁵ Entrapment of a dirhodium tetracarboxylate unit inside the aromatic bowl of a calix[4]arene has been achieved (see Fig. 14 for the crystal structure of one such example) and this inclusion complex has been evaluated for rhodium-catalyzed oxidative amination of saturated C–H bonds. These mixed-carboxylate systems display estimable performance when compared to other known Rh dimers.⁷⁶

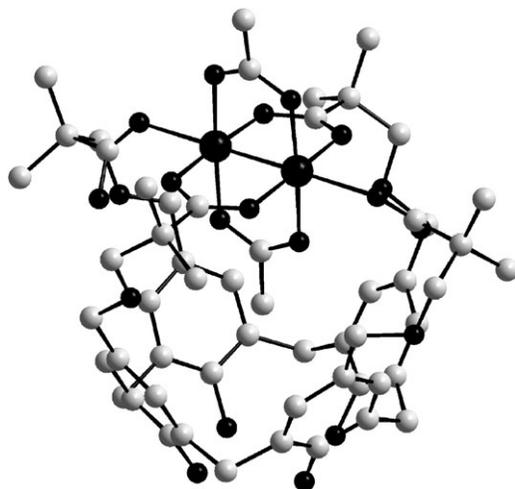
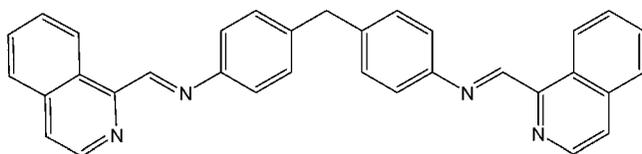


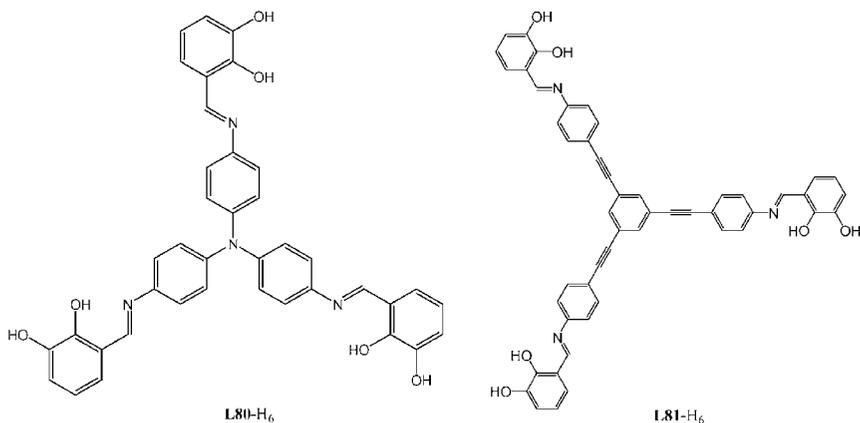
Fig. 14 Crystal structure of a calix[4]arene-derived tetracarboxylate dirhododium(II) inclusion complex.

Ag(I) and Cu(I) double-stranded boxes, and Fe(II) and Ni(II) triple-helicates are synthesized from the isoquinoline-imine ligand **L79** and the aggregation of these imine-based metallo-supramolecular architectures through π - π interactions explored.



L79

The isoquinoline affords an extended π surface and the use of this surface to obtain self-recognition and consequent π - π aggregation is investigated. The approach is effective in that each of the four complexes is observed to aggregate through these interactions.⁷⁷



L80-H₆

L81-H₆

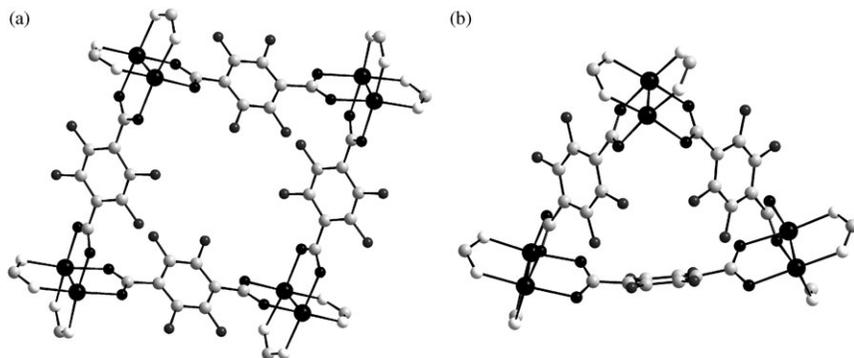


Fig. 15 Core structures of the molecular square, $[cis-Mo_2(DAniF)_2]_4(O_2CC_6F_4CO_2)_4$ and triangle, $[cis-Mo_2(DAniF)_2]_3(O_2CC_6F_4CO_2)_3$.

The metallocupramolecular tetrahedra $M_8[L_4Ti_4]$ are easily obtained by self-assembly from the triangular ligands $L-H_6$ and titanoyl bis(acetylacetonate) in the presence of alkali metal carbonates as base. Force field calculations reveal that the tetrahedra show Ti–Ti separations of 17 ($[L80_4Ti_4]^{8-}$) and 23.5 Å ($[L81_4Ti_4]^{8-}$) respectively, leading to huge internal cavities. The cavity is readily shielded in the case of **L80** but possesses big pores with the bigger ligand **L81**. $[L80_4Ti_4]^{8-}$ was used to investigate the host–guest chemistry of these container molecules and it was found that cationic organic guest species like anilinium can be introduced into the interior of the complex. Inclusion of guests can be followed by NMR spectroscopy and upon addition of one equivalent of guest the symmetry of the tetrahedron is lost but is regained after addition of significantly more than four equivalents.⁷⁸

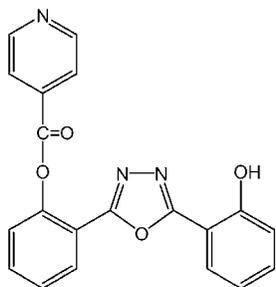
An interesting dynamic equilibrium has been observed in $CDCl_3$ between a neutral molecular square, $[cis-Mo_2(DAniF)_2]_4(O_2CC_6F_4CO_2)_4$ and triangle, $[cis-Mo_2(DAniF)_2]_3(O_2CC_6F_4CO_2)_3$ ($DAniF$ = the anion of *N,N'*-di-*p*-anisylformamidine). Both compounds have been characterized crystallographically making this one of the few examples in which both species in a dynamic equilibrium could be isolated and analyzed structurally (Fig. 15). The conversion of three moles of molecular squares to four moles of molecular triangles has an equilibrium constant of $1.98(7) \times 10^{-4}$ at 23.7 °C. At this temperature, the ΔG^0 for the conversion of three moles of squares to four moles of triangles is 21.0 kJ mol⁻¹ and the conversion is enthalpically disfavoured ($\Delta H^0 = 23.5$ kJ mol⁻¹), but entropically favoured ($\Delta S^0 = 8.2$ J K⁻¹ mol⁻¹).⁷⁹

A cage-like lanthanide cluster $\{[La^{III}]_{18}(D-bpba)_{18}(H_2O)_{36}\}Cl_{18} \cdot nH_2O$ with a spherical structure has been synthesized and characterized by X-ray crystallography. (*D-bpba* = *N,N'*-bis(2-pyridylmethyl)-*N,N'*-1,2-ethanediybis(*D*-alaninate)). This complex is large and the maximum diameter of the overall molecule is *ca.* 3.2 nm, and that of the La^{III}_{18} cluster core is *ca.* 1.9 nm.⁸⁰ It has been observed that the binding of 3,5-di-*tert*-butyl-1,2-benzocatechol (H_2DTBC) at Zn^{II} complexes of a tetradentate, tripodal ligand is significantly enhanced ($36\text{--}4.6 \times 10^4$ fold), and its reduction potential shifted (90–270 mV) to more positive values by introducing one to three amino hydrogen bond donors into the host complex. The structure of one of the complexes is reported and shows intramolecular N–H···O hydrogen bonding between the ligand-based amino group and the Zn^{II} -bound catecholate, which provides an explanation for the observed behaviour. These begin to show the extent

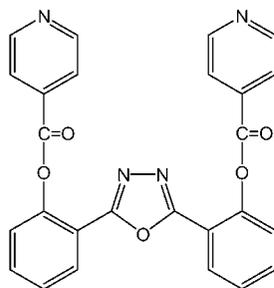
to which N–H hydrogen bond donors can affect redox potentials and binding of electroactive substrates bound to a metal centre.⁸¹

Recognition of thiolato- and alkoxy-bridged Re^{I} molecular rectangles towards highly conjugated aromatic guests like pyrene *via* perfect C–H $\cdots\pi$ interactions was observed and confirmed by solid state data. This molecular recognition through weak CH $\cdots\pi$ interactions is a rare example of an interaction that is rarely designed into a host guest pair.⁸² Gondola-shaped luminescent tetrarhenium metallacycles with crown-ether-like multiple recognition sites have been synthesized employing a new orthogonal-bonding approach for assembling functional molecules. This method involves the simultaneous introduction of a bis-(chelating) dianion to coordinate to two equatorial sites of two *fac*-(CO)₃Re cores and a ditopic nitrogen-donor ligand to the remaining orthogonal axial site, leading to the generation of a new class of metallacycles. These highly luminescent metallacycles contain crown-ether-like recognition sites, which are capable of selectively recognizing metal ions and planar aromatic molecules.⁸³

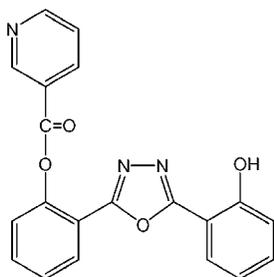
Four new symmetric and asymmetric oxadiazole-bridging ligands (**L82–L85**) with single and double 4- or 3-pyridinecarboxylate arms bridged by a 1,3,4-oxadiazole ring have been synthesized. **L82**, **L83** and **L84** act as convergent ligands and bind metal ions into discrete molecular complexes while **L85** exhibits a divergent spacer to link metal ions into one dimensional coordination polymers. Further, it was observed that the different donor orientation of the ligands and the power of anion templation are the key factors in determining the final structure of the supramolecular species formed.⁸⁴



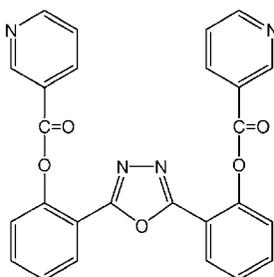
L82



L83



L84



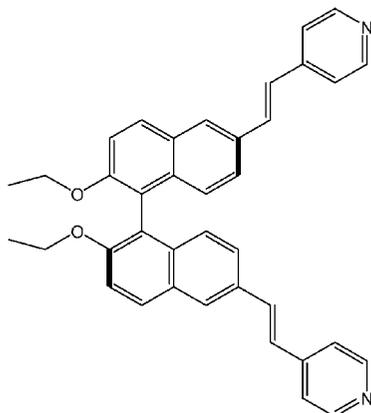
L85

A cavity-containing metal–ligand assembly is employed as a catalytic host for the 3-aza Cope rearrangement of allyl enammonium cations. Upon binding, the rates of

rearrangement are accelerated for all substrates studied, up to 850-fold. Activation parameters were measured for three enammonium cations in order to understand the origins of acceleration. Those parameters reveal that the supramolecular structure is able to reduce both the entropic and enthalpic barriers for rearrangement and is highly sensitive to small structural changes of the substrate. The space-restrictive cavity preferentially binds closely packed, preorganized substrate conformations, which resemble the conformations of the transition states. This hypothesis is also supported by quantitative NOE studies of two encapsulated substrates, which place the two reacting carbon atoms in close proximity. Therefore the capsule can act as a true catalyst, since release and hydrolysis facilitate catalytic turnover. It was concluded that the iminium product must dissociate from the cavity interior and the assembly exterior before hydroxide-mediated hydrolysis, and propose the intermediacy of a tight ion pair of the polyanionic host with the exiting product.⁸⁵

Transformation of inorganic sulfur to organic sulfur has been observed in the solvothermal reaction of CuSCN with 1,2-bis(diphenylphosphino)ethane (dppe) yielding a coordination polymer, which was characterized to be a complex of CuCN and 1,2-bis(diphenylthiophosphinyl)ethane (dppeS₂): [(CuCN)₂(dppeS₂)]_n. The identification of complex [(CuCN)₂(dppeS₂)]_n revealed that CuSCN was decomposed and the sulfur was transferred to dppe. Substituting the dppeS₂ ligand from the above complex with strong coordinating ligands 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt), three more new CuCN coordination polymers were synthesized and characterized. During the syntheses of these tpt substituted complexes, single crystals of dppeS₂ were isolated, which indicate that it was substituted by tpt ligand and also confirmed the transformation of sulfur from CuSCN to dppe. The decomposition reactions of CuSCN seem to be temperature- and solvent-dependent.⁸⁶

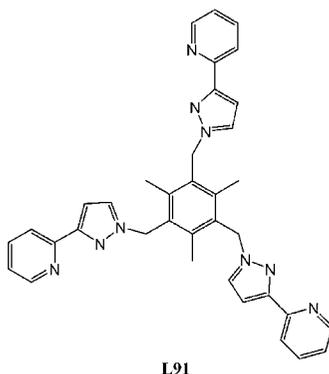
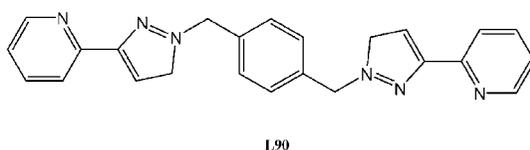
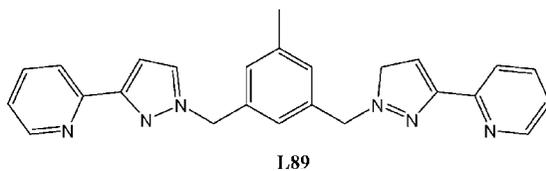
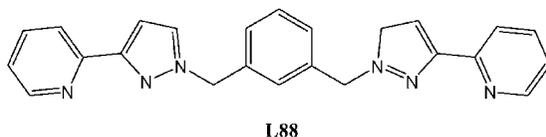
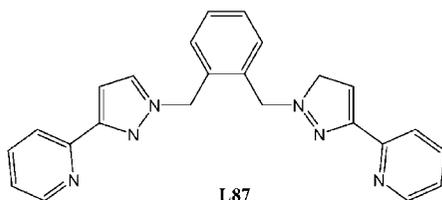
A family of new homochiral 1D coordination polymers based on 46-membered metallomacrocycles with the enantiopure elongated and bent bipyridine ligand (*S*)-2,2'-diethoxy-1,1'-binaphthyl-6,6'-bis(4-vinylpyridine), **L86** have been reported.

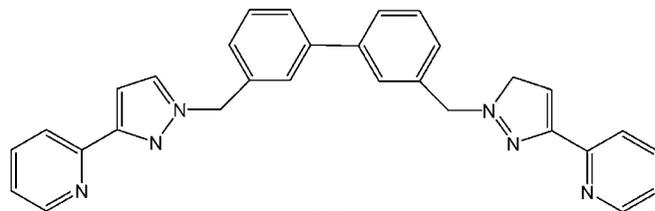


L86

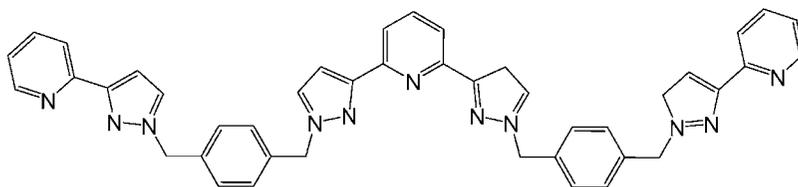
The framework structures of all these six compounds were found to be built up from similar 1D polymeric chains composed of 46-membered metallomacrocycles and mainly four distinct packing patterns were observed. It was found that with the exception of one case, the anions do not coordinate to the metal centres and reside in the open channels. The framework structures were found to be tolerant of the change of metal centres and their local coordination environments.⁸⁷ The coordination

chemistry of a series of di- and tri-nucleating ligands (**L87–L93**) which contain two or three *N,N'*-bidentate chelating pyrazolyl-pyridine units pendent from a central aromatic spacer with Ag(I), Hg(I) and Hg(II) has been investigated. Thirteen complexes of varying structural types are reported, which include 1D coordination polymers, 2D coordination network and mesocate or helicate dinuclear complexes from Ag(I). Three dinuclear Hg(I) complexes were isolated which contain an $\{\text{Hg}_2\}^{2+}$ metal-metal bonded core bound to a single bis-bidentate ligand which can span both metal ions. Also characterised were a series of Hg(II) complexes comprising a simple mononuclear four-coordinate Hg(II) complex, a tetrahedral Hg^{II}_4 cage which incorporates a counterion in its central cavity, a trinuclear double helicate, and a trinuclear catenated structure in which two long ligands have spontaneously formed interlocked metallo-macrocyclic rings as a result of cyclometallation of two of the Hg(II) centres.⁸⁸



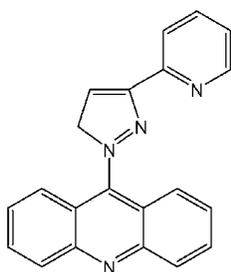


L92

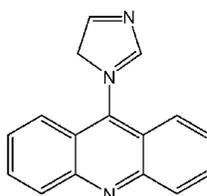


L93

New Ag(I) supramolecular complexes which exhibit rare C-H...Ag hydrogen bonding interactions have been synthesized by reactions of Ag(I) salts with two well-designed rigid bulky acridine-based ligands **L94** and **L95**. This work offers three new rare examples in which the N donors of the acridine rings coordinate to Ag(I) ions in coordination supramolecular systems. The total interaction energy related to the hydrogen bonds between H and Ag(I) in one of the complexes is evaluated to be about 14 kJ mol⁻¹ for the H...Ag weak interaction, which is very close to those values estimated for C-H...O and C-H...N hydrogen bonds. In addition, NBO and MO analyses also confirm the presence of C-H...Ag weak interaction in this complex. These results strongly support the existence of the C-H...Ag hydrogen-bonding interactions in the coordination supramolecular systems, which may offer an effective means for constructing unique supramolecular architectures *via* C-H...M close interactions.⁸⁹



L94



L95

3D 3d–4f interpenetrating coordination polymers $\{[\text{LnCr}(\text{IDA})_2(\text{C}_2\text{O}_4)]\}_n$ (Ln = Eu, Sm) have been discovered by the hydrothermal reaction of Cr(NO₃)₃, Ln₂O₃, and iminodiacetate acid (H₂IDA). It was observed that in these reactions, the H₂IDA ligands partly decompose into oxalate anions (ox), which connect Ln^{III} ions to form 1D {Ln(ox)}_n chains. Each of the Cr^{III} ions is tridentate—coordinated by two IDA ligands, which act as tetradentate metalloligands to link {Ln(ox)}_n chains to form 3D open networks. The interpenetration of two open networks results in nonporous products.⁹⁰ Also, 3D layer-pillared homoligand coordination polymers

with 1D and 2D channels are constructed from a 2D layered precursor. Here, a layered metal-organic framework $Zn_3(BDC)_3(H_2O)_2 \cdot 4DMF$ ($BDC =$ terephthalate, $DMF = N,N$ -dimethylformamide) was fabricated from H_2BDC by liquid-liquid diffusion. This layered metal organic framework was then used as a precursor to solvothermally react with further H_2BDC at 140–180 °C, resulting in two products of BDC insertion into the layered structure. These are $[Zn_3(p-BDC)_4] \cdot 2HPIP$, ($HPIP =$ partially protonated piperazine), and $[Zn_3(p-BDC)_3(H_2BDC)] (C_6H_{15}NO) \cdot H_2O \cdot 3DMF$, ($C_6H_{15}NO =$ triethylamine N-oxide). Crystallography revealed that these products possess 1D and 2D channels, respectively.⁹¹

Microporous Ni^{II} coordination polymers with general formula $\{[Ni_2(NCX)_4(azpy)_4] \cdot G\}_n$ ($X = S/Se$, G (guest molecule) = $MeOH/EtOH/H_2O$ /no guest) are prepared with a 4,4'-azobis(pyridine) (azpy) ligand. These compounds have one-dimensional periodic ultramicropores that contain the small guest molecules H_2O , $MeOH$, or $EtOH$, the hydroxy groups of which interact with the S or Se atoms of isothiocyanate or isoselenocyanate, respectively, *via* $-S(Se) \cdots HO-$ hydrogen bonds. X-ray characterization of the solvated and desolvated structures of the compounds were almost the same indicating that the ultramicropores are stable without any guest molecules. The adsorption and desorption experiments indicate that these compounds have dynamic 1D ultramicroporous channels constructed by an interpenetration that is not a chemical bonding network but merely a mechanical entanglement.⁹²

Five different multidimensional coordination polymers based on W/Cu/S clusters with flexible imidazole ligands have been synthesized and structurally characterized. Depending on the reaction temperature and the reagents used, reactions of $[WES_3]^{2-}$ ($E = S, O$) with CuX ($X = NCS, CN, I$) in the presence of *bix* ($bix = 1,4$ -bis(imidazole-1-ylmethyl)benzene) in DMF or CH_3CN resulted in the formation of two novel 2D \rightarrow 3D interpenetrating coordination polymers $[S_2W_2S_6Cu_4(bix)_2]_n$ and $\{[WS_4Cu_4(NCS)_2(bix)_3] \cdot CH_3CN\}_n$, a noninterpenetrating 3D polymer $\{[WS_4Cu_2(bix)] \cdot DMF\}_n$, and two 2D sheet polymers $[WS_4Cu_3(CN)(bix)]_n$ and $\{[OWS_3Cu_3(bix)_2][I] \cdot DMF \cdot 2H_2O\}_n$. The first two compounds of this series $[S_2W_2S_6Cu_4(bix)_2]_n$ and $\{[WS_4Cu_4(NCS)_2(bix)_3] \cdot CH_3CN\}_n$ represent the first examples of interpenetrating (4,4) frameworks with clusters and nodes and bidentate pyridyl-based ligands as linkers.⁹³

A new Janus scorpionate ligand $[HB(mtda)_3]^-$, which is a hybrid of tris(pyrazolyl)borate and a tris(mercaptoimidazolyl)borate containing mercapthotheadiazolyl (*mtda*) heterocyclic rings with both hard nitrogen donors and soft sulfur donors has been prepared. The differential hard/soft character of the dissimilar donor groups in this bridging ligand was exploited for the controlled solid-state organization of homometallic and heterometallic alkali metal coordination polymers. Sodium gave coordination polymers with both acentric (with NaS_3N_3H kernels) and centric (with alternating NaN_6 and NaS_6H_2 kernels) chains in the same crystal (where the centricity is defined by the relative orientations of the B–H bonds of the ligands along the lattice). It was found that for the homometallic potassium congener, the larger cation size compared to sodium, induced significant distortions and favoured a polar arrangement of ligands in the resulting coordination polymer chain. An examination of the solid-state structure of the mixed alkali metal salt system revealed that synergistic binding of smaller sodium cations to the nitrogen portion and of the larger potassium cations to the sulfur portion of the ligand minimizes the ligand distortions relative to the homometallic coordination polymer counterparts, a design feature of the ligand that is likely to assist in thermodynamically driving the self-assembly of the heterometallic chains.⁹⁴

An unprecedented crystal growth system of a coordination framework, where the crystallization occurs through the breaking and forming of covalent bonds has been reported as a novel approach to control crystal growth rate, direction, and their time-dependent changes. The coordination framework studied $\{[\text{Cu}_3(\text{CN})_3(\text{hat}(\text{CN})_3(\text{OEt})_3)]_n\}$ ($\text{hat}(\text{CN})_3(\text{OEt})_3 = 2,6,10\text{-tricyano-}3,7,11\text{-trioxy-}1,4,5,8,9,12\text{-hexaazatriphenylene}$) is crystallized through the reaction of 2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexaazatriphenylene ($\text{hat}(\text{CN})_6$), ethanol, and a copper(I) complex, involving the breaking and forming of covalent bonds. The crystal morphologies obtained from this system contain dumbbells, cogwheels, and superlattices.⁹⁵ Solvothermal reactions of $\text{Cu}(\text{NO}_3)_2$ with 3,5-dimethylpyrazole (HPz) and 3,3',5,5'-tetramethyl-4,4'-bipyrazole (H_2Bpz) in presence of NH_3 resulted in two luminescent coordination compounds, $[\text{Cu}(\text{Pz})_3]$ and $[\text{Cu}_2(\text{Bpz})_n]$, respectively of which the former was revealed to be a planar trimer and the latter a three-dimensional framework, presenting a rare 3-connected binodal $(6^2.10)(6.10^2)$ topology and eight-fold interpenetration.⁹⁶

Reversible structural transformation of a non porous 2D spin cross over coordination polymer, $\{\text{Fe}(\text{3-CNpy})_2(\text{CH}_3\text{OH})_{2/3}[\text{Au}(\text{CN})_2]_2\}$ ($\text{3-CNpy} = 3\text{-CNpyridine}$), into a triple interpenetrated 3D microporous spin crossover framework with the NbO structure type, $\{\text{Fe}(\text{3-CNpy})_2[\text{Au}(\text{CN})_2]_2\}$ is reported. This system is an example of crystalline-state ligand exchange reaction involving substitution-active iron(II) coordination sites able to selectively recognize guest CH_3OH molecules. Reversibility of this crystal-to-crystal transformation is evidenced by X-ray crystallographic data and from their spin crossover properties.⁹⁷ A series of pillared helical-layer coordination polymers are reported by the self assembly of a long V-shaped 3,3',4,4'-benzophenonetetracarboxylate ligand and salts of Cu, Mn, Ni, Co, Cd, Mg and Fe in the presence of linear bidentate ligand and 4,4'-bipyridine. These complexes are believed to be the first examples of pillared helical layer coordination polymers. The V-shaped bptc ligand and V-shaped phthalic group of the bptc ligand are supposed to be important for the formation of the helical structures.⁹⁸

A microporous magnetic 3D cobalt(II) coordination polymer $[\text{Co}_2(\text{ma})(\text{ina})_n] \cdot 2n\text{-H}_2\text{O}$ ($\text{ma} = \text{malate}$, $\text{ina} = \text{isonicotinate}$) featuring pillared layers with a void volume of 25.8%, was generated by hydrothermal treatment. In this material, the *in situ* generated ma ligands connect the Co^{II} ions into a 2D lattice with mixed and multiple exchange-bridges, affording a new geometrical topology different from the Kagomé lattice and leading to spin frustration. It was found that the rigid ina-pillared metallic-layered structure retains the 3D structural ordering upon guest removal and exchange. Single crystals of dehydrated $[\text{Co}_2(\text{ma})(\text{ina})_n]$ were transformed into single crystals of $[\text{Co}_2(\text{ma})(\text{ina})_n] \cdot \text{MeOH}$ and $[\text{Co}_2(\text{ma})(\text{ina})_n] \cdot \text{HCONH}_2$ by soaking the guest-free host in MeOH and methanamide (HCONH_2) solutions, respectively without apparent host-structural changes. $[\text{Co}_2(\text{ma})(\text{ina})_n]$ can also be rehydrated into $[\text{Co}_2(\text{ma})(\text{ina})_n] \cdot 2\text{H}_2\text{O}$. These single-crystal-to-single-crystal transformations are confirmed by single crystal XRD. The magnetic behaviours of this family of porous magnetic materials were complex due to the influences of multiple metal sites, intra- and inter-layer exchanges, spin-orbit coupling, as well as geometrical frustration.⁹⁹

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