

17 Macrocyclic coordination chemistry

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Highlights include the design of a dicopper(II) cryptate that can be used for the fluorescent detection of dicarboxylate anions in aqueous solution, the translocation of copper(II) centres within a macrocycle to detect imidazole-based moieties, and the design of a cyclohexyl-1,2-diamine derived bis(binaphthyl) macrocycle that demonstrates enantioselectivity in the fluorescent recognition of mandelic acid. The activation of acetonitrile solvent by a dinuclear Cu(II) cryptate is interesting. The undoubted highlight of the year, however, is the realization of a Borromean link from 18 components in a metal-templated assembly.

1. Introduction and scope

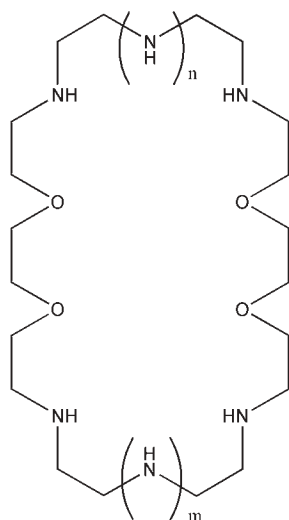
This report focuses on developments in design, synthesis and self-assembly of metal-based architectures and ligands related to macrocyclic chemistry. Although particular attention will be paid to discrete molecular architectures, infinite networks and polymers will also be included where new interesting ligands or metal-based moieties have been discovered that are of consequence to the general area. A section describing devices based on macrocyclic compounds has been included to reflect the current interest in functional devices and materials. Pictures of crystal structures have been included in this report to aid in the visualisation and conceptualisation of the many interesting metallo-supramolecular architectures that have been constructed. 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 atoms—small black spheres and all hydrogen atoms are omitted for clarity.

2. N, O, S and P macrocycles

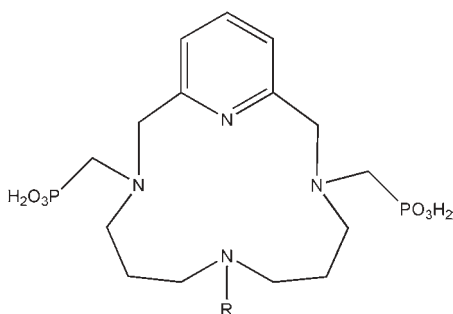
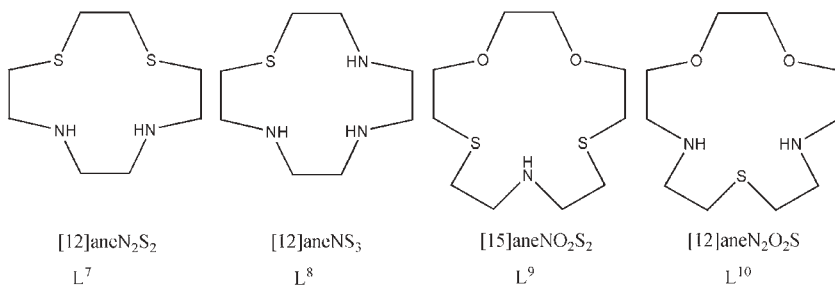
The stability and decomposition kinetics of Cu^{II} complexes of the novel azacyclophane receptors 2,6,10,13,17,21-hexaaza[22]-(2,6)-pyridinophane (**L**¹), 2,6,9,12,15,19-hexaaza[20]-(2,6)-pyridinophane (**L**²) and 2,6,9,12,15,19-hexaaza[20]-metacyclophane (**L**³) have been investigated and compared with their open chain ligand analogues. The Cu^{II} ion can perform a ‘slippage’ motion through the macrocyclic cavity, driven by pH changes.¹ The coordination chemistry of the ditopic oxa-azamacrocycles **L**⁴–**L**⁶, complexed to Ni^{II} and Co^{II}, has been studied by potentiometric and UV-vis measurements. Both the monomeric [ML]²⁺ and the dimeric [M₂L]⁴⁺ complexes were studied; the [Co₂L]⁴⁺ complexes binding oxygen.² The structural characterization of four Cd^{II} macrocyclic complexes containing mixed N-, O- and S-donors [Cd(NO₃)₂([12]aneN₂S₂)], [Cd(NO₃)₂([12]aneNS₃)], [Cd(NO₃)₂([15]aneNO₂S₂)] and [Cd(NO₃)([15]aneN₂O₂S)]NO₃ (**L**^{7–10}) has been

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achieved to evaluate the conformational flexibility of aza-thioether macrocycles.³ The metal ion is coordinated outside of the macrocyclic cavity in the complexes of the smaller macrocycles ([12]aneN₂S₂ and [12]aneNS₃), whereas the flexibility of the larger macrocycles ([15]aneN₂O₂S) and ([15]aneNO₂S₂) allow very different conformations to be adopted. Two *N*-methylphosphonic acid derivatives, **H₄L¹¹** and **H₆L¹²**, of a 14-membered tetraazamacrocycle containing pyridine have been synthesized;⁴ complexes of these ligands have stability constants similar to or higher than those formed with ligands of the same macrocyclic backbone but with acetate arms.



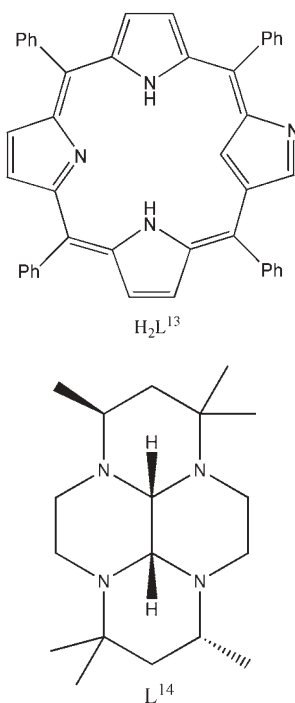
$n = 1, m = 1; L^4$
 $n = 1, m = 2; L^5$
 $n = 2, m = 2; L^6$



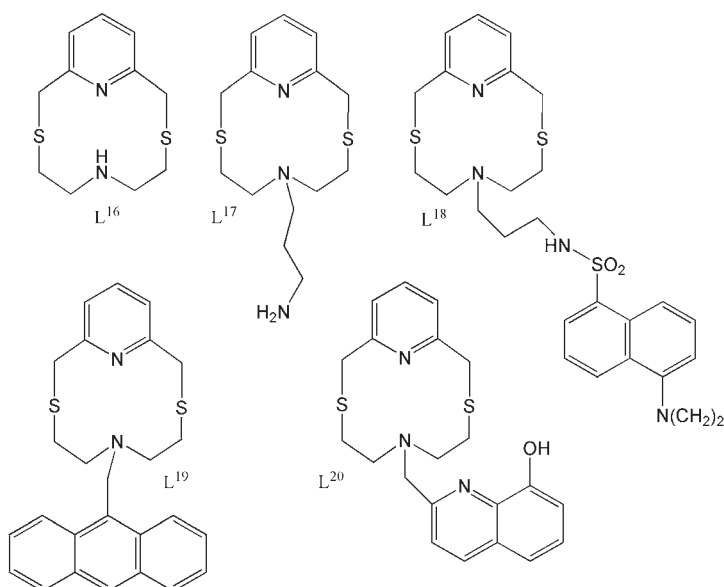
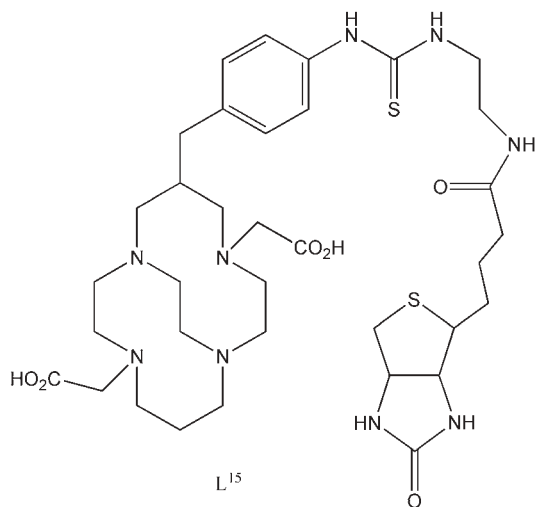
$R = \text{CH}_3 = \text{H}_4\text{L}^{11}$

$R = \text{CH}_2\text{PO}_3\text{H}_2 = \text{H}_6\text{L}^{12}$

Complexes of the N-confused porphyrin H_2L^{13} (a tetrapyrrolic macrocycle with an inverted pyrrole ring, such that an internal carbon atom can form organometallic bonds with transition metal ions), have been formed with cobalt. In these cases, the coordinated macrocycle can be either di- or tri-anionic.⁵ An unusual Cu(II) complex of highly rigid and bulky ligand L^{14} (a macrocycle–glyoxal condensate) has been synthesized and investigated *via* DFT calculations and structural characterisation. The observed conformation shows a ring inversion intermediate conformation, trapped by complex formation, and suggests the inversion process described for the unsubstituted tetracycles also occurs for substituted systems.⁶ The synthesis, Cu(II) complexation and biotin conjugation of a bifunctional chelator L^{15} , incorporating a cross-bridged macrocycle, has been achieved.⁷ NMR and UV-vis spectroscopic studies show that Zn(II) rapidly binds to cyclam at micromolar concentrations, an observation relevant to the antiviral activity and co-receptor binding of anti-HIV cyclams.⁸



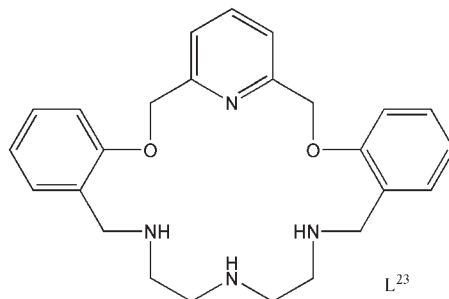
A new range of pyridine-based, 12-membered 2,8-dithia-5-aza-2,6-pyridinophane type macrocycles, L^{16-20} , have been functionalized with different fluorescent subunits. The coordination chemistry of the new pyridine-based, N_2S_2 -donating 12-membered macrocycle, L^{16} , towards Cu^{II} , Zn^{II} , Cd^{II} , Hg^{II} and Pb^{II} has been investigated both in aqueous solution and in the solid state.⁹ The protonation constants for L^{16} and the stability constants with these metal ions have been determined potentiometrically, and compared with those of ligand L^{17} , which contains a *N*-aminopropyl side arm. The data show that Hg^{II} in water has the highest affinity for both ligands, followed by Cu^{II} , Cd^{II} , Pb^{II} and Zn^{II} . For each metal ion considered, 1 : 1 complexes with L^{16} have also been isolated in the solid state, those of Cu^{II} and Zn^{II} having also been characterised by X-ray crystallography.



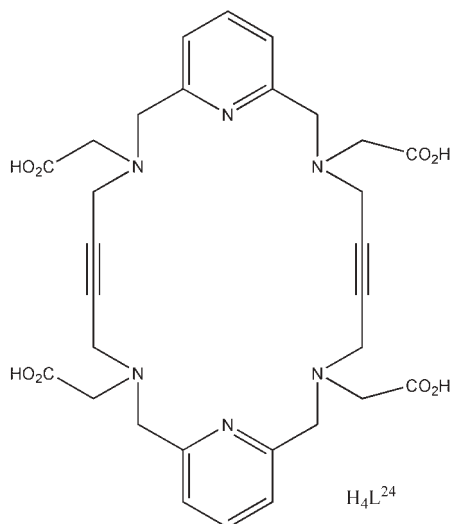
The interaction of sulfate and dithionate with protonated forms of [18]aneN₆, L^{21} , have been studied and the sulfate anions show remarkable versatility in their hydrogen bonding interactions with the macrocycle.¹⁰ In related work, the interaction of [18]aneN₆ with phosphate and phosphoric acid was also studied.¹¹ The macrocycle adopts a variety of conformations in order to accommodate the supramolecular constructs, formed by the oxo-anions and solvent molecules as the relative proportions of interacting species are altered. In a related study, the halide binding properties of the two well known polyazamacrocycles [12]aneN₄ (L^{22}) and [18]aneN₆ have been investigated.¹² [18]aneN₆ was generally found to bind two anions within the macrocyclic cavity. In the adducts formed by L^{22} , the anions and solvent of crystallization do not sit within its cavity, instead preferring to occupy positions outside the macrocycle. In most cases, chloride and bromide adopt

trigonal-pyramidal coordination motifs with various degrees of distortion from a regular geometry. The ring size, conformational flexibility and level of protonation were found to influence the halide binding characteristics of the macrocycles.

Complexes of the progressively *N*-benzylated N_4O_2 -donor macrocycles (based on L^{23} , each incorporating a 20-membered macrocyclic ring) with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) have been probed using a range of techniques.¹³ They show that *N*-benzylation of the secondary amine donor groups of the macrocyclic ring results in an enhanced selectivity for Ag(I) relative to the other six metal ions. The observed behaviour serves as an additional illustration of the previously proposed concept of selective 'detuning' as a mechanism for metal ion discrimination, and this has also been employed with N_3O_2 macrocycles.¹⁴



The synthesis of the novel dinucleating aminocarboxylate macrocycle H_4L^{24} has been achieved. Complexation with di- and trivalent transition and lanthanide metal ions yielded the following dinuclear complexes, which were examined crystallographically: $[Zn_2(L^{24})(H_2O)_2]$, $[Fe_2(L^{24})(\mu-O)]$, $[La_2(L^{24})(NO_3)_2(H_2O)_2]$ and $Na[Eu_2(L^{24})(\mu-OAc)_3]$.¹⁵



A study of the complexation and extraction of $CuSO_4$ and $NiSO_4$ by the related N_3O_2 -donor macrocycles, L^{25} and L^{26} has been reported.¹⁶ Comparative solvent extraction (water/chloroform) studies show that an efficient extraction of both metal

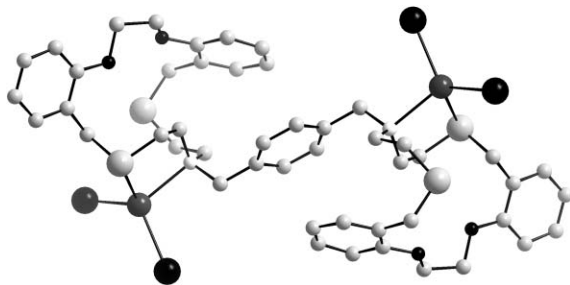
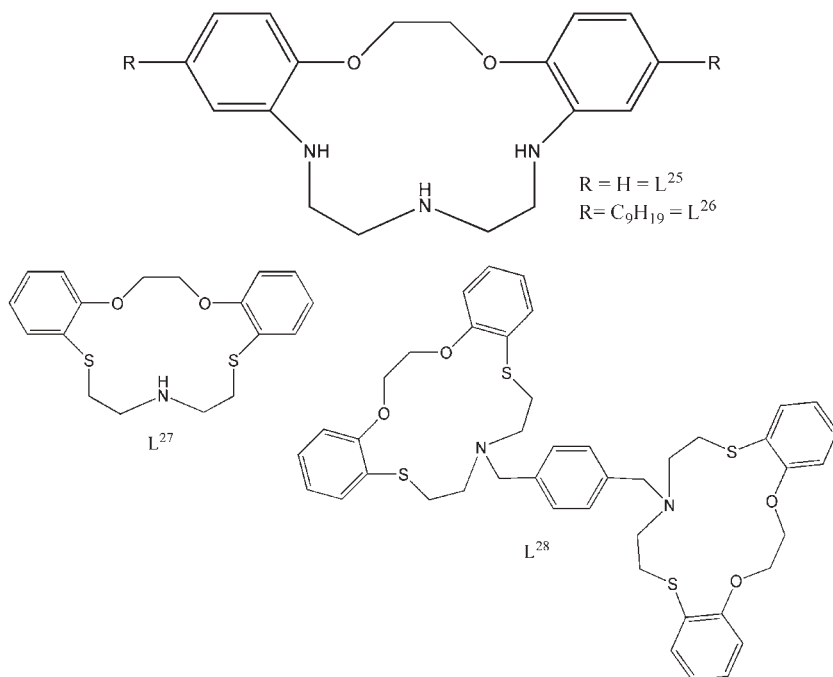


Fig. 1 A representation of the structure of $[\text{Hg}_2(\text{L}^{28})\text{Br}_4]$. The Hg^{II} ions are shown in dark grey and the Br^- ions in black.

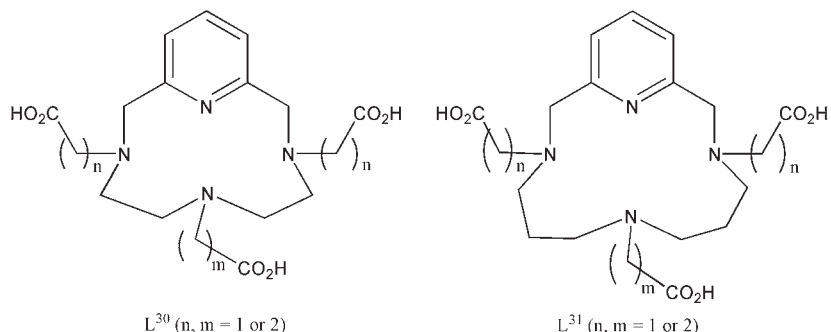
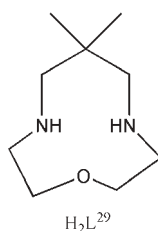
sulfates was observed, the degree of extraction being comparable (or slightly enhanced) relative to that observed for each of the other anionic systems. The NO_2S_2 -based donor macrocycles L^{27} and the bridged macrocycle L^{28} have been synthesized and a range of Cd^{II} and Hg^{II} complexes produced.¹⁷ A range of 1 : 1 complexes were synthesized with L^{27} , and 2 : 1 complexes with L^{28} (Fig. 1). Each $\text{Hg}(\text{II})$ ion in $[\text{Hg}_2(\text{L}^{28})\text{Br}_4]$ has a distorted tetrahedral environment made up of S and N donors from an exodentate L^{28} and two coordinated halides.



The kinetics of formation and dissociation of Cu^{II} and Ni^{II} complexes of a series of N_2S_2 macrocycles, in which the ring size and the geometric arrangement of the donor groups have been varied, has been measured.¹⁸

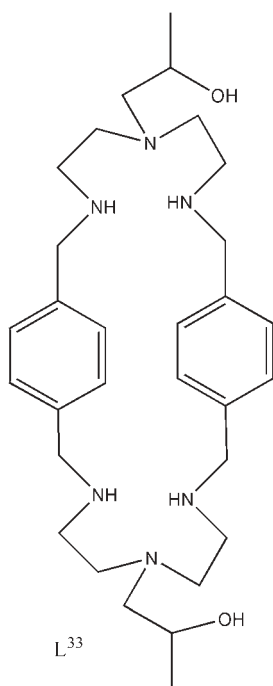
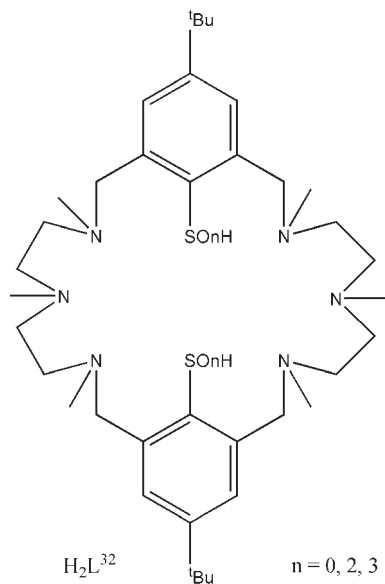
Reaction of the dilithium salt of 3,3-dimethyl-1,5-diaza-8-oxacyclodecane, $[\text{L}^{29}\text{Li}_2]$, with $[\text{Zr}(\text{NET}_2)_2\text{Cl}_2(\text{thf})_2]$ afforded a $20e^-$ complex $[\text{Zr}(\text{L}^{29})_2]$. Furthermore, metallation of H_2L^{29} with $\text{Ti}(\text{benzyl})_4$ afforded $[(\text{L}^{29*})\text{Ti}(\text{benzyl})_2]$ in which the

tri-anionic diamido ligand, L^{29*} , was formed by the C–H activation of the carbon α to the amido nitrogen.¹⁹ Two 14-membered azamacrocycles, L^{30} and L^{31} , each containing a pyridine moiety and three acetic and/or propionic acid pendant arms, were prepared from regioselectively-functionalised polyamines. The stability constants of the lanthanide(III) complexes (La, Pr, Nd, Eu, Gd, Tb, Er, Yb and Lu) formed with the triacetic acid ligands were determined by spectroscopic methods (luminescence and/or UV-vis).²⁰ The preparation and ligating properties of S-oxygenated derivatives of a macrobinucleating hexaazadithiophenolate Robson-type macrocycle, H_2L^{32} , towards Ni(II) and Zn(II) ions were described. Ni(II) complexes of H_2L^{32} (where $n = 3$) are readily obtained in high yields by the oxidation of the thiol analogue ($n = 0$) with *meta*-chloroperoxybenzoic acid or hydrogen peroxide. A Zn(II) complex of H_2L^{32} ($n = 2$) was isolated, while a dinuclear Cu^{II} complex of the $n = 3$ form was formed unexpectedly by aerial oxidation in the presence of Cu^I .²¹ A dinuclear Cu^{II} complex of the hexaaza macrocyclic ligand bearing two 2-hydroxypropyl pendants, L^{33} , was synthesized. The protonation constants of $[Cu_2(L^{33})Cl_2]$ were determined by potentiometric titration; the hydroxypropyl groups of the complex exhibiting low pK_a values of $pK_{a1} = 7.31$ and $pK_{a2} = 7.83$. The hydrolysis kinetics of 4-nitrophenyl acetate promoted by this complex have also been studied, with the pH-rate profile corresponding to a sigmoidal curve.²²



The coordination chemistry of an octa-aza macrocycle, L^{34} , containing four pyrrole and four Schiff base donors, towards late first row transition metals has been reported. Binuclear complexes with Ni^{II} , Cu^{II} , Zn^{II} and Cu^I were prepared and characterized (Fig. 2). Aerial oxidation of the Cu^I ions in the latter complex to their divalent oxidation state resulted in a change in the coordination mode of the macrocycle.²³

Ternary Pt(II) complexes of 1,4,7-trithiacyclononane, L^{35} , with additional substituted 2,2'-bipyridine ligands have been prepared and the relationship between their molecular and electronic structures studied.²⁴ In each case, the Pt(II) cation is



bonded to the chelating bipyridine and two sulfur atoms of L^{35} , with the third sulfur atom forming a long apical interaction with the Pt (2.84–2.97 Å), resulting in a flattened square-pyramidal structure. There is a correlation between the apical Pt...S distance and the donor properties of the ancillary bipyridyl ligands, which suggests a route to utilize the variation in the electronic properties of the ligand to tune the molecular structures of the complexes.

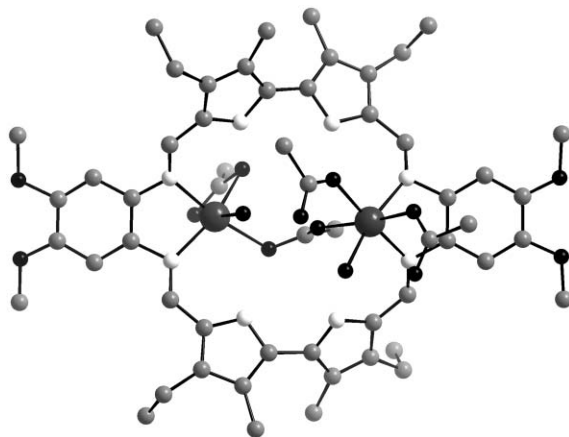
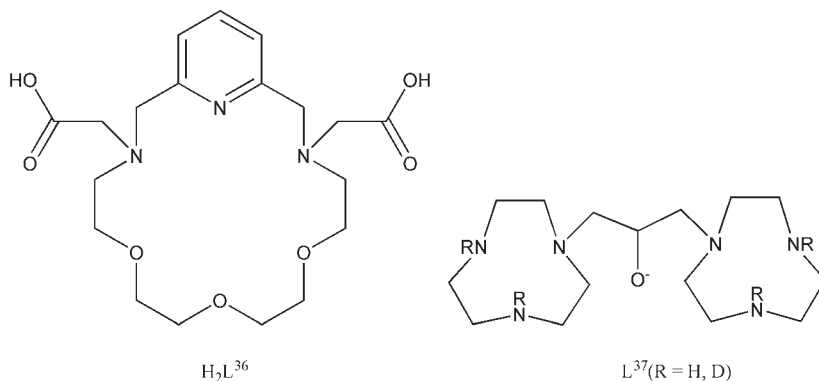


Fig. 2 A representation of the structure of $[\text{Ni}_2(\text{L}^{34})(\text{OAc})_4]$. The Ni^{II} ions are represented by dark grey spheres.

The triaza, trioxa macrocycle H_2L^{36} , with two carboxymethyl pendant arms, forms the pentanuclear Ba^{II} complex $[\text{Ba}_5(\text{H}_{0.375}\text{L}^{36})_4(\text{ClO}_4)(\text{EtOH})(\text{H}_2\text{O})_2](\text{ClO}_4)_{2.5}$, in which four ligands surround five Ba^{II} ions to give an unusual structure, in which the 5th metal ion sits inside a spherical organic cavity (Fig. 3).²⁵



Dinuclear $\text{Zn}(\text{II})$ complexes of a range of tetraaminodiphenol macrocycles have been synthesized and their interactions with carboxylate anions and amino acids studied.²⁶ New insights into the activity of dinuclear Zn^{II} complexes in phosphate ester hydrolysis were found by examining the complexes of macrocycles containing bipyridine units,²⁷ as well as with the linked [9]ane N_3 -based bimacrocycle $[\text{L}^{37}]^-$, whose $\text{Zn}(\text{II})$ complex shows very strong catalytic activity for the cleavage of uridine 3'-4-nitrophenyl phosphate.²⁸

Reactions between $[\text{Mn}^{\text{II}}(\text{L}^{38})]^{2+}$ and different cyanometalate anions such as $[\text{M}(\text{CN})_n]^{m-}$ ($\text{M}(\text{III}) = \text{Cr}$ or Fe , $\text{M}(\text{II}) = \text{Fe}$, Ni , Pd or Pt) lead to cyano-bridged molecular assemblies exhibiting a variety of structural topologies.²⁹ For instance, the reaction between $[\text{Mn}^{\text{II}}(\text{L}^{38})]^{2+}$ and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ forms a trinuclear complex and the reaction between $[\text{Mn}^{\text{II}}(\text{L}^{38})]^{2+}$ and $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$, where $\text{M}^{\text{II}} = \text{Ni}$, Pd or Pt , gives

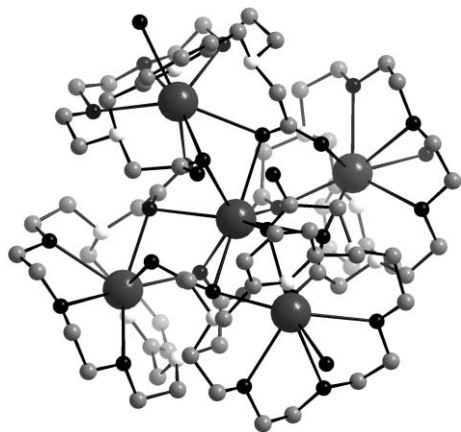
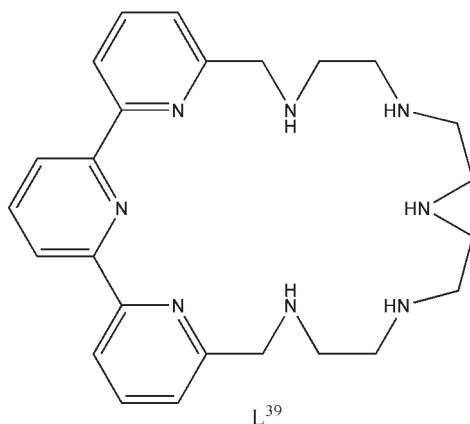
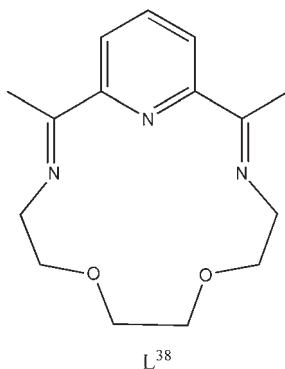
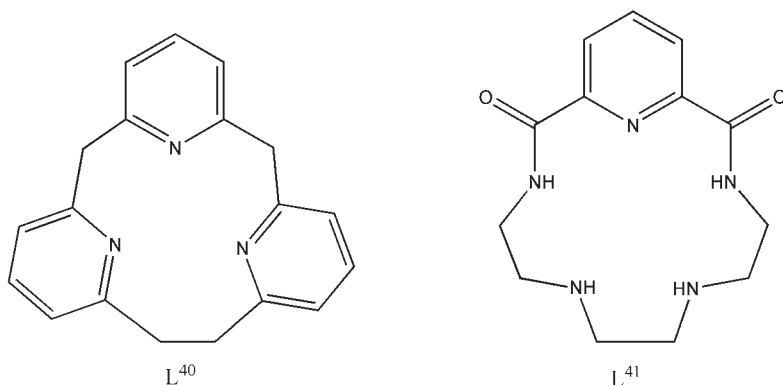


Fig. 3 The structure of $[\text{Ba}_5(\text{H}_{0.375}\text{L}^{36})_4(\text{ClO}_4)(\text{EtOH})(\text{H}_2\text{O})_2]^{2.5+}$. The Ba^{II} ions are shown as large dark grey spheres.

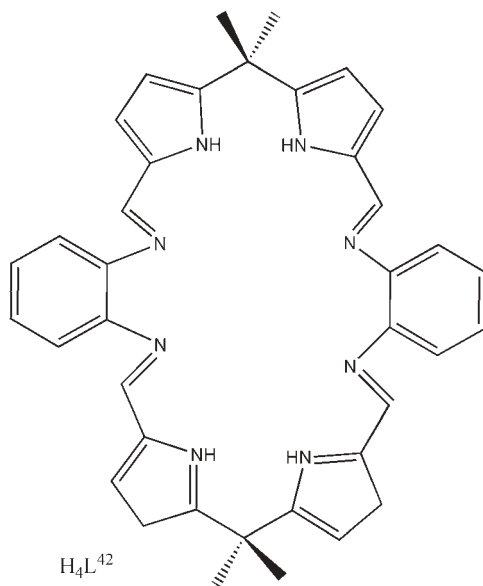
rise to three isostructural linear chain compounds. The synthesis of the new terpyridine–pentaamine macrocycle, L^{39} , is reported.³⁰ It can form both mono and dinuclear metal complexes with Cu^{II} , Zn^{II} , Cd^{II} and Pb^{II} salts in aqueous solution.



The macrocycle [2.1.1]-(2,6)-pyridinophane, **L⁴⁰**, binds to CuCl to give monomeric [Cu(**L⁴⁰**)Cl], which has a distorted tetrahedral '3 + 1' geometry with one long Cu–N bond.³¹ A stable iron(III) complex with the pentadentate amide-containing macrocyclic ligand, **L⁴¹**, was prepared and fully characterized.³²

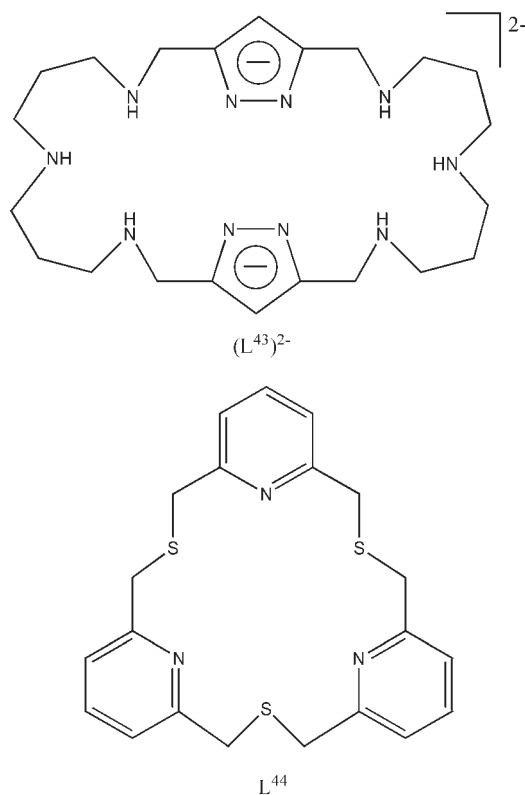


A mononuclear uranyl (UO_2^{2+}) complex, supported by the polypyrrolic macrocycle **L⁴²**, exhibits a 'hinged' macrocyclic structure with an expanded cavity, enforced π -stacking and hydrogen bonding motifs.³³ One imine group of a '3 + 3' Schiff base macrocycle with six imines was selectively reduced to give a new macrocycle possessing one CH_2NH and five imine groups. The benzimidazaoline reducing agent used has potential for the controlled partial reduction of other multi-imine macrocycles.³⁴



The synthesis of a new macrocyclic receptor, **L⁴³**, containing two 3,5-dimethylpyrazole units connected by dipropyleneamine bridges, has been synthesized.³⁵ Addition of Cu^{II} and Zn^{II} results in the deprotonation of the pyrazole moieties, which act as bis(monodentate) $\eta^1:\eta^1$ ligands. The pyridine-containing

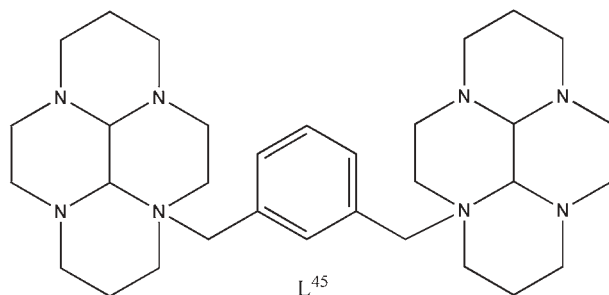
aza-thia macrocycle, L^{44} , and its complexes with Ni^{II} , Pd^{II} , Cu^I , Ag^I and Hg^{II} were synthesised and structurally investigated. The Ni^{II} and Hg^{II} complexes are mononuclear, with L^{44} serving as an unusual quinquedentate ligand. However in the mononuclear Cu^I complex, L^{44} is tetracoordinated to a tetrahedral Cu^I ion and $Pd(II)$ forms a binuclear complex with L^{44} , which exists as a zwitterion with square-planar $Pd(II)$ centres. In contrast, $Ag(I)$ forms one-dimensional coordination polymers.³⁶ Ditopic hexaaza macrocycles containing pyridine have also been reported.³⁷



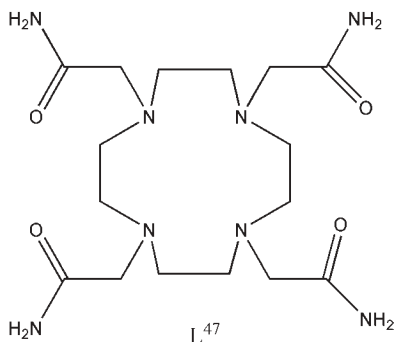
The first examples of the substitution of internally-directed P atoms at the bridgehead positions of phosphorus-based macrobicyclic compounds have been accomplished using groups larger than methyl substituents. This will allow the introduction of a range of groups into the cavity to allow its size and guest binding properties to be tailored.³⁸ The selection of a pentameric phosphorus donor host in the assembly of cyclic phosphazenes is a kinetic template effect, arising from the presence of chloride ion, which is nicely encapsulated by hydrogen bonding in its adduct with the cyclic pentamer.³⁹ An interesting metallomacrocycle with a 1,3-alternate calix[4]arene phosphorus ligand has also been prepared.⁴⁰ A convenient synthesis of a linear phosphazene salt and a 16-membered macrocycle of the form $[NCCl(NPCl_2)_3]_2$ has been reported.⁴¹ A 28-membered seleno-aza macrocycle has also been reported,⁴² and a diphosphine-palladium macrocyclic complex, possessing a molecular recognition site, has been shown to recognise barbiturates.⁴³

3. Macrocycles with pendant arms

A new, two step synthesis of the cyclam-based macropentacyclic ligand L^{45} has been developed, and a tetranuclear Cu(II) complex prepared.⁴⁴ Five novel Gd^{III} complexes based on the structure of the heptadentate macrocyclic ligand 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid, L^{46} , have been synthesized and their ^1H and ^{17}O NMR relaxometric properties investigated in detail. The complexes have been functionalised on the remaining secondary nitrogen atom of the macrocycle, with a range of pendant groups designed to interact non-covalently with human serum albumin. Indeed, all the complexes show some degree of interaction with human serum albumin, with a stronger binding affinity being measured for those that bear an aromatic moiety on the pendant group. This association results in a decrease in the rotational correlation time for the complexes and hence in an increase in their relaxivity for the purposes of MRI.⁴⁵

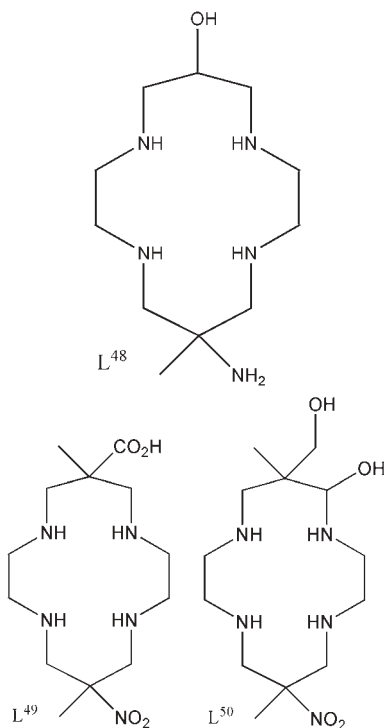


The synthesis and structures of $[\text{Pb}(L^{47})]^{2+}$ and $[\text{Hg}(L^{47})]^{2+}$ are reported.⁴⁶ The Pb^{II} ion is 9-coordinate, with L^{47} being octadentate and a water molecule being placed ($\text{Pb}-\text{O} = 3.52 \text{ \AA}$) above the proposed site of the lone pair on Pb. In contrast, the Hg^{II} is only 6-coordinate from an N_4O_2 donor set.

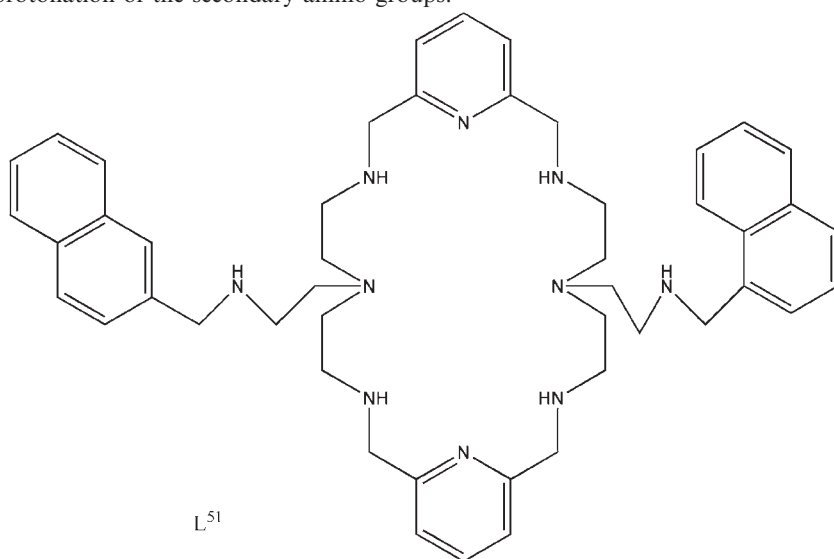


The use of a hydroxyl-functionalized open chain tetraamine in a template reaction based on its Cu(II) complex, leads, after reduction, to a new tetraaza macrocycle, L^{48} , containing both amino and hydroxyl substituents. The macrocycle is formed predominantly as its *trans* (anti) isomer, though the *cis* form is also detectable, and complexes of both have been structurally characterized; the OH substituent may be either axial or equatorial.⁴⁷ In related work, a reaction between ethane-1,2-diamine and 3,3'-dichloropivalic acid results in two isomeric tetraamines, one a tetraamino carboxylic acid and the other a carboxamidotriamino alcohol, depending on the

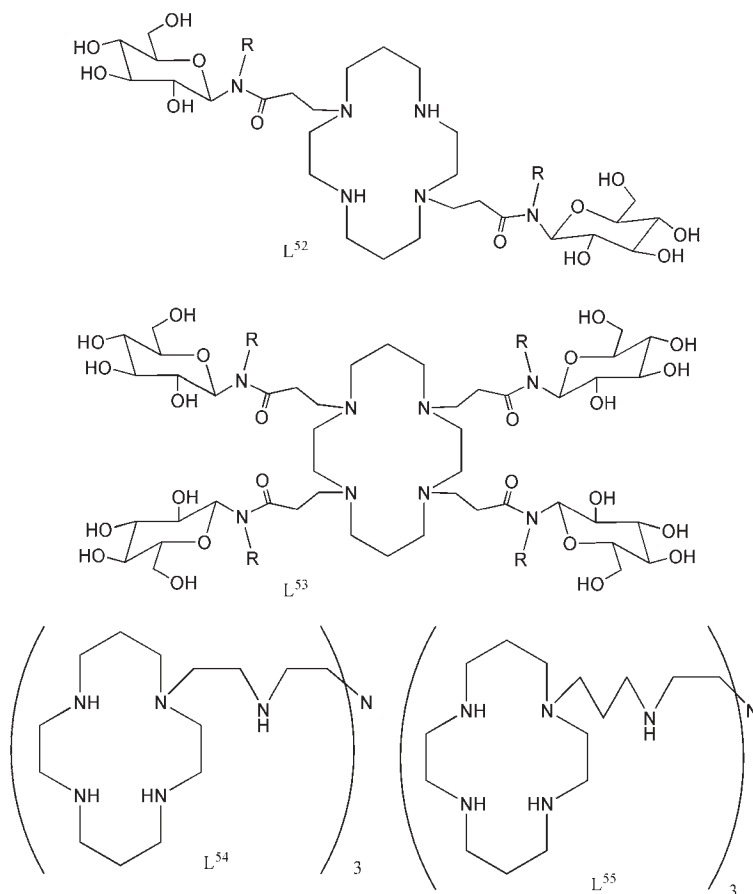
conditions. These were converted *via* template reactions to macrocycles with electrophilic (CO_2H , L^{49}) or nucleophilic (CH_2OH , L^{50}) pendant arms.⁴⁸



The synthesis, protonation behavior and $\text{Cu}^{\text{II}}/\text{Zn}^{\text{II}}$ coordination chemistry of the bibrachial aza lariat ether, L^{51} , have been reported.⁴⁹ The macrocycle, which has two aminoethyl naphthyl moieties symmetrically appended to a 2:2 azapyridinophane core, displays six protonation steps in the pH range 2–11 which correspond to the protonation of the secondary amino groups.

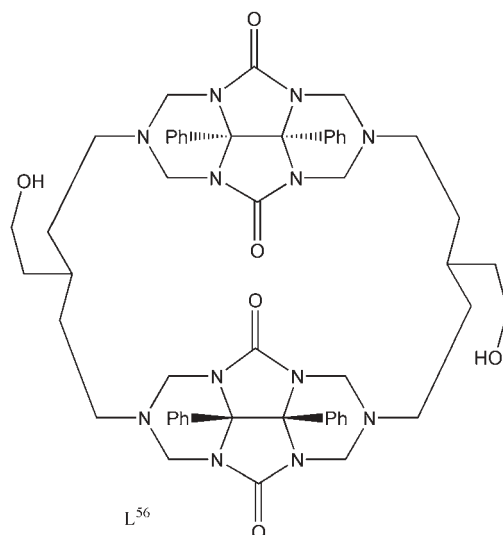


Macrocyclic surfactants, using cyclam and other macrocycles as their core, have been designed and synthesized so that sugar-based units are pendant from the macrocycle, as in **L**⁵² and **L**⁵³. In this way, versatile surfactants can be synthesized that combine the polar properties of the sugar moiety with the cation binding properties of the macrocycle.⁵⁰ The polytopic ligands **L**⁵⁴ and **L**⁵⁵ are composed of three cyclam-based units which are connected to a central 'tren' moiety *via* (CH₂)₂ or (CH₂)₃ linkers, respectively; polynuclear complexes of Ni(II) and Cu(II) having been prepared.⁵¹ Interesting work investigating the coordination chemistry of amino pendant arm derivatives of 1,4,7-triazacyclononane has also been reported.⁵²



4. Bowl shaped macrocycles

Three novel macrocyclic polyamines and an unexpected macrocycle were synthesized by the one step condensation of diethylenetriamine (or triethylenetetraamine) with formaldehyde and diphenylglycoluril; **L**⁵⁶ being an example.⁵³ The condensation of aryl boronic acids with 2,3-dihydropyridine gives boronates, which self-assemble to form tetrameric macrocycles; **L**⁵⁷ being an example (Fig. 4).⁵⁴ The structural diversity could be enhanced further by replacing the aryl groups with alkyl boronic acids.



Selective heterodimerisation of tetraurea-calix[4]arenes, containing four or eight ω -alkenyl groups, with a tetraosyl-urea-calix[4]arene has been used to synthesize multimacrocycles, L^{58} , via a metathesis reaction, in which the adjacent urea residues become covalently-connected.⁵⁵ L^{59} is a member of a new class of novel macrocycles that contain both polyether and phenolic functionalities. It forms dimers in both the solid state and in solution when exposed to chloroform, dichloromethane or toluene, but does not self-associate in the presence of dimethyl sulfoxide.⁵⁶ Subtle variations in intramolecular hydrogen bonding and articulation of these self-associated dimers about an axis provided by π - π stacking interactions, allow variably-shaped, irregular, nanosized balls to be formed. These pack in a multitude of motifs, ranging from simple networks with occluded solvent in the channels, to sheets and capsules.⁵⁷ Sequential Claisen-Schmidt condensations have also been used to produce

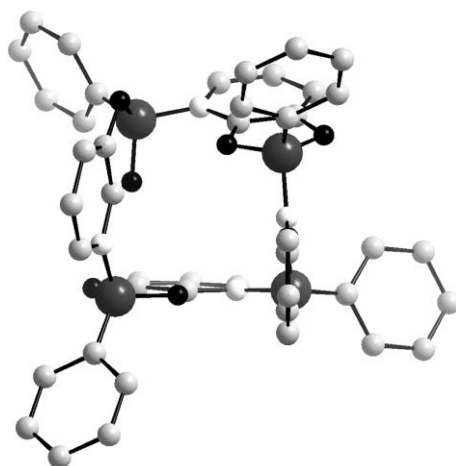
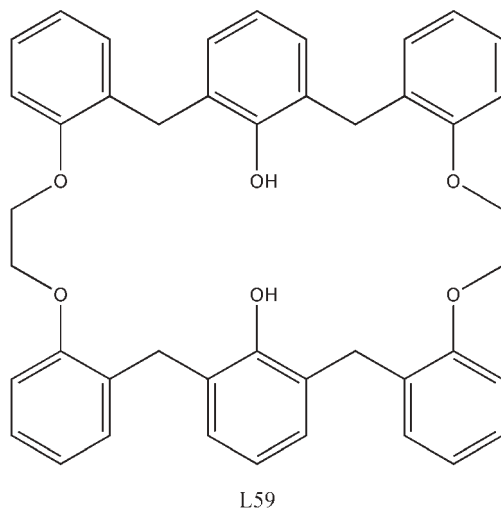
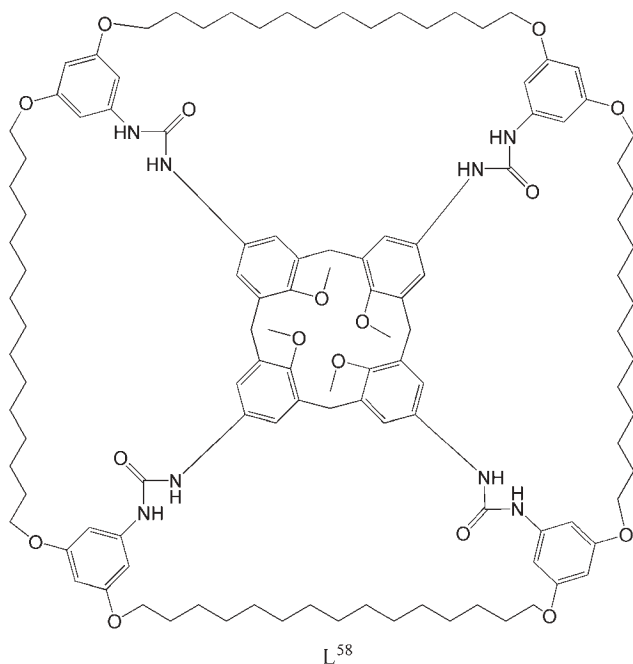


Fig. 4 Structure of the aryl boronic acid-based macrocycle, L^{57} . The cavity is *ca.* 5 Å wide. The boron atoms are shown as large dark grey spheres.

macrocycles with internal ketonic rather than phenolic groups.⁵⁸ The dimeric metallamacrocycles $[\{P(\mu-N^tBu)\}_2 \cdot (L-L)]_2$ ($L-L = OCH_2C(Me)_2CH_2O$, **L⁶⁰**; 2,6-(NH)₂C₅H₃N, **L⁶¹** and 1,2-(NH)₂C₆H₄, **L⁶²**) have been obtained from the reactions of the appropriate diols and diamines ($L-LH_2$) with the dimeric phosph(III)azane $[CIP(\mu-N^tBu)]_2$.⁵⁹



Calix[4]arenes bearing one or two methylenebisphosphonic acid fragments, **L⁶³**, were prepared *via* addition of diethylphosphite to the parent calix[4]arene aldehyde. The resulting compounds displayed stronger inhibition of calf intestine alkaline phosphatase than did simple methylenebisphosphonic or 4-hydroxyphenyl

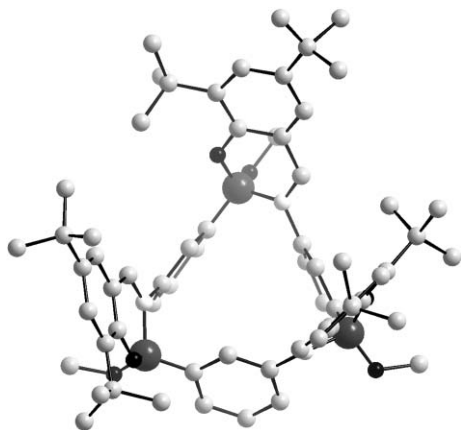
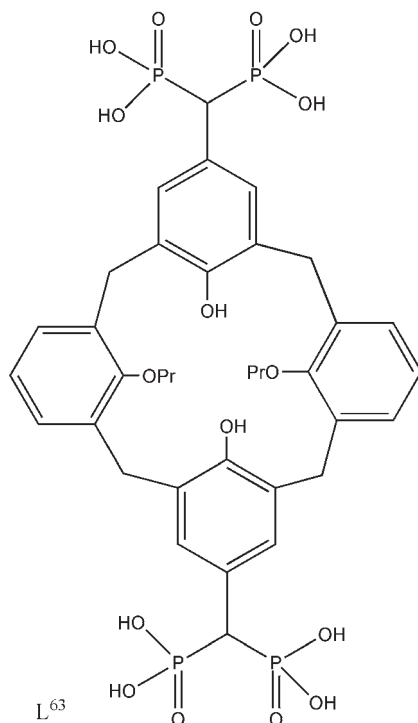


Fig. 5 Structure of the B–N calix[3]arene type macrocycle, **L⁶⁴**. The boron atoms are shown as dark grey spheres.

methylenebisphosphonic acids. The action of these phosphorylated calix[4]arenes is concordant with partial mixed type inhibition, and could be promising for the design of efficient alkaline phosphatase inhibitors.⁶⁰ The first of a new generation of boron-nitrogen based calix[3]arenes has been synthesised by the simple condensation reaction of 3,5-di-*tert*-butyl salicylaldehyde and 3-aminophenylboronic acid, which leads to a trimeric macrocyclic compound, **L⁶⁴** (Fig. 5).⁶¹ Its cavities are able to encapsulate small molecules such as benzene, THF and AcOMe.



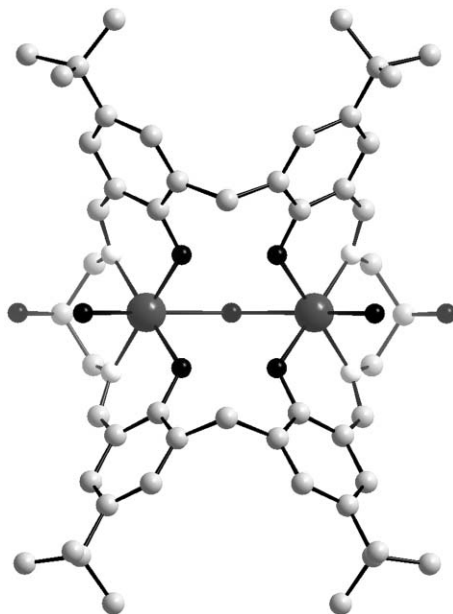


Fig. 6 Structure of the Ni(II) complex of L^{65} . The Ni(II) ions are shown as dark grey spheres.

A series of dinuclear complexes of a pseudo-calixarene macrocycle, H_6L^{65} , containing two 2,2-methylenediphenol groups, has been synthesised and structurally characterised.⁶² Using divalent metal ions, complexes containing a common saddle-shaped $[M_2(H_4L)]^{2+}$ core are formed. The structure is controlled by two strong O–H–O interactions, resulting from metal ion-promoted mono-deprotonation of the methylenediphenol units. The metal ions are located in a cleft, within which neutral or anionic guests can bind (Fig. 6). Use of trivalent metal ions leads to complete deprotonation of the phenol groups and the loss of the saddle conformation. A similar family of novel chiral ‘calixsalen’ Schiff base macrocycles, containing three chiral diamino moieties, has also been discovered, and these can also form mono or dinuclear compounds.⁶³

The [3 + 3] cyclocondensation reaction between aromatic dialdehydes and (1*R*,2*R*)-diaminocyclohexane affords oxygenated ‘trianglimine’ macrocycles containing six Schiff base units.⁶⁴ Reaction of a Schiff base macrocycle with iron(III) leads to the modification of the original macrocycle through the incorporation of a methylene group between two amine groups to give an imidazolidine ring.⁶⁵ Formation of organoactinide inclusion complexes with boron-containing macrocycles has been described, whereby the complex is built from a combination of catechol and catechol–borane units around the actinide centres, giving an overall hexagonal-bipyramidal geometry (Fig. 7).⁶⁶

5. Functional systems

A dicopper(II) cryptate complex of the polycyclic octaamine ligand, L^{66} , has been prepared, whose tren subunits are linked by 4,4'-ditolyl spacers to provide an unusually long ellipsoidal cavity (Fig. 8). As such, this cavity is suitable for the inclusion of ambidentate anions whose donor groups are well separated, and

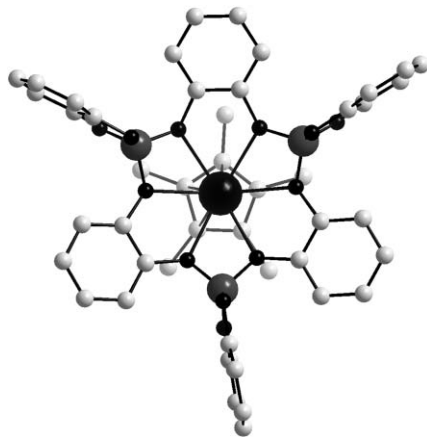


Fig. 7 Structure of a catechol-borane-based macrocycle with Th^{III} at the centre, shown as the large black sphere (with a C_5Me_5 ligand behind it). The boron atoms are shown as large dark grey spheres.

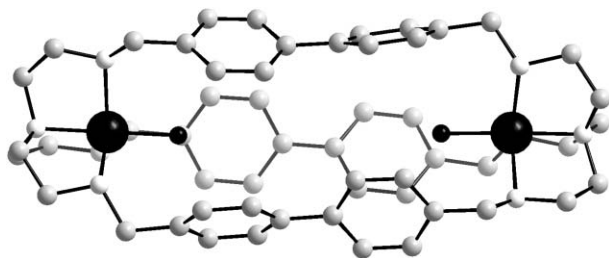
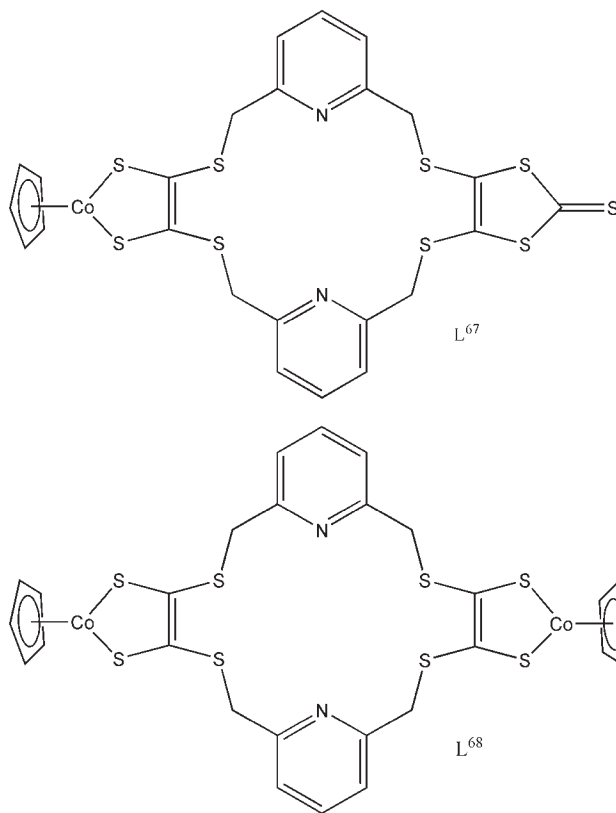


Fig. 8 Structure of $[\text{Cu}_2\text{L}^{66}(\text{H}_2\text{O})_2]^{4+}$. The copper atoms are shown as large black spheres.

this complex can be used for the fluorescent detection of dicarboxylate anions in aqueous solution.⁶⁷

The new S_4N_2 redox-active macrocycles, L^{67} and L^{68} , contain 18-membered rings conjugated to one or two chromophoric, redox-active $\text{CpCo}(\text{dithiolene})$ units. Electrochemical and UV-vis spectroscopic studies have shown that L^{67} interacts strongly with Ag^{I} ions.⁶⁸

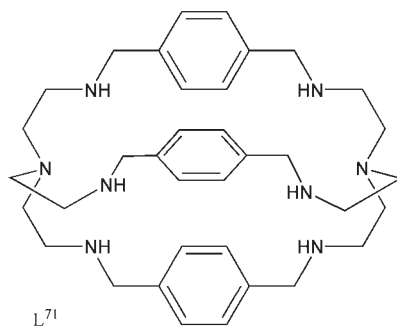
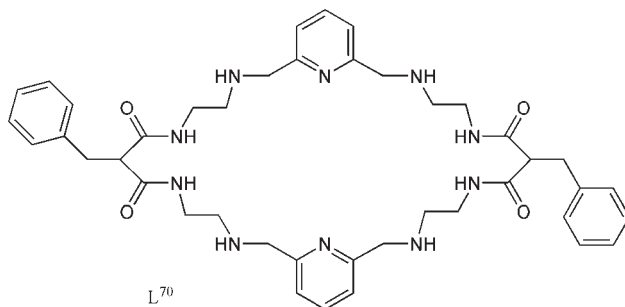
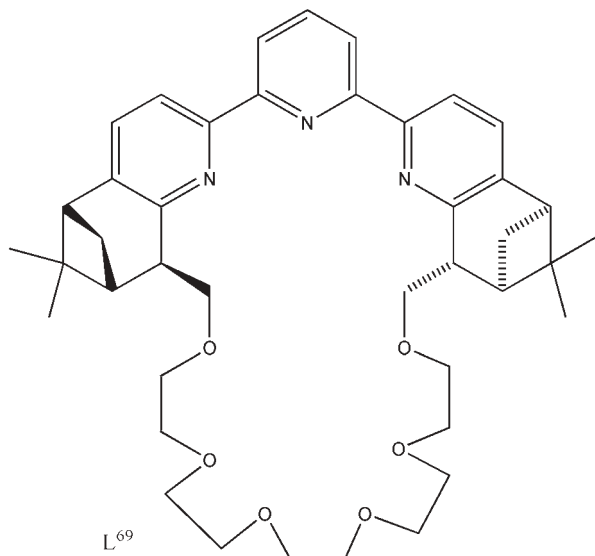
The chiral terpyridine macrocycle, L^{69} , has been developed as a fluorescent sensor for enantioselective recognition of amino acid derivatives. It is a strong chelating agent for organic ammonium salts and also a useful chromophore in fluorescent sensing.⁶⁹ Luminescent cation sensors have been prepared containing a $\{(\text{bpy})\text{Re}(\text{CO})_3\}$ group linked to an azacrown ether *via* an alkenyl or alkynyl spacer. Binding constants for metal ions at the macrocyclic sites are in the range $\log K = 1-4$; the alkene spacer being a more responsive sensor than the alkyne spacer because it provides stronger electronic communication with the Re centre across the ligand.⁷⁰ A range of ditopic, redox-active polyferrocenyl zinc(II) dithiocarbamate macrocyclic receptors have been synthesized, based upon dithiocarbamate units containing ferrocene groups on the macrocycle's periphery and/or as part of the cyclic cavity.⁷¹ These host systems were found to bind and electrochemically sense anionic guest species such as isonicotinate, benzoate and neutral 4-picoline. Condensation of



1,1'-ferrocenedicarboxaldehyde with (1*R*,2*R*)-1,2-diaminocyclohexane affords a '3 + 3' bowl-shaped hexa-Schiff base macrocycle (*cf.* the 'trianglimines' mentioned earlier) with a chiral concave cavity that exhibits a remarkable ability to act as a host material for the enantioselective enclathration of 1,1'-bis-2-naphthol.⁷² Electrochemical investigations were performed on a set of three cyclooctaphyrin complexes containing Co(II) which adopt a 'figure-of-eight' geometry.⁷³ This conformation, displaying two tetrapyrrolic complexation sites, can accommodate up to two divalent cations.

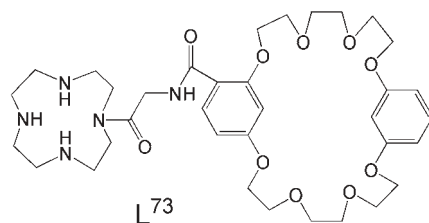
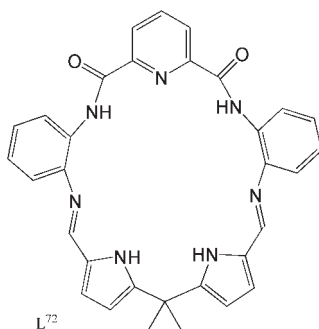
The di-copper(II) complex of the polyaza-macrocyclic, **L**⁷⁰, shows a dramatic colour change in the presence of imidazole-based substrates, based upon the translocation of the copper centres within the macrocycle, and caused by the coordination of the imidazole in a bridging mode.⁷⁴ The dinuclear Cu(II) cryptate, [Cu₂**L**⁷¹](ClO₄)₄, binds and activates acetonitrile solvent to yield the unexpected cyanide-bridged complex [Cu₂**L**⁷¹(CN)](ClO₄).⁷⁵

The diamidopyridine–dipyrromethane anion receptor, **L**⁷², shows a high selectivity for dihydrogen phosphate and hydrogen sulfate relative to nitrate in acetonitrile solution. As such, it is suggested that it could find use in nuclear waste remediation applications that require the selective removal of hydrogen sulfate from nitrate-rich waste mixtures.⁷⁶ The modular hybrid receptor, **L**⁷³, containing both an azamacrocyclic and a crown ether, was designed and synthesised for the binding of phosphate. The thermodynamic characterisation of the Zn(II) complex's receptor binding properties towards phosphate in water is presented and the parameters are

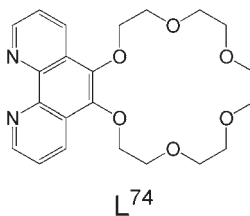


compared to those of the isolated aza macrocycle precursor.⁷⁷ Three new azamacrocyclic–cyclophane hybrid receptors have been synthesized that incorporate either 1,4,7,10-tetraazacyclododecane (cyclen) or 1,4,7-triazacyclononane (tacn) unit(s), tethered *via* a short amidic spacer to an electron donor and a hydrogen bonding crown ether. The crown ether is designed to act as a host towards biologically-relevant guests, whereas the macrocycle can coordinate Zn(II) or Cu(II) ions; the Zn(II) complex strongly binding phosphate derivatives.⁷⁸ Attachment of a laterally non-symmetric cryptand and a macrocycle at the 9- and 10-positions of

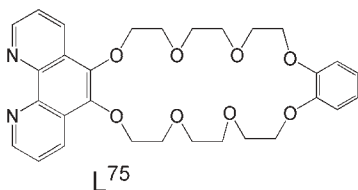
anthracene leads to a fluorescent signalling system which gives fluorescence enhancement in the simultaneous presence of alkali and transition metal ions.⁷⁹



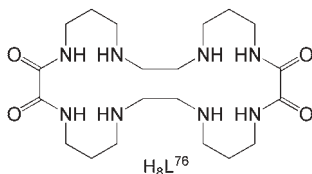
A new macrocycle containing three basic pyridines, four hydrogen bond accepting carbonyls and two hydrogen bond donating amide groups, binds mono-alkyl ammonium salts in a manner that is dependent on the counterion of the ammonium guest, and so demonstrating its ditopic recognition properties.⁸⁰ A range of ligands, for example **L⁷⁴** and **L⁷⁵**, in which a macrocyclic unit is fused to a 1,10-phenanthroline unit, has been prepared, starting from 5,6-dihydroxyphenanthroline. The ligands comprise a crown ether or a mixed amide/crown macrocycle fused to a 1,10-phenanthroline unit, with luminescence measurements being used to examine cation and anion binding.⁸¹ The interactions of various pyrazole-containing macrocyclic receptors with L-glutamate in aqueous solution have been studied by potentiometric techniques and show the relevance of the central polyaminic nitrogen in the interaction with glutamate.⁸² A cyclohexyl-1,2-diamine derived bis(binaphthyl) macrocycle has demonstrated enantioselectivity in the fluorescent recognition of mandelic acid,⁸³ while the Cu(II) complex of an aza-terpyridinophane receptor has been found to fix CO₂.⁸⁴



The 'one pot' synthesis and characterization of a large 28-mer macrocycle, **H₄L⁷⁶**, with oxamido units capable of complexing guest ions through oxygen or nitrogen donor atoms, has been achieved.⁸⁵ The macrocycle contains two sites capable of complexing two nitrate anions or two copper(II) cations. A large structural

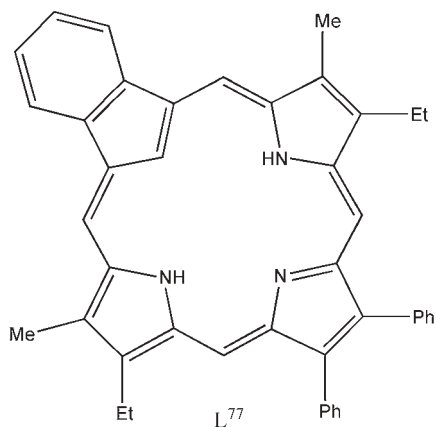


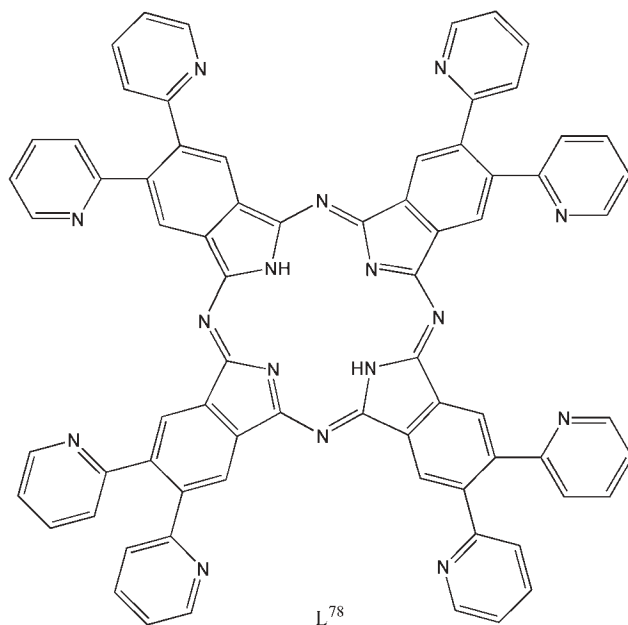
reorganization in the conformation of the macrocyclic framework for coordination of the copper(II) ions is required, compared to when nitrate is coordinated. A 'weak link' approach has been employed to synthesize a series of bimetallic Cu(I) macrocycles in high yield.⁸⁶



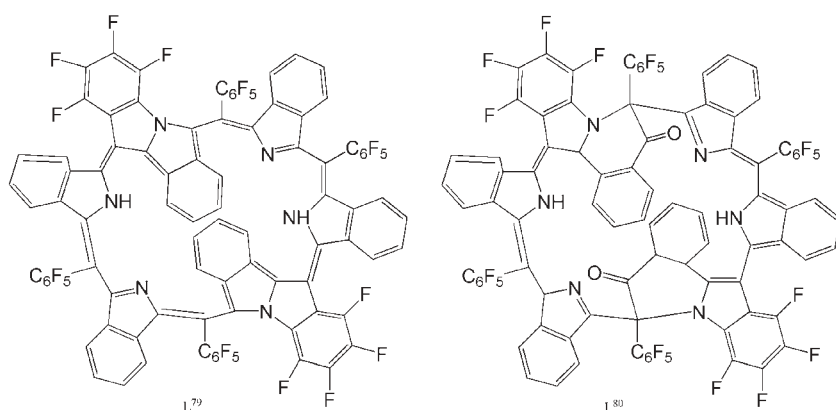
6. Porphyrins

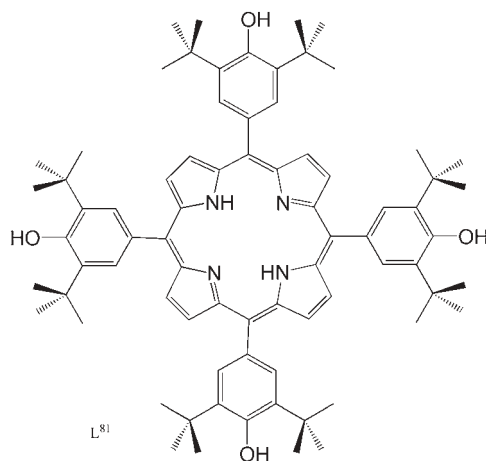
New macrocycles incorporating a porphyrin and π -electron rich aromatic units were prepared from a dynamic library, based on the formation of disulfide linkages. The outcome could be influenced by the use of templates that biased the equilibrium towards the host which provided the best fit for the template.⁸⁷ New metallocarba-porphyrins of the form L^{77} have been synthesised and show a strong diatropic ring current in their proton NMR spectra. Au(III) complexes of *meso*-tetraaryl-carbaporphyrins show strong porphyrin-like aromatic characteristics, as apparent from UV-vis and electrochemical measurements.^{88,89} Electrochemical, spectral and computational studies of metalloporphyrin dimers, formed by cation complexation of pendant crown ether cavities, has been undertaken.⁹⁰ A new pyrazinoporphyrazine macrocycle carrying eight externally-appended pyridine rings, L^{78} , was prepared in high yield. A comparison of the electrochemical behavior of L^{78} with phthalocyanine and porphyrazine analogues highlighted the remarkable electron accepting properties of the free base macrocycle.⁹¹





A doubly N-fused β -benzo[28]hexaphyrin, L^{79} , has been synthesized. It undergoes an oxidative rearrangement to macrocycle L^{80} , whose fluorescence is solvent dependent.⁹² Multivalent porphyrin assemblies are being targeted; for instance a lipophilic hexaporphyrin assembly, supported on a stannoxane core, has been characterised,⁹³ and a giant porphyrin disc dodecamer ($M_w = 15$ kDa) has been synthesized which self-assembles into huge domains.⁹⁴ Rather than using a core 'support', a dodecameric porphyrin wheel has been created, whereby the porphyrin moieties are connected by 1,3-substituted benzyl groups.⁹⁵ A highly non-planar, electron deficient, N-substituted tetraoxocyclohexadienylidene porphyrinogen, L^{81} , has been synthesised and investigated by both crystallography and cyclic voltammetry.⁹⁶





7. Threaded and interlocked compounds

The realization of the Borromean link in a wholly synthetic molecular form is reported.⁹⁷ This topologically achiral compound was assembled in high yield from 18 components by the template-directed formation of 12 imine and 30 dative bonds. The structure comprises three interlocked macrocycles, each tetranucleating and decadentate overall, coordinating to a total of six Zn(II) ions. The use, in concert, of coordination, supramolecular and dynamic covalent chemistry was necessary for this highly efficient construction of a nanoscale dodecacation with an approximate diameter of 2.5 nm.

A switchable macrocycle clip complex that functions as a NOR logic gate has been synthesized.⁹⁸ The switching behaviour is not only controlled through the use of either K^+ -[2,2,2]cryptand or NH_4^+ - Et_3N systems, but also provides colour changes that are visible to the naked eye. Consequently, this system operates as a two-input, NOR functioning molecular logic gate.

Six types of porphyrin-stoppered rotaxane have been prepared from Rh(III)-porphyrin complexes. These have flexible amino groups as threads and these are threaded through a 24-crown-8 macrocycle. ¹H NMR studies showed that in the case of the rotaxanes with relatively short threads, the conformation of the macrocycle was affected by the substituents of the terminal porphyrin. This suggests a mechanical interaction between the macrocycle and terminal porphyrin, and may lead to a methodology for the design of novel molecular devices that can regulate the rotational motion of macrocycles by terminal porphyrins, or transmit rotational motion from macrocycles to terminal porphyrins.⁹⁹ A chiral Cu(I)-complexed [2]-catenane, consisting of two interlocking 38-membered rings, each ring incorporating a 2,9-diphenyl-1,10-phenanthroline (dpp) and (*S*)-1,1-binaphthyl group, has been prepared by means of a transition metal template strategy.¹⁰⁰ Demetalation afforded the corresponding free chiral [2]-catenane. Copper(I)-assembled pseudorotaxanes bearing bis(nitrile) ligands have been utilised in the selective formation of large chelate rings.¹⁰¹

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