Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Hannon, Michael J. and Childs, Laura J.(2004) 'Helices and Helicates: Beautiful Supramolecular Motifs with Emerging Applications', Supramolecular Chemistry, 16: 1, 7 — 22
To link to this Article: DOI: 10.1080/10610270310001632386
URL: http://dx.doi.org/10.1080/10610270310001632386

Supramolecular Chemistry, January–February 2004, Vol. 16 (1), pp. 7–22

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Helices and Helicates: Beautiful Supramolecular Motifs with Emerging Applications

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Received (in Southampton, UK) 8 August 2003; Accepted 4 October 2003

INTRODUCTION

The fascination of scientists, and particularly supramolecular chemists, with helical arrays continues unabated [1,2]. These structures have provided the playground in which many supramolecular design principles have evolved, starting in the mid-1980s and stimulated by the work of Lehn and co-workers [3].

Their origins are even older with the first recognized triple helical metal complex reported by Busch in the late 1950s [4] and a report from Morgan and Burstell [5] in the 1930s of a silver(I) complex with unexpected stability towards oxidation that is now recognized to be a consequence of the compound's helical structure [6]. Yet only recently have potential applications of these fascinating structures started to emerge. Herein we review the design of helical arrays, focusing on those arrays assembled by metal ions, and explore their potential for application.

In chemical terms a helical structure is achieved by the wrapping of molecular (or supramolecular) strands about a central axis (the helical axis). Helices may be single or multiple stranded and vary in pitch (the distance along the helical axis for the strands to complete a full turn). The wrapping may be controlled by metal ion coordination (the focus herein) or other supramolecular interactions such as hydrogen bonds [7] or π-stacking [8].

If a helix is viewed down its helical axis, the rotation of the helix may be clockwise or anticlockwise. A right-handed or *P* (plus) helix rotates clockwise while a left-handed or *M* (minus) helicate rotates anticlockwise. Many helices occur in nature and one of the most well known examples is deoxyribonucleic acid (DNA). This macromolecule in its most usual B conformation exists as a right-handed double helix with the two strands held together by hydrogen bonds between complementary bases.

The term helicate is used to describe metal containing helical coordination arrays or structures and is derived from the Greek word *helix* and the suffix *-ate* which describes complexes between ligands and metal ions. The organic ligands or strands of the helicate must fulfil some requirements: (i) they must possess several binding domains along the strand that are capable of coordinating to various metal ions; and (ii) they must include spacers between the binding domains that are rigid enough to prevent two binding units of the same ligand coordinating to the same metal ion but at the same time be flexible enough to wrap around the metal ions and produce a helical architecture.

Helicates can be polymetallic double-, triple- or quadruple-stranded complexes. When the coordinated strands are identical, the helicate is referred to as a *homostrand* helicate and, conversely, helicates possessing different strands are *heterostrand* helicates. The strands themselves can exist in two categories. Strands with an identical sequence of binding domains along the length of the strand are called *homotopic* strands whereas strands with different binding domains are known as *heterotopic*. The second category possesses directionality as the strands can orient themselves within a helicate in either parallel (head-to-head, HH) or antiparallel (head-to-tail, HT) fashion (Fig. 1a).

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ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270310001632386

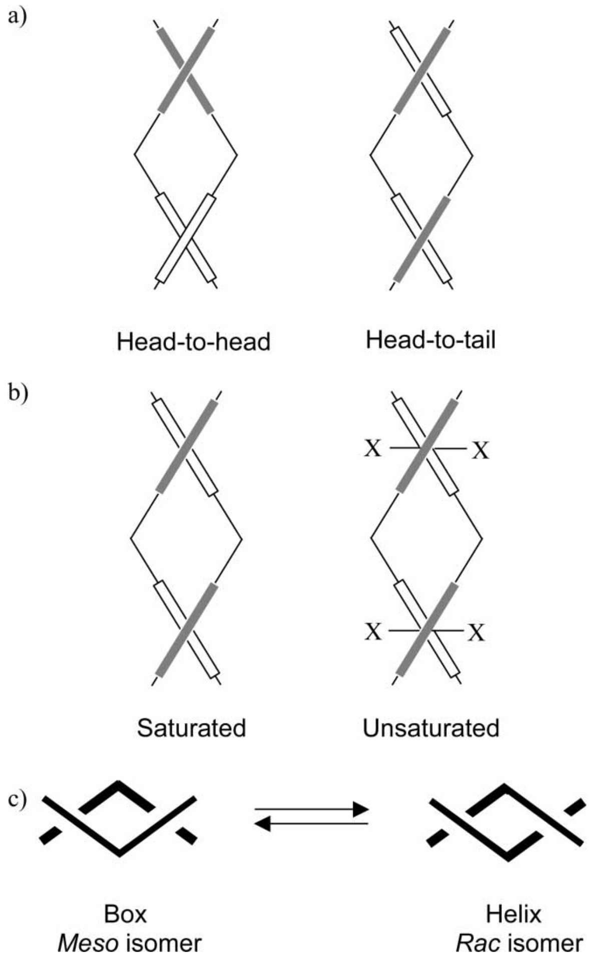

FIGURE 1 Representation of a) HH and HT helicates b) saturated and unsaturated helicates and c) cyclophane (box) and helicate conformations.

Additional categories of helicate are *saturated* and *unsaturated*. A saturated helicate is one in which the coordination sphere of the metal ions is satisfied by the binding domains of the ligand strand. The metal ions in an unsaturated helicate require supplementary ligands to enable their stereochemical requirements to be achieved (Fig. 1b).

Double-helicates

The term helicate was introduced by J.-M. Lehn in 1987 [9] but before this time, some examples of double- and triple-helicates were already known. For example, as early as 1958, Stratton and Busch had shown that 2-pyridinaldazine (**1** illustrated in Fig. 2) reacts with iron(II) or nickel(II) salts to form compounds with the formula $[\mathrm{M}_2\mathbf{1}_3]^{4+}$ [4]. Each of the three ligands acts as bidentate donor to two metal ions. It was proposed that this compound must have a helical structure and this has recently been confirmed by an X-ray crystal structure [10].

In 1976, Fuhrhop and colleagues [11] reported the synthesis of zinc octaethyl formylbiliverdinate. Addition of acid to the complex results in the removal of a coordinated water molecule and hence the coordination number of zinc changes from five to four. Consequently, a dimeric helix is formed. The structure returns to its original form upon the addition of base and these reversible changes can be followed spectroscopically. More recently, Thompson and Dolphin [12] reported a similar approach using bis(dipyrromethene) ligands linked by alkyl spacers of varying lengths.

Oligopyridines which consist of pyridine rings linked directly via interannular carbon–carbon bonds provided the basis of much of the early work in the field. In particular, Lehn *et al.* [9] and Constable [13] demonstrated that oligopyridines can behave as helicating ligands and the various binding modes that give rise to these structures are discussed here.

The simplest oligopyridine, 2,2′-bipyridine (bpy), is an important building block in helicating ligands. Oligopyridines containing bipyridine units linked by flexible spacer units have been synthesized (**2a**–**2d** in Fig. 2). Provided that the spacer is sufficiently flexible, they are capable of forming double-helical complexes when mixed with metal salts of the appropriate coordination geometry [14]. For example, the ether linked oligo(bipyridine) ligand **2b** (Fig. 2) forms a trinuclear double-helical complex with copper(I) ions (Fig. 3). The coordination preference of the copper(I) ion is to bind to two bipyridines in a *pseudo*-tetrahedral N_4 environment. The length of the spacer prevents two bipyridine units from the same ligand from binding in such a geometry to a single metal. Instead, two bipyridines from two different ligand strands are brought together around each copper(I) ion and this leads to the assembly of the double-helical array. The substituents at the 6 and 6′ positions of the bpy units sterically prevent the formation of triple-helicates when octahedral metals are added to ligand **2b**.

In 1993, Lehn and colleagues examined whether self-recognition could be achieved in a helicate system using ligands **2a** to **2d**. A mixture of the four ligands was reacted with Cu(I) ions and only the homostranded complexes $[\mathrm{Cu}_2\mathbf{2a}_2]^{2+}$, $[\mathrm{Cu}_3\mathbf{2b}_2]^{3+}$, $[\mathrm{Cu}_4\mathbf{2c}_2]^{4+}$ and $[\mathrm{Cu}_5\mathbf{2d}_2]^{5+}$ were formed. No polymeric structures were identified [15].

Heterostrand recognition has also been achieved through the use of five-coordinate Cu(II) ions to assemble a mixture of ligands **2b** ($X = H$) and **3** (Fig. 2). Each copper(II) centre binds to one bpy and one tpy subunit and only the mixed ligand complex $[\mathrm{Cu}_3(\mathbf{2b})(\mathbf{3})]^{6+}$ is formed [16]. In this example, no homostranded complexes were generated.

Further work by Lehn and co-workers demonstrated that it is possible to attach thymidine substituents to bpy units. Helicate formation takes

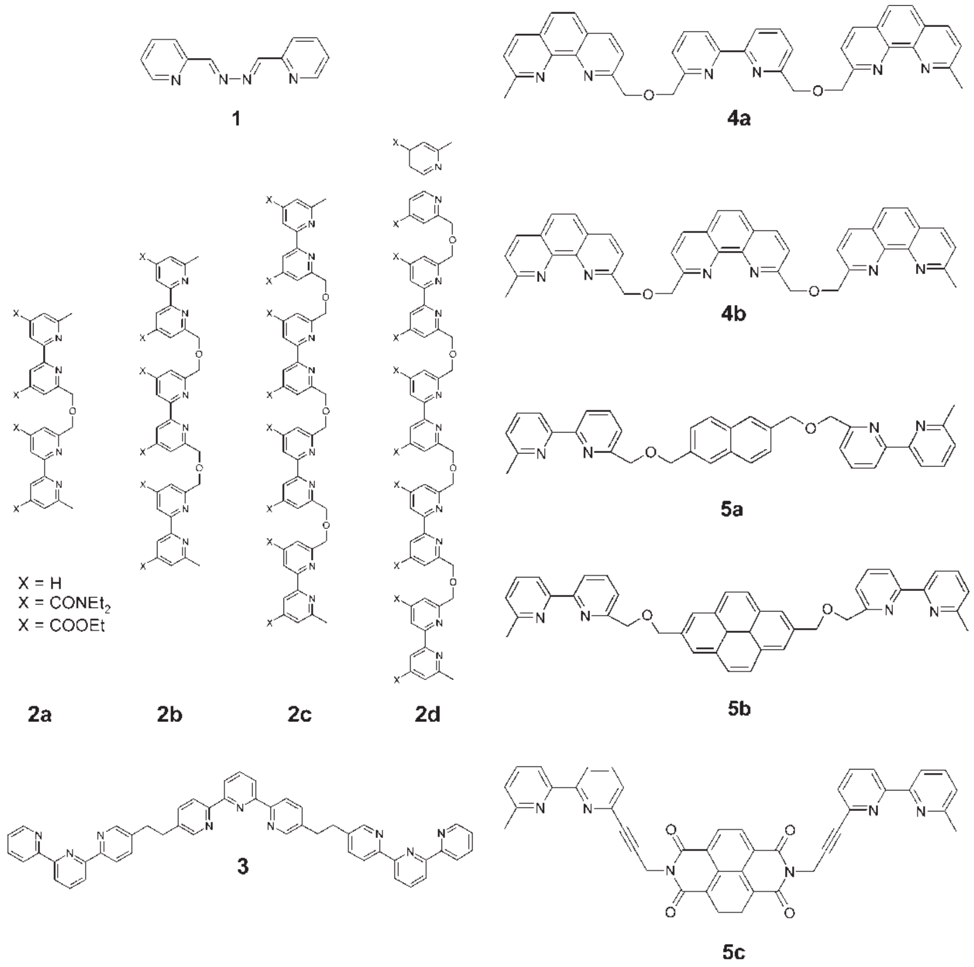

FIGURE 2 Ligands **1**–**5**.

place upon addition of Cu(I) ions to the ligand and the product was named deoxyribonucleohelicate (DNH) [17]. It was expected that the thymidine bases sitting on the exterior of DNH could interact with the bases of DNA via hydrogen bonds. However, no DNA binding studies with DNH have been reported.

Despite being structurally more rigid, 1,10-phenanthroline (phen) has coordination chemistry

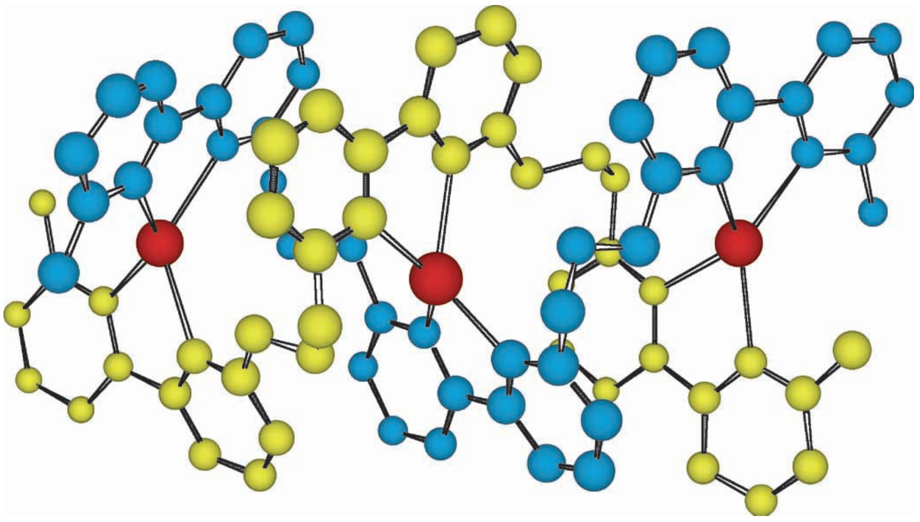

FIGURE 3 Crystal structure of double helicate $[Cu_3\mathbf{2b}_2]^{3+}$.

that is similar to that of bpy. Ligands **4a** and **4b** are similar to ligand **2b** but with some or all of the bpy binding units replaced with phen (Fig. 2) [18]. Ligand **4a** forms trinuclear double-stranded helicates with both Cu(I) and Ag(I). Ligand **4b**, also forms a helical architecture with Cu(I).

The nature of the spacer between the metal binding units is crucial for ensuring helical arrays are generated. The effect of changing the bridging unit between two bpy units has been investigated by Harding and colleagues [19–22]. Ligand **5a** (Fig. 2) forms equal amounts of non-helical and helical isomers (Fig. 1c) of $[\mathrm{Cu}_2\mathbf{5a}_2]^{2+}$ when reacted with Cu(I) ions. A mixture of two $[\mathrm{Zn}_2\mathbf{5a}_2]^{4+}$ complexes is also observed with Zn(II) ions in which the metal ions adopt a *pseudo*-octahedral coordination geometry. In a similar manner to **5a**, ligand **5b** forms equal amounts of helical and non-helical complexes $[\mathrm{Cu}_2\mathbf{5b}_2]^{2+}$. In the presence of Zn(II) ions, however, only the non-helical species $[\mathrm{Zn}_2\mathbf{5b}_2]^{4+}$ is formed.

Ligand **5c** has also been synthesized. In the presence of Zn(II) ions and at low concentrations ($<0.74\,\mathrm{mmol\,dm^{-3}}$), a single complex $[\mathrm{Zn}_2\mathbf{5c}_2]^{4+}$ was formed. At higher concentrations ($8.3\,\mathrm{mmol\,dm^{-3}}$) a mixture of several Zn(II) complexes were observed in the NMR spectrum. However, upon addition of a suitable guest molecule, a single $[\mathrm{guest} \subset \{\mathrm{Zn}_2\mathbf{5c}_2\}]^{4+}$ complex was observed (Fig. 4).

This work provides an example of a dynamic combinatorial library. All components of the library are in dynamic equilibrium. Addition of a template results in the formation of a complex between the template and the most suitable receptor for the template. The equilibrium within the mixture then alters and eventually only one host–guest complex remains in solution. Crystal structures of the complex have been obtained in which the guest molecule is 1,2,4,5-tetramethoxybenzene or *o*-dimethoxybenzene. The structures reveal the helical structure of the Zn(II) complex. Evidence for binding of a guest molecule in the cavity of the Zn(II) complex was also provided by NMR experiments. In the absence of a guest molecule, the pyromellitimide rings are rotating rapidly on the NMR timescale. When a guest molecule is added that binds in the helical cavity, the ring rotation is hindered and the pyromellitimide protons broaden in the NMR spectrum at room temperature. Host–guest recognition was also reported for the complex $[\mathrm{Cu}_2\mathbf{5c}_2]^{2+}$. The Cu(I) complex, however, required more equivalents (>20) of guest molecule than the Zn(II) complex (<3) for the same effect to be observed.

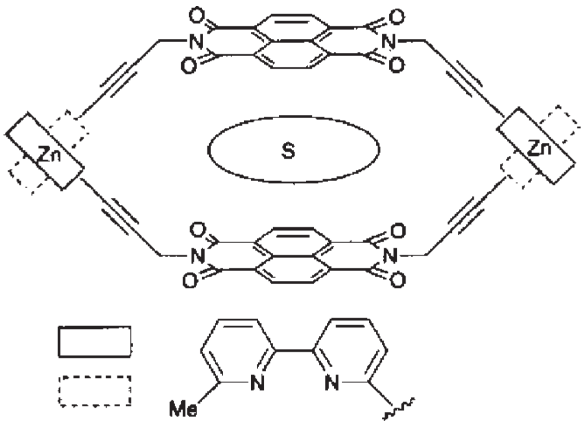

FIGURE 4 Representation of complex formed between template and $[\mathrm{Zn}_2\mathbf{5c}_2]^{4+}$. Reproduced from [22] by permission of The Royal Society of Chemistry.

2,2′:6′,2″-Terpyridine (tpy) is the next higher oligopyridine after bpy and can behave as either a tridentate or bidentate ligand. If only some of the donor atoms of this ligand are coordinated to a metal ion, the arrangement about the C—C bond between the coordinated and non-coordinated rings is found to be non-planar. This twisting also occurs when tpy acts as a bridging ligand between two or more metal centres and is of significance when considering the formation of multiple-helical systems.

Like bpy, tpy units have been linked together using appropriate spacer units. Ligand **3** (Fig. 2) was synthesized and consists of three tpy units linked together by ethylene groups. Metal ions that prefer an octahedral coordination environment can be satisfied when coordinated to two tpy binding units. Therefore, the addition of Fe(II) to ligand **3** provides the trinuclear double-stranded helicate, $[\mathrm{Fe}_3\mathbf{3}_2]^{6+}$ [23]. The ethylene linker is attached to the tpy units at the 5 position. Attachment at the 6 position would prevent coordination.

The two enantiomers of this helicate have been separated chromatographically. The complex was loaded onto a column packed with the ion exchange resin Sephadex®-SP and eluted with optically pure (+)-tartratoantimonate(II). Two well separated purple bands were collected from the column and circular dichroism spectra of the two bands showed them to be the helical enantiomers of the iron(II) complex.

2,2′:6′,2″:6″,2‴-Quaterpyridine (qtpy) can behave as a planar quaterdentate, a terdentate with a non-coordinated pyridine or a bidentate with two non-coordinated pyridines. When complexed to an octahedral metal ion, the planar tetradentate mode will be favoured with the ligand occupying the four equatorial sites. A different situation arises, however, when copper(I) is used as the metal ion. In this case, qtpy acts as two linked bpy units and a dinuclear double-helical array is formed in which each copper(I) binds to a bpy subunit from two different ligand strands. The double-helical structure arises because of a mismatch between the requirements of the metal and the ligand structure. Copper(I) prefers to adopt a tetrahedral coordination geometry and with this planar N_4 ligand this can only be achieved in a dinuclear double-helical system [6,13].

Multinucleating oligopyridine ligands frequently require time-consuming multi-step syntheses from relatively expensive starting materials. Ligands containing imine binding domains have been developed for the synthesis of helicates and offer considerable synthetic advantages since they are readily prepared simply by mixing aldehydes and amines, many of which are available commercially.

Ligand **6a** (Fig. 5) has been synthesized in our own laboratories. Reaction of this ligand with copper(I) and silver(I) ions gives rise to dinuclear double-stranded structures [24]. The two metal binding sites are sterically prevented from coordinating to the same metal centre because of the phenylenes in the spacer unit while the central methylene unit introduces sufficient flexibility into the ligand to allow helicate formation. As with the Harding ligands **5a**–**5c**, the dimeric complexes formed between ligand **6a** and tetrahedral metal ions exist in two possible conformations, the cyclophane (box) and helix (Fig. 1c).

The complex $[Cu_2\mathbf{6b}_2]^{2+}$ also adopts two conformations in solution. In the solid state a helix is observed with the face-edge π-stacking interactions between the strands creating a major and minor groove in the double-helical array [25].

Using this simple imine technology, we demonstrated that it is possible to impose directionality in a helical array [26] by introducing an asymmetric spacer into the ligand (Fig. 5). Two conformations are possible for complexes of ligand **7** shown in Fig. 5 (HH and HT); however, only a double-helicate of HT configuration is obtained when tetrahedral metals are added.

Ligands **8a** and **8b** (Fig. 5) were synthesized by Ziessel *et al.* [27] Both ligands lead to helical complexes $[Cu_2\mathbf{8a}_2]^{2+}$ and $[Cu_2\mathbf{8b}_2]^{2+}$ when reacted with Cu(I) ions. In both helicates each Cu(I) ion is coordinated to four nitrogen atoms—two pyridylimine units from two ligand strands.

Yoshida *et al.* [28] have studied the coordination chemistry of the Schiff base ligands **9a-H$_2$** and **9b-H$_2$** (Fig. 5) Both bis-*N*,*O*-bidentate ligands **9a-H$_2$** and **9b-H$_2$** yield 1:1 polymeric complexes with Zn(II) ions although ligand **9a-H$_2$** forms a dinuclear double helix when bound to copper(II) ions. Flexibility in the helicate allows its stabilization by face–face (π–π) and edge–face (CH–π) interactions.

Oligopyridine ligands with imine bridging units have been synthesized by Lehn *et al.* (**10a** and **10b** in Fig. 5). The rigid double bond does not prevent helicate formation when the ligands are treated with metal ions of tetrahedral coordination geometry and coordination occurs through the pyridine nitrogen atoms only [29]. Competition experiments with a mixture of the two ligands demonstrated that self-recognition occurs—each ligand self-assembles into a helicate with an identical ligand, resulting in homostranded helicates.

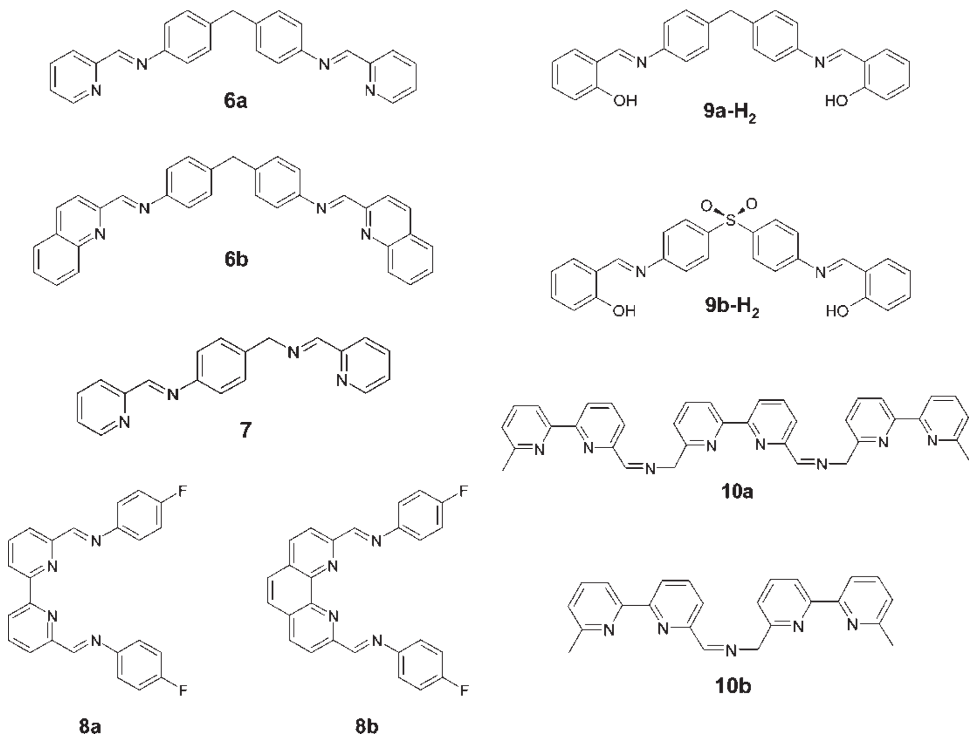

FIGURE 5 Ligands **6**–**10**.

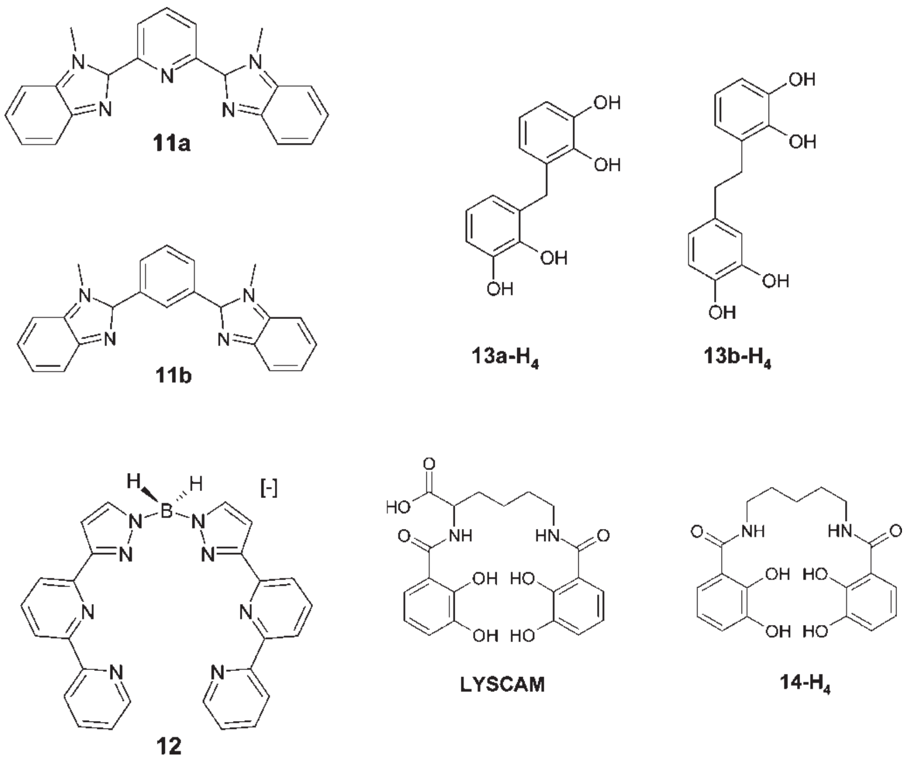

FIGURE 6 Ligands **11**–**14**.

Benzimidazole ligands have been investigated by Williams and colleagues [30]. They found that these ligands also form helical structures when mixed with metal ions of appropriate coordination geometry. An example is the benzimidazole ligand **11a** (Fig. 6), which forms a dinuclear double-helicate with copper(I). Each Cu(I) ion is essentially linearly coordinated with a weak interaction also observed between the bridging pyridine units. Coordination of ligand **11b** to copper(I) ions was also investigated and found to generate in this case the non-helical $[\mathrm{Cu_2}\mathbf{11b}_2]^{2+}$ complex. This suggests that the weak interaction from the bridging pyridine rings is necessary to produce a helical twist.

Mixed pyridine pyrazole ligands such as ligand **12** (Fig. 6) have been synthesized by Ward, McCleverty and colleagues [31] and used to study the effect that the metal ion can have on the structure of the final architecture created. The first crystal structure presented was of the K^+ complex $[\mathrm{K_2}\mathbf{12}_2]^{2+}$. Two terdentate "arms" octahedrally coordinate each K^+ ion in the dinuclear double-helicate—one from each ligand. The complex is the first self-assembled double-helicate to be prepared with an s-block metal ion.

Reaction of ligand **12** with Cu(II) ions resulted in the double-helicate $[\mathrm{Cu_2}\mathbf{12}_2]^{4+}$. The crystal structure reveals that the metal–metal separation in the copper(II) complex (5.388(2) Å) is longer than in the potassium complex (3.954(2) Å). This is thought to be due to greater electrostatic repulsion between the metal ions with a 2+ charge compared to two monopositive metal ions.

The complex formed with Gd^{3+} ions was also reported. The unsaturated complex $[\mathrm{Gd}\mathbf{12}(\mathrm{NO_3})_2]$ was formed rather than a dinuclear triple-helical structure. This is again attributed to electrostatic effects. The repulsion between two 3+ charged metal ions would have resulted in a metal–metal separation that ligand **12** was unable to provide.

Metal ions have also been used to control self-recognition in helicates [32]. The self-assembly of dinuclear helicates and *meso*-helicates with Ti(IV) ions has been shown to proceed with self-recognition of the ligands in the presence of alkali metal ions. It is foreseeable that addition of Ti(IV) ions to a mixture of ligands $\mathbf{13a}\text{-}\mathbf{H_4}$ and $\mathbf{13b}\text{-}\mathbf{H_4}$ (Fig. 6) could lead to a mixture of homoleptic and heteroleptic dinuclear and oligonuclear complexes.

When a 1:1 mixture of the ligands is treated with K^+ ions, the homoleptic helicate $[\mathrm{Ti_2}\mathbf{13b}_3]^{4-}$ and the oligomeric species $[\mathrm{Ti_2}\mathbf{13a}_3]_n^{4n-}$ are formed. The K^+ ions probably destabilize $[\mathrm{Ti_2}\mathbf{13a}_3]^{4-}$ as they are unable to bind to the internal oxygen atoms of ligand **13a**. When Li^+ ions are added, the homoleptic complexes $[\mathrm{Ti_2}\mathbf{13a}_3]^{4-}$ and $[\mathrm{Ti_2}\mathbf{13b}_3]^{4-}$ are formed along with the heteroleptic complex $[\mathrm{Ti_2}\mathbf{13a}_2\mathbf{13b}]_n^{4n-}$. The Li^+ ions are thought to bind to the "square" of oxygen atoms that are formed by ligand **13a**. There is no such binding site for Li^+ ions in the heteroleptic complex $[\mathrm{Ti_2}\mathbf{13a13b}]_{2n}^{4n-}$. With Na^+ ions or mixtures of cations (Na/K, Li/K and Na/Li) only the dinuclear homoleptic species are formed. In this example, the alkali metal cations have acted as templates, which control the helicate self-recognition.

The bis(catecholamide) ligand **14-H$_4$** is an analogue of a naturally occurring siderophore *N*,*N*′-bis(2,3-dihydroxybenzoyl)-L-lysine (LYSCAM) (Fig. 6). Ligand **14-H$_4$** forms a dinuclear double-helicate $[(MoO_2)_2\mathbf{14}_2]^{4-}$ with the two metal centres in an octahedral coordination environment [33]. Many of the above examples have involved oligo(bidentate) ligands providing a tetrahedral coordination environment to Cu(I) or Ag(I). This example demonstrates that double-helicate formation can occur between oligo(bidentate) ligands and metal ions that prefer an octahedral coordination environment. The unsaturated double-helicate consists of two MoO_2^{2+} ions coordinated to a catecholamide unit from each ligand.

Triple-helicates

Triple-helicates can be formed by taking a suitable (oligo)bidentate ligand and coordinating to metal ions that prefer an octahedral coordination geometry.

The first structurally characterized triple-stranded helicate was obtained in 1991 by Williams *et al.* [34], who mixed three equivalents of ligand **15** (Fig. 7) with two equivalents of cobalt(II) perchlorate (Fig. 8).

Ligand **16** is able to form double-helicates with metal ions which require a tetrahedral coordination environment e.g. $[Cu_3\mathbf{16}_2]^{3+}$. Metal ions that require

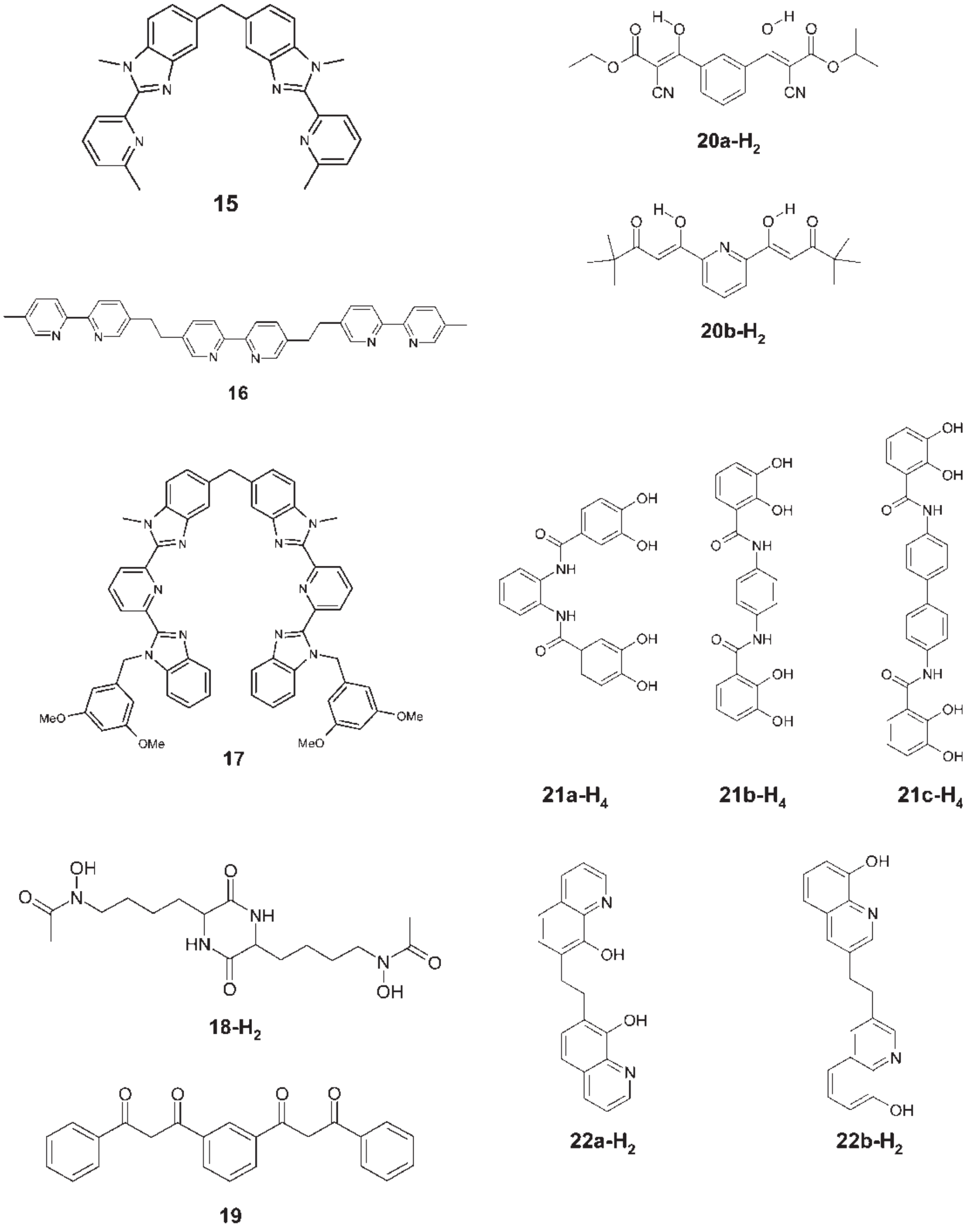

FIGURE 7 Ligands **15**–**22**.

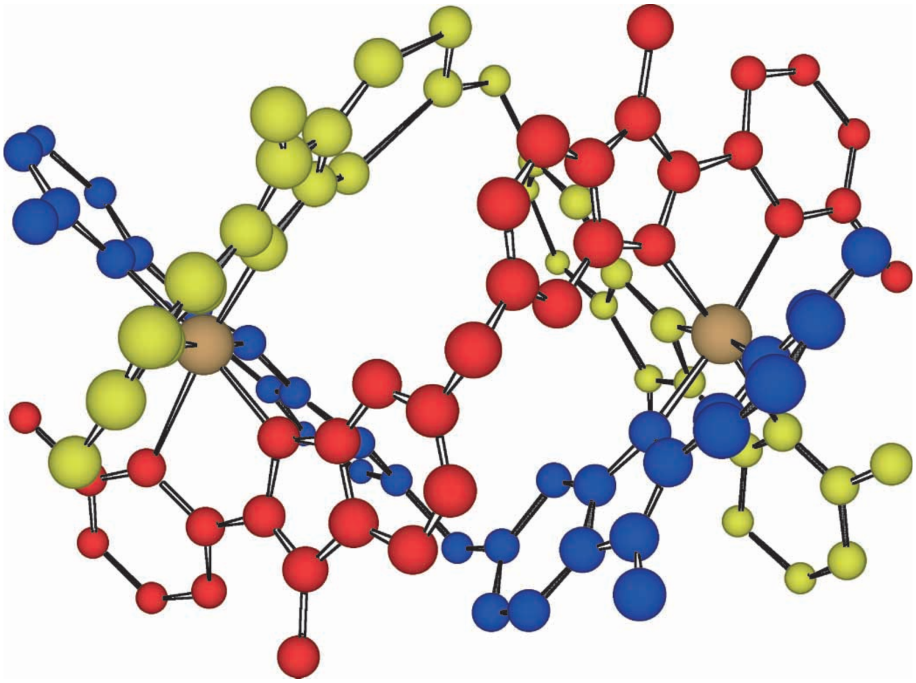

FIGURE 8 Crystal structure of triple helicate $[Co_2\mathbf{15}_3]^{4+}$.

an octahedral coordination environment [e.g. Ni(II)] do not form mononuclear complexes with ligand **16**. Instead, three bpy units from three different ligands coordinate to a Ni(II) ion and the result is a triple-helical architecture with a pitch shallower than that of double-helicates [35]. Each nickel ion is bound in a tris-bpy coordination environment.

Ligand **6a** has already been shown to form double-helicates with Cu(I) and Ag(I). The same ligand also self-assembles into dinuclear triple-helical architectures with Fe(II) and Ni(II) [24]. Spectroscopic studies reveal that the tetracationic structures bind to the major groove of DNA causing the DNA to wrap up in an intramolecular fashion (*vide infra*) [36]. The two enantiomers of these triple helicates can be separated by simple paper chromatography and the DNA binding of each enantiomer is distinct [37–40].

(Oligo)tridentate ligands can also be used in triple-helicate formation if the metal ion involved prefers a nonacoordination environment. The first lanthanide dinuclear triple-helicate was report in 1992 by Bernardinelli *et al.* [41]. The 3,3′-dimethoxybenzyl groups attached to ligand **17** (Fig. 7) increases its solubility. This allows the solution structure to be investigated by ^1H NMR. Ligand **17** was reacted with Eu(III) ions, resulting in the triple-helicate $[Eu_2\mathbf{17}_3]^{6+}$. Aromatic π-stacking interactions between ligands were observed in the crystal structure. ^1H NMR experiments indicate that the triple-helical architecture is maintained in acetonitrile.

Substituents at the 6 positions of oligopyridine units sterically prevent the formation of triple-helical architectures. Lehn and co-workers have demonstrated this phenomenon with a homo-recognition experiment. Ligands **2b** ($X = H$, Fig. 2 and **16** (Fig. 7) differ in their substitution patterns at the bpy binding units. Ligand **2b** prefers to coordinate to metal ions with a tetrahedral coordination geometry while **16** prefers to form octahedral metal complexes. When a mixture of Cu(I) and Ni(II) ions is added to a mixture of both ligands, the complexes that result are $[Cu_3\mathbf{2b}_2]^{3+}$ and $[Ni_3\mathbf{16}_3]^{6+}$ [13]. Homo-recognition has occurred for both the ligands and the metal ions.

Much of the research into triple-helical architectures that has been mentioned so far focuses on nitrogen donor ligands. The only naturally occurring triple-helicate identified to date, however, is the iron complex of the siderophore *rhodoturulic acid* (ligand **18-H$_2$** in Fig. 7)—a ligand based on oxygen donors. It is produced by microorganisms to control the iron uptake and forms a dinuclear triple-stranded *P*-helicate [42].

Many synthetic oxygen donor ligands have also been investigated and are usually based on catechol and 1,3-dicarbonyl derivatives. An example of the latter is provided by Christou *et al.* [43]. Ligand **19** (Fig. 7) was prepared and reacted with Ti(III), V(III), Mn(III) and Fe(III). All four complexes resulted in dinuclear triple-helicate formation with the metal ions in a pseudo-octahedral environment.

Saalfrank *et al.* [44] synthesized a triple-helicate with Fe(III) ions and ligand **20a-H$_2$** (Fig. 7). Ligand **20b-H$_2$** was synthesized in an analogous manner by substituting the *m*-phenylene spacer with a *m*-pyridylene spacer. With this ligand, the complex formed with Fe(III) was also able to incorporate a K^+ ion in its cavity. Unlike [Fe_2**20a**$_3$] which is chiral, the metallacryptate [$K \subset Fe_2$**20b**$_3$]$^+$ is achiral.

Caulder and Raymond [45] have demonstrated that self-recognition between ligands can be achieved based on the distance between two metal coordination sites rather than the number of metal coordination sites The bis(catecholamide) ligands, **21a-H$_4$**, **21b-H$_4$** and **21c-H$_4$** (Fig. 7) were all synthesized and all form triple-helical structures with Ga(III) ions. The rigid ligands were designed so that the metal–metal distance in the dinuclear helicates gradually increased from **21a** to **21c**. When each Ga(III) complex is formed with an excess of ligand, two sets of resonances are observed in the ^{1}H NMR spectrum—one corresponding to the complex and the second corresponding to free ligand. When a mixture of all three ligands is reacted with Ga(III) ions, only homostranded species are formed. No mixed-ligand complexes are observed either in the ^{1}H NMR spectrum or with electrospray mass spectrometry.

Albrecht and Blau [46] have shown that di-(8-hydroxyquinolines) are also suitable ligands for helicate formation. Ligands **22a-H$_2$** and **22b-H$_2$** (Fig. 7) both form insoluble dinuclear triple-helicates when reacted with Ga(III) ions. [Ga_2**22a**$_3$] possesses internal oxygen atoms allowing it to bind alkali metal ions in its cavity. The formation of [$K \subset (Ga_2$**22a**$_3)$]$^+$ results in solubilization of the complex and a ^{1}H NMR in DMSO-d_6 has been obtained. The diastereotopic protons of the CH_2CH_2 spacer confirm the formation of a helical architecture. This is supported by the X-ray structure analysis, which also reveals that the K^+ cation is bound in the interior of the helicate. Ligand **22b-H$_2$** does not possess any internal oxygen atoms and therefore the complex [Ga_2**22b**$_3$] is not solubilized by the addition of K^+ cations.

Quadruple- and Hexa-stranded Helicates

McMorran and Steel [47] have reported the successful synthesis of a saturated, quadruple-stranded helicate. This was achieved using the oligomonodentate ligand **23a** (Fig. 9) and metal ions that adopt a planar coordination geometry, in this case Pd(II). The crystal structure of the [Pd_2**23a**$_4$]$^{4+}$ species reveals the encapsulation of a hexafluorophosphate anion in the cavity of the helicate. Weak interactions occur between the anion and the Pd(II) ions. ^{19}F NMR studies suggest that the PF_6^- anion remains within the helicate cavity on the timescale of the NMR experiment.

Ligand **24** was synthesized by Lehn and coworkers [48]. Coordination of the ligand with Ag(I) ions leads to two structures that are in equilibrium with each other. One of the structures is a [4 × 5] grid. The second structure is a quadruple-helicate with two linear rows of four Ag(I) ions capped top and bottom by two more Ag(I) ions. The 10 Ag(I) ions are coordinated to four ligands with the terminal binding sites of each ligand on opposite sides of the helical axis.

Albrecht *et al.* [49] recently reported the first hexa-stranded helicate. The chiral ligand **25** (Fig. 9) was reacted with Zn(II) ions to form the chiral complex *P*-[Zn_3**25**$_6$]$^{6+}$. X-ray analysis revealed the unusual structure of the helicate in which the three metal centres lie on the helical axis. Each quinolinato oxygen atom bridges two metal centres, binds to one carbon atom and hydrogen bonds to an aryl-NH proton (Fig. 10).

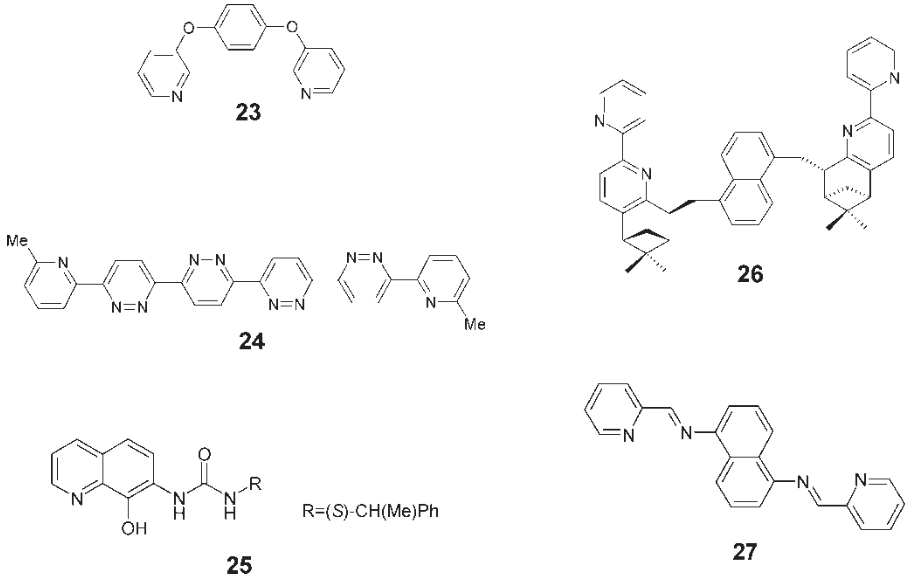

FIGURE 9 Ligands **23**–**27**.

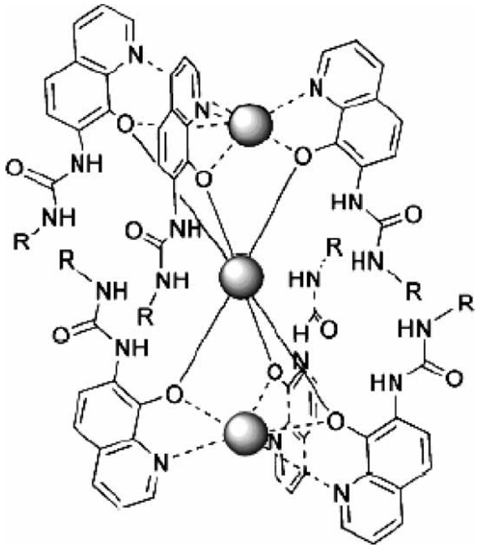

FIGURE 10 Representation of the chiral complex *P*-[Zn_3**25**$_6$]$^{6+}$. Reproduced from [49] by permission of The Royal Society of Chemistry.

A double-helical polymer has been synthesized by reacting ligand **26** with Ag(I) ions [50]. Each double-helicate consists of two monostranded helicates that are connected by van der Waals forces. The double-helicates of the polymer are connected through $\pi - \pi$ interactions and the metal centres are in a spiral configuration with a total of six Ag(I) ions, three from each strand.

Ligand **27**, which contains a 1,5-naphthalene spacer, has been prepared and its silver(I) coordination chemistry investigated. Isotactic, helical and syndiotactic, achiral coordination polymers are formed with a range of different anions with the isotactic polymers displaying long-range ordering of the metal centres [51].

Circular Helicates

DNA is often found as an acyclic, double-stranded helix. However, in some organisms the DNA has a cyclic structure, i.e. plasmid DNA. Similarly, examples of metallo-supramolecular helical circles also exist with the metallo arrays adopting a closed cyclic arrangement.

The formation of a triple helicate between ligand **16** (Fig. 7) and Ni(II) has already been described. Further work carried out by Lehn and colleagues [52] revealed that when the same ligand is mixed with Fe(II)Cl_2, a different architecture is created. Instead of forming a triple helix analogous to that formed with Ni(II), a circular helicate containing five Fe(II) ions is generated.

The inner cavity of the helicate has a radius of 1.75 Å and acts as a receptor for a chloride ion. Different iron(II) salts form different complexes with the same tris-bpy ligand. $FeSO_4$, $Fe(BF_4)_2$ and $FeSiF_6$ can all be used to generate the hexanuclear circular helicate [Fe_6**16**$_6$]$^{12+}$. Reaction of the ligand with $FeBr_2$ resulted in a mixture of the penta- and hexanuclear complexes while using FeF_2 and FeI_2 yielded insoluble red powders. The fact that both mono- and divalent anions are capable of forming a hexanuclear helicate suggests that it is the size of the anion, and not its charge, which affects the helicate structure.

The self-assembly of the tris-bpy ligand into two different structures according to which metal ion is employed [Ni(II) or Fe(II)] led Lehn and coworkers to perform kinetic studies. The reaction between the ligand and Fe(II) was followed by ^1H NMR spectroscopy and it was found that after one minute, the triple-helicate [Fe_3**16**$_3$]$^{6+}$ had formed. As the reaction progressed, more peaks corresponding to [Fe_5**16**$_5$Cl]$^{9+}$ appeared in the spectrum and after 24 hours all of the triple-helicate had been converted to the pentanuclear circular helicate. Although the pentanuclear complex should be entropically less favourable than the trinuclear complex, the enthalpic contributions must be large enough to make the circular helicate the more stable complex. The rate of conversion of [Fe_3**16**$_3$]$^{6+}$ into [Fe_5**16**$_5$Cl]$^{9+}$ was investigated and found to increase with concentration. The complex [Ni_3**16**$_3$]$^{6+}$ has also been shown to be partially converted into [Ni_5**16**$_5$Cl]$^{9+}$ when placed in low pH conditions.

Lehn and colleagues [53] have also tested whether a mixed system ligand expresses the same behaviour of its individual components. The bisbipyridine ligand **28a** (Fig. 11) forms a double-helical structure with copper(I) ions. The bispyridyl-pyridazine ligand **28b** yields square-shaped complexes with copper(I) ions. Ligand **28c** possesses both bisbipyridine and bispyridyl-pyridazine subunits. The stoichiometry of the complex formed between this ligand and Cu(I) was found to be four ligands and 12 Cu(I) ions. The data obtained for the complex agreed with two possible structures, **A** and **B**, as shown in Fig. 12. X-ray crystallography has confirmed the structure to be that of **B**. The circular helicate combines four chiral double-helical elements, which alternate in helicity around the circle so that the overall structure is achiral. The internal cavity of the structure has a diameter of 11 Å, which allows the inclusion of four PF_6^- anions.

Ligand **29** has been reported by McCleverty and Ward [54] to form a cyclic supramolecular complex [Co_8**29**$_{12}$]$^{16+}$. The crystal structure of the perchlorate salt reveals that each metal ion is coordinated to three bidentate units, each from different ligand strands. One anion is encapsulated in the central cavity of the circle and the chirality of each metal ion is the same, so the overall structure is chiral.

A chiral circular helicate, which does not incorporate a central anion has been synthesized by

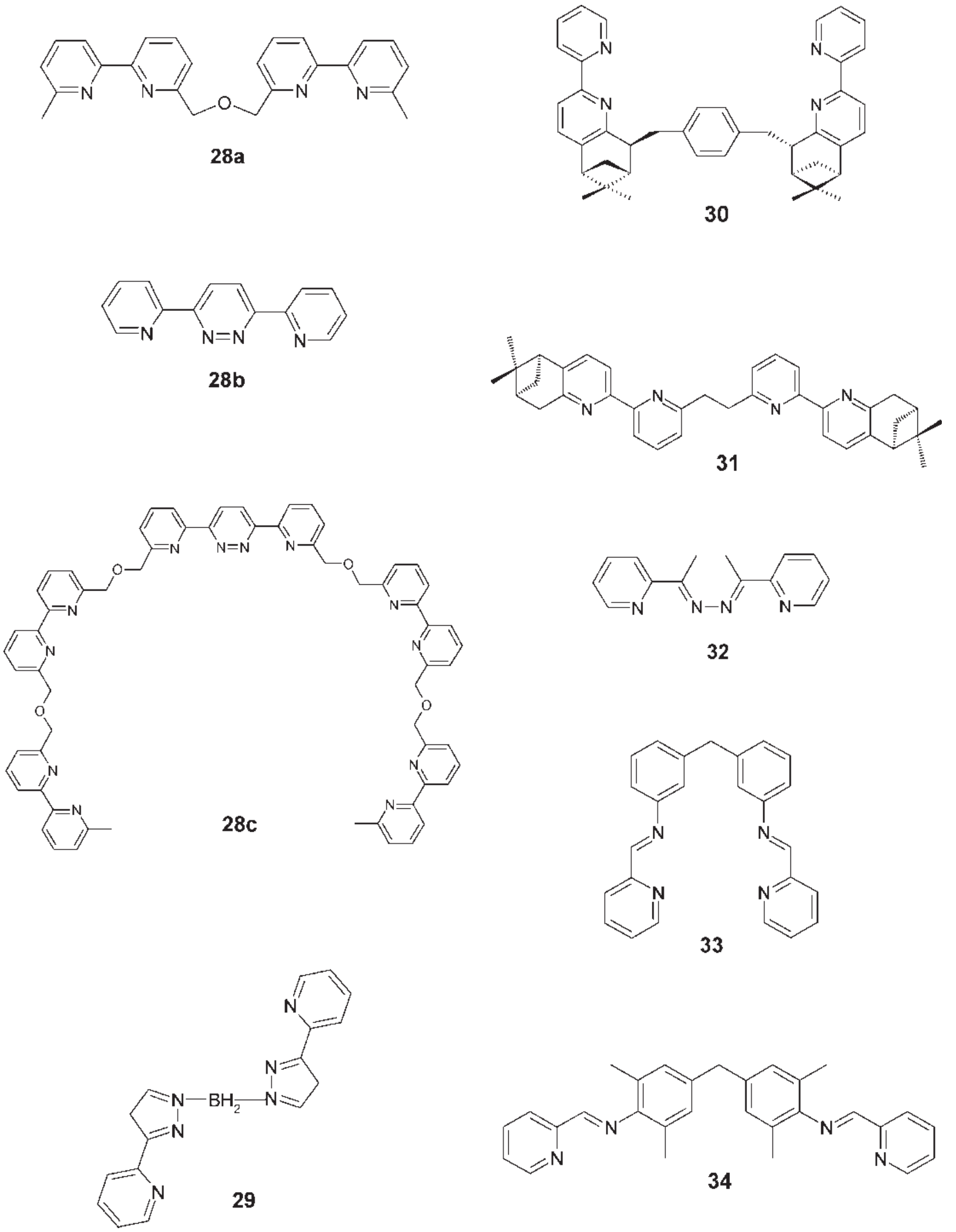

FIGURE 11 Ligands **28**–**34**.

von Zelewsky and colleagues [55]. Ligand **30** (Fig. 11) is chiral and in the presence of Ag(I) ions forms a chiral, circular single-stranded helicate *P*-$[Ag_6\mathbf{30}_6]^{6+}$ (Fig. 13). The crystal structure of the circular helicate is reported, while in solution the hexanuclear species is in equilibrium with the tetranuclear complex $[Ag_4\mathbf{30}_4]^{4+}$

Ligand **31** is a chiral quaterpyridine ligand, that has been split into two bpy units by a CH_2CH_2 spacer [56]. The ligand reacts with Ag(I) to give a dinuclear double-helicate. Reaction of the ligand with Cu(I), however, provides a mixture of $[Cu\mathbf{31}]_n^{n+}$ complexes. Solid state structures of $[Cu_3\mathbf{31}_3]^{3+}$ were obtained (Fig. 14). Both *P* and *M* circular helicates are

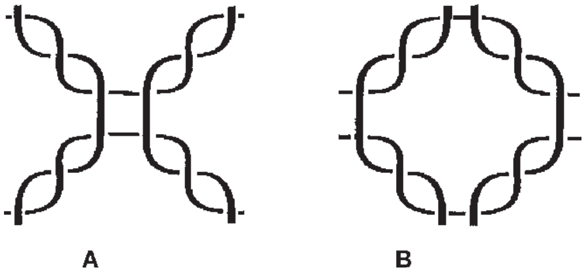

FIGURE 12 The two possible conformations of $[Cu_{12}\mathbf{28c}_4]^{12+}$. Reproduced from [53] by permission of Wiley-VCH.

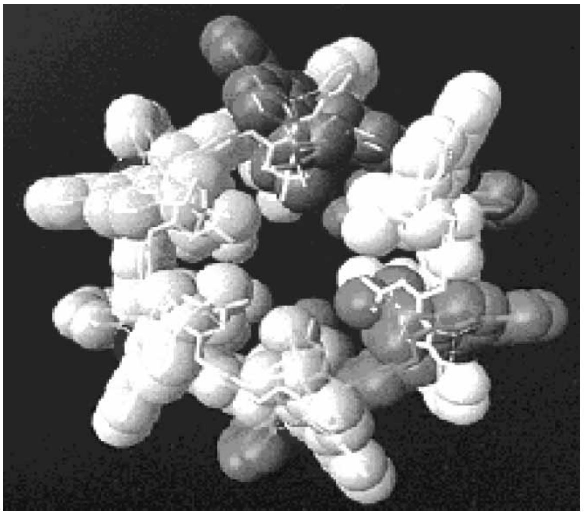

FIGURE 13 Crystal structure of the circular helicate P-$[Ag_6\mathbf{30}_6]^{6+}$. Reproduced from [55] by permission of Wiley-VCH.

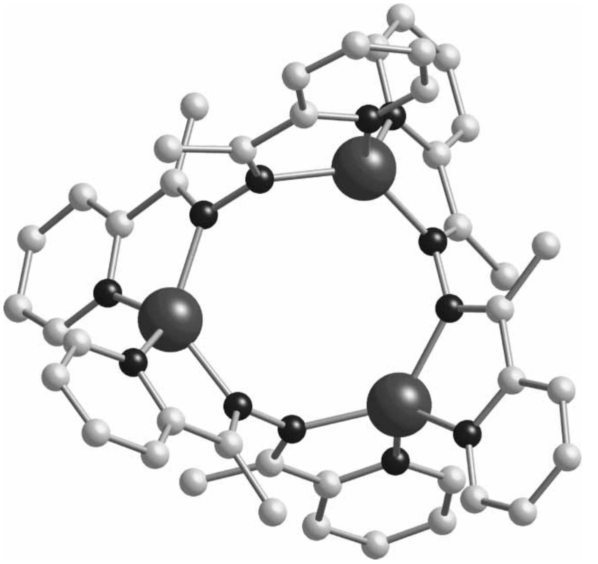

FIGURE 15 X-ray crystal structure of trinuclear circular helicate $[Cu_3\mathbf{32}_3]^{3+}$.

observed suggesting that in the solid state, no diastereoselectivity occurs. Some diastereoselectivity is observed in solution.

Copper(I) chemistry with the pyridine–azine ligand **32** has been investigated and an X-ray structure obtained. The structure reveals a trinuclear circular helicate (Fig. 15) whilst solution data support the existence of an equilibrium mixture of species with a dimer and trimer being dominant [57].

Pyridyl-imine ligand **33** forms a "bowed" (arc-shaped) helix when reacted with Cu(I) ions [58]. The crystal structure reveals that in the solid state the arc-shaped helicates aggregate to form a cyclic array of four metallo-supramolecular units held together by π–π interactions (Fig. 16). The diameter of the circular aggregate is approximately 2.5 nm (C–C; ~2.7 nm H–H) and four BF_4^- counteranions are located in the internal cavity. The chirality of each helicate alternates around the circle so that the overall structure is achiral. The nanoscale structure, nevertheless, bears a striking resemblance to the circular helical arrays but it is achieved without the need for extensive covalent ligand synthesis.

Aggregation of circular helicates has also been described and gives three dimensional aggregates: ligand **34** has been reacted with copper(I) ions and an X-ray crystal structure determined [59]. The solid state structure reveals a chiral helical trimer $[Cu_3\mathbf{34}_3]^{3+}$ with each copper(I) centre occupying a four coordinate pseudo-tetrahedral environment bound to two pyridylimine units from two different ligands. The side view of this triangle reveals that the triangle is not

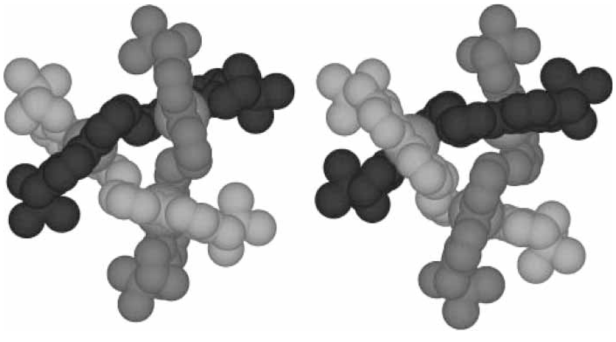

FIGURE 14 Crystal structure of P- and M-$[Cu_3\mathbf{31}_3]^{3+}$. Reproduced from [56] by permission of The Royal Society of Chemistry.

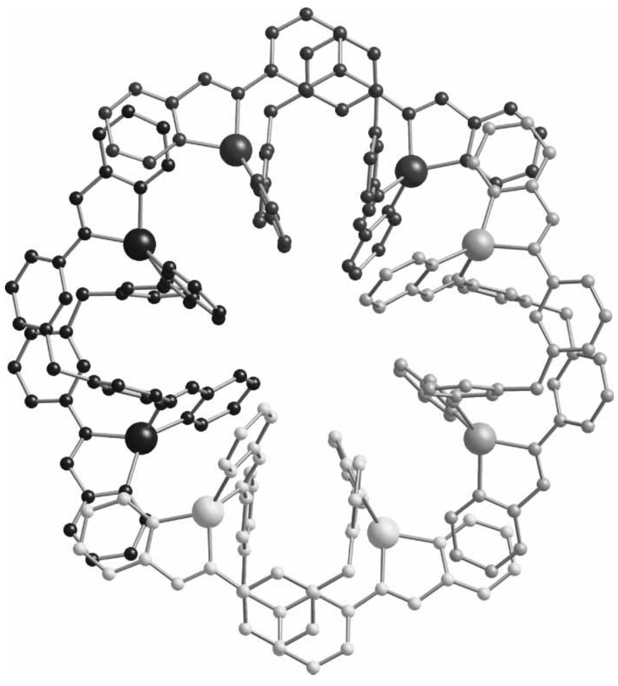

FIGURE 16 Crystal structure showing the cyclic aggregation of $[Cu_2\mathbf{33}_2]^{2+}$.

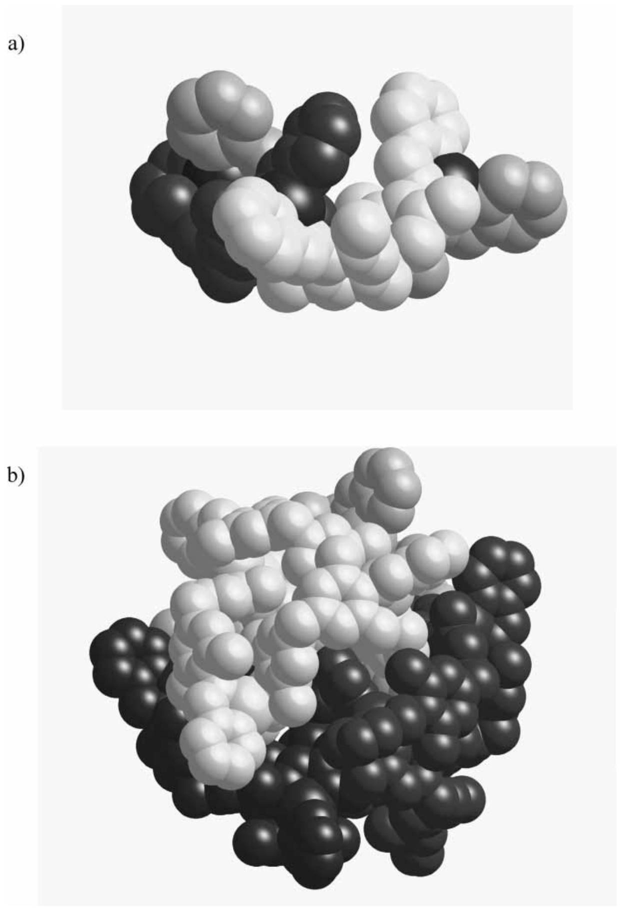

FIGURE 17 Crystal structure of a) side view of $[Cu_3\mathbf{34}_3]^{3+}$ cation and b) tetrahedral array resulting from aggregation of four $[Cu_3\mathbf{34}_3]^{3+}$ trimers.

planar but instead slightly bent over towards one face to provide a bowl-shaped motif (Fig. 17a). This bowl-shaped distortion arises to accommodate the CH–π interactions and is a consequence of the desirability of the methyl groups forming CH–π interactions coupled with the constraints of the ligand connectivity. Three pyridyl rings (one from each ligand) point up towards the cavity of the bowl and are arranged like the blades of a propeller. Four of the bowl-shaped triangles aggregate together to form a nanoscale tetrahedral ball-shaped structure (Fig. 17b) with three pyridyl rings from each triangle pointing into the cavity of the tetrahedron.

Anion and Hydrogen-bonded Helices

The first example of anion-templated helix formation was provided by De Mendoza *et al.* in 1996 [60]. The synthesis of diguanidinium and tetraguanidinium strands that self-assemble around sulphate anions to form a double-helix was reported. The double helix was characterized by ROESY NMR spectroscopy.

Sessler, Allen and co-workers [61] have prepared three tetrasubstituted biimidazole ligands **35–37** (Fig. 18) which can self-associate into helices through hydrogen bond interactions, as evidenced by X-ray crystallography. Solid-state structures reveal helices which are "inverted" when compared to DNA. Each biimidazole can be viewed as covalently linking two strands in the helix together, while the helical backbone is constructed through hydrogen bond interactions.

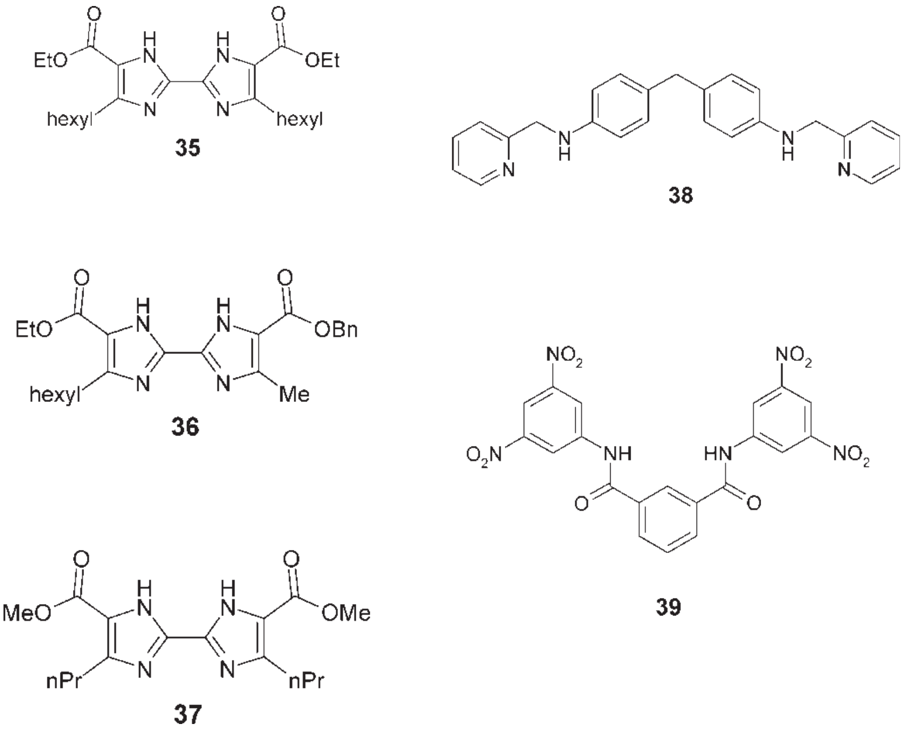

FIGURE 18 Ligands **35–39**.

A diamino-bis-pyridine ligand **38** has been synthesized and treated with dilute hydrochloric acid resulting in precipitation of a pale yellow solid [62]. X-ray quality crystals were obtained and diffraction studies revealed a double helix in which two ligand strands wrap around two chloride anions. The crystal structure revealed no intrahelicate π–π interactions, although interhelicate π–π interactions between phenyl and pyridyl rings of neighbouring helicates were observed in the solid state structure.

More recently, Gale and coworkers [63] have reported the formation of a double helix between ligand **39** and fluoride anions. The ligand is designed with nitro groups with the intention that their electron-withdrawing properties will augment ligand–anion interactions. The fluoride ions form $NH\cdots F^-$ hydrogen bonds and an X ray crystal structure reveals π-stacking interactions between terminal nitroaromatic groups. Surprisingly, this is the first example of neutral ligands wrapping around anions to form helical structures.

Applications

While the assembly of beautiful helical architectures is now well established, applications of these arrays are less well developed and much of the research into helicates has been aimed solely at improving our understanding of self-assembly processes, which are so common in nature. However, several potential applications of these structures are beginning to emerge.

Helicates have been used as precursors in the synthesis of molecular knots, with the first example provided by Dietrich-Buchecker and Sauvage [64]. Ligand **40** (Fig. 19) forms a double-helicate with Cu(I) ions.

The appropriate hydroxy groups then undergo a cyclization process with a diiodoethylene spacer (**A** to **B** and **C** to **D** in Fig. 20). The resulting product is a trefoil knot in 3% yield [64]. More recently, more effective spacers [65] and reversible metathesis for ring closure [66] have allowed the yield to be improved to 30 and 74% respectively.

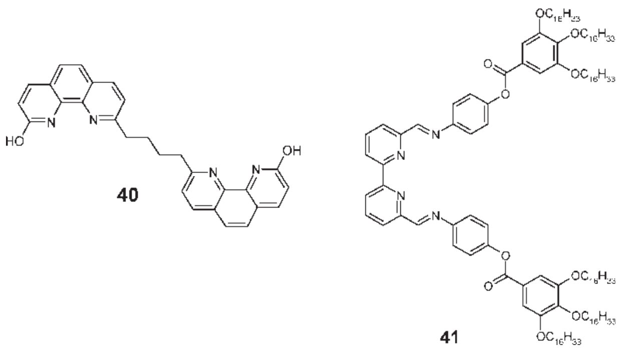

FIGURE 19 Ligands **40** and **41**.

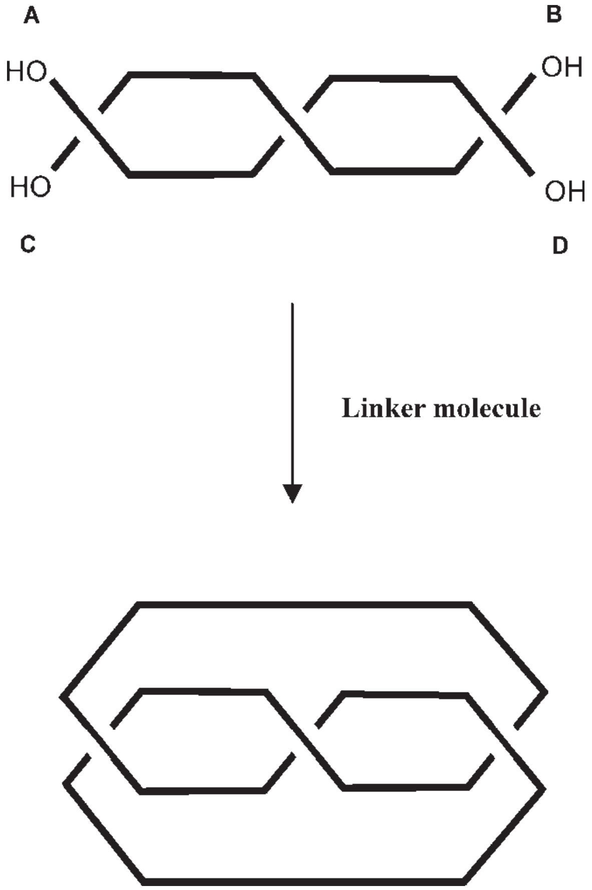

FIGURE 20 Representation of trefoil knot formation.

Ligand **41** (Fig. 19) described by Ziessel and colleagues [67] is non-mesomorphic. However, when the ligand is assembled into a dinuclear double-helicate $[Cu_2\mathbf{41}_2]^{2+}$, the complex exhibits liquid crystalline behaviour. This helicate may therefore have potential applications in practical devices in roles such as chiral switchable display materials.

Helicates can also provide chiral cavities that may potentially be used in host–guest recognition. Some examples have already been discussed, such as the work of Harding and colleagues in which neutral molecules are shown to behave as templating agents [19–22]. Encapsulation of alkali metal ions has been reported by Albrecht and Blau [46], and Lehn and colleagues [52] observed that a chloride anion was tightly bound in the cavity of the circular helicate $[Fe_5\mathbf{16}_5]^{10+}$. We have shown that libraries of supramolecular helical structures assembled by the use of multiple competing interactions (the frustration approach) can be responsive to both solvents and the anions located outside the helical array [57,68].

The solid state aggregation of helicates has recently been applied to the design of magnetic materials using cupric helicates that exhibit

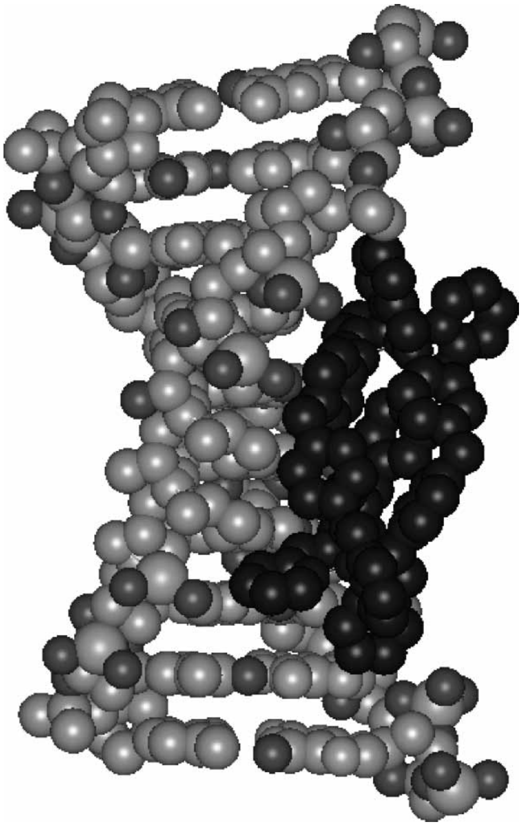

FIGURE 21 Representation of $[Fe_2\mathbf{6a}_3]^{4+}$ binding to major groove of DNA.

inter-supramolecular magnetic coupling through the non-covalent aggregating π interactions [69].

Schoentjes and Lehn [70] reported binding of double-helicates to DNA for the Cu(I) helicates formed with ligands **2a** to **2d** The binding was proposed to be dominated by electrostatic interactions between the polyanionic DNA helix and the positively charged Cu(I) helicates but the binding site of the helicates was not unambiguously identified. We have probed the binding of triple-helicates to DNA [36,38–40]. NMR experiments demonstrate that the helical supramolecule binds in the major groove of DNA (Fig. 21) [36,39].

AFM images reveal that at moderate loadings, intramolecular coiling of the DNA is observed [36,38]. As would be expected chiral discrimination is observed, with the *M* enantiomer being more aggressive than the *P* enantiomer. The ability of $[Fe_2\mathbf{6a}_3]^{4+}$ to "wrap up" DNA in an intramolecular fashion is unprecedented for traditional small-molecule DNA condensation agents and reminiscent of protein recognition of DNA. The helicates represent chiral supramolecular cylinders of similar size to natural protein cylindrical DNA recognition units such as zinc fingers, and this may provide a rich seam for application of helicate technology.

While the field of helicate design is now fairly mature, it is clear that there are a series of emerging potential applications are emerging for these types of supramolecule. With the advent of new synthetic routes which allow helicates to be prepared in simple mixing steps from commercial reagents [34–38], it seems likely that these potential applications will provide a further impetus for detailed study of these elegant structures in the coming years.

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