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Chirality Transfer through Helical Motifs in Coordination Compounds

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Helicates obtained by self-assembly have initiated a revolution from classical coordination chemistry to extensive supramolecular concepts. The design of helicates will be described, and the structural features that are necessary for chirality transfer, as well as the extension of chirality from one-dimensional to three-dimensional chiral polymers in complicated chiral architectures will also be addressed. Chiral assembly by using achiral components has been given considerable attention in this review paper. The understanding of the essential processes and mechanisms in the chiral assembly on the basis of helicate supramolecular structures is a fundamental study in a variety of disciplines ranging from biology to materials science.

1. Introduction

The term helicate was introduced by Lehn in 1987 to describe a discrete metal-based helix comprising one or more covalent organic strands wrapped and coordinated to a series of ions defining the helical axis.[1] Such kinds of complexes have elegantly illustrated how the specific formation of architecturally complicated assemblies are directed by the interplay between relatively simple parameters such as the stereoelectronic preference of the metals and the position of the binding sites of the helicands (helicating ligands). Previously, the chemistry of helicates was reviewed thoroughly with a focus on the description of the topologies and conformations of the helical structures, as well as an investigation into the design of special helicates.[2,3]

Chirality is the intrinsic character of helicates. It can be right-handed (plus, *P*) or left-handed (minus, *M*), depending on whether the rotation is clockwise or anticlockwise when a helicate is considered to wind from the eye of the viewer towards a distant point from the viewer. If we neglect the helical domain produced by the spacers between the binding units, the chirality of a helicate would be deduced from the absolute configurations of the metal centers (Figure 1). Clearly, chiral helicates will be created only when the metal ions in the helical axis display the same absolute configuration. Because they are constructed from achiral components, the helical molecular assemblies in the crystalline phase have two possibilities: either the crystals are composed of both *P* and *M* helices (centric space group) to afford an internal racemate or by a spontaneous resolution process where each crystal is enantiomerically pure (*P* or *M* helicity, chiral space group), but the mixture of crystals is racemic, as a so-called conglomerate.[4] A much more interesting case for the latter is homochiral crystallization, by which all the crystals obtained in one crystallization have the same chirality. Usually, the interhelicate interactions associated with donor (or acceptor) groups hosted on the chiral helicates should be always directional and homochiral. If such kinds of interactions are substantially strong, the chiralities of the metal centers could be extended into high-dimensional frameworks to achieve the complicated chiral species. Whereas a large number of chiral superstructures were developed through the covalent arrangements of chiral building blocks at the molecular level by using the "bottom-up" strategy,[5] the chiral assembly from achiral components on the basis of helical motifs is of current interest in both supramolecular chemistry and materials science as one of the most attractive and evocative strategies. This microreview will focus on the current research developments in the structural features and the design of helicates modulating the transfer of chirality between metal ions, and chirality extension in the formation of high-dimensional chiral polymers.

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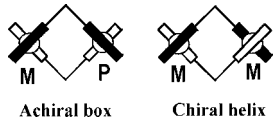

Figure 1. Helical and chiral properties of double-stranded dinuclear helicate with C_2 symmetrical ligand strands.

2. Discrete Oligonuclear Helicates – Local Chiral Translation in Helicates

Oligonuclear helicates, especially dinuclear helicates, are one kind of classical helicates that have been investigated most extensively. Proverbially, single-, double-, and triple-stranded helicates possess one, two, and three coordinated strands wrapped around the metal ions, respectively. The ligands are obviously partitioned into two or more distinct multidentate (commonly bidentate) binding sites with a spacer linking them together. For a dinuclear double helical architecture, it is postulated that the chosen spacer should have enough rigidity to sterically prevent the two binding sites from coordinating to one single metal center, and in the mean time it should also have enough flexibility to permit it to wrap around the metal–metal axis.[2,3,6] However, investigations on the construction of helicates by using ligands L^1-L^4 (Figure 2)[7–10] showed that each ligand spans both metal ions but does not wrap over (from one side to the other) the metal–metal axis (Figure 3). Despite the fact that both the rigidity of the ligands and the close proximity of the two metal centers seem to be unfavorable for the formation of helicates, the absolute configurations of the two metal centers in each molecule are identical. Further structural studies of double and triple helicates with two pyridylimine units linked by a single –N–N– confirm that

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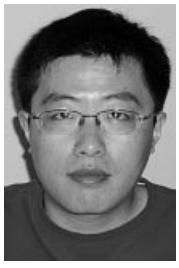

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the nonplanar bridging mode might be essential for such kinds of ligands to encode metal ions in the formation of helicates.[11] From a mechanistic viewpoint, upon coordination, the rotating freedom of the –N–N– bonds on the ligands is restrained, and the ligands can be locked in an atropisomerically chiral conformation. At the same time, the strong and directional bonding interactions could transmit the original chirality of one metal center to another, leading to the formation of the helical species. Reasonably, it suggests that in both double and triple helicates, there is not any necessary relationship between their formation and the rigidity/flexibility of the spacers in ligands. In other words, the chirality translation between the metal centers only occurs when the bridging modes of the ligands exhibit atropisomeric chiralities in the formation of a helicate.

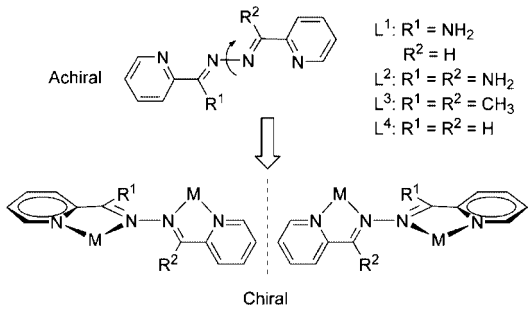

Figure 2. Diazine ligands and generation of conformational chirality.[9]

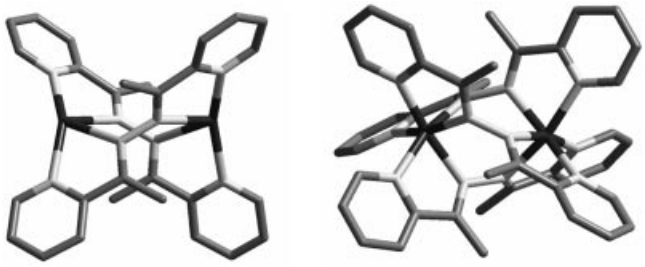

Figure 3. Structures of helicates $Ag_2L^3_2$ (left) and $Co_2L^3_3$ (right). The rigid ligands are twisted but not wrap over the metal centers.[10]

This type of chirality translation through atropisomeric chiral bridging modes of the ligands could also be observed directly in the formation of helicates that are based on biphenyl ligands (Figure 4).[12,13] For example, ligand L^5 in solution is achiral due to the free rotation about the two phenyl groups.[12] In the solid state, however, this ligand shows atropisomeric chirality due to the constraint of the rotation around the C–C bond as described as a monohelix. Upon coordination to the metal centers as a bridge, such a special conformation of the ligand induces the formation of helical species with the metal centers being homochiral, even in the case where the two metal centers are bridged by one ligand. Similar atropisomeric chiralities of ligands were observed in several other dinuclear monohelicates of which

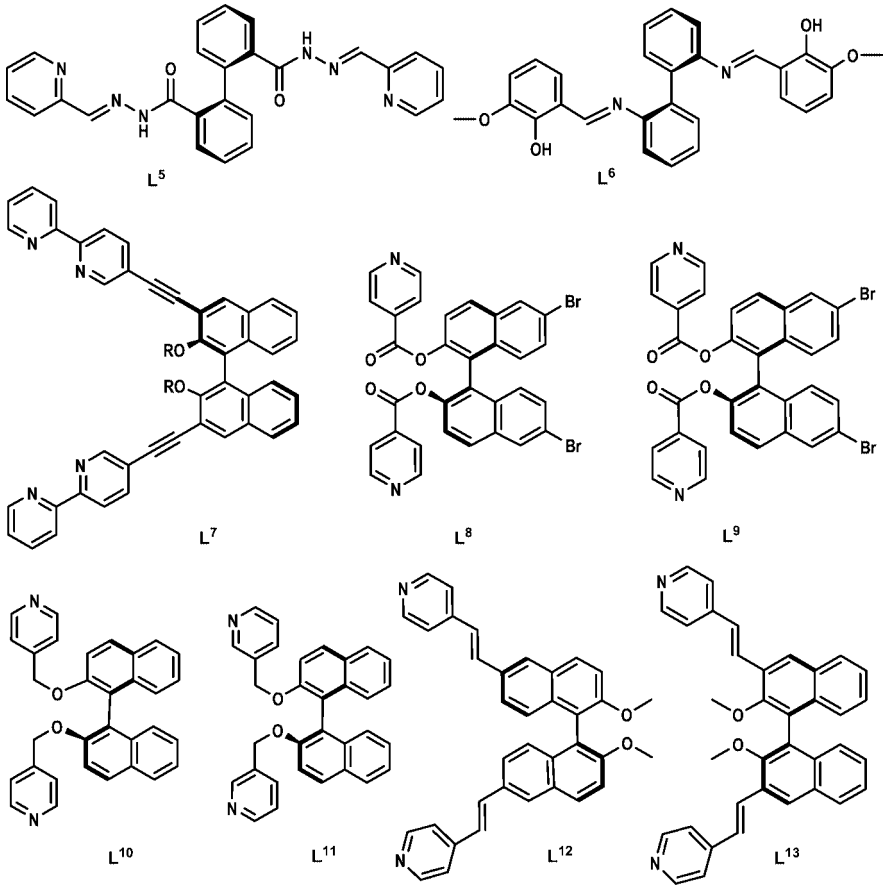

Figure 4. Ligands exhibiting an atropisomerically chiral bridging mode.[12,13,15–18]

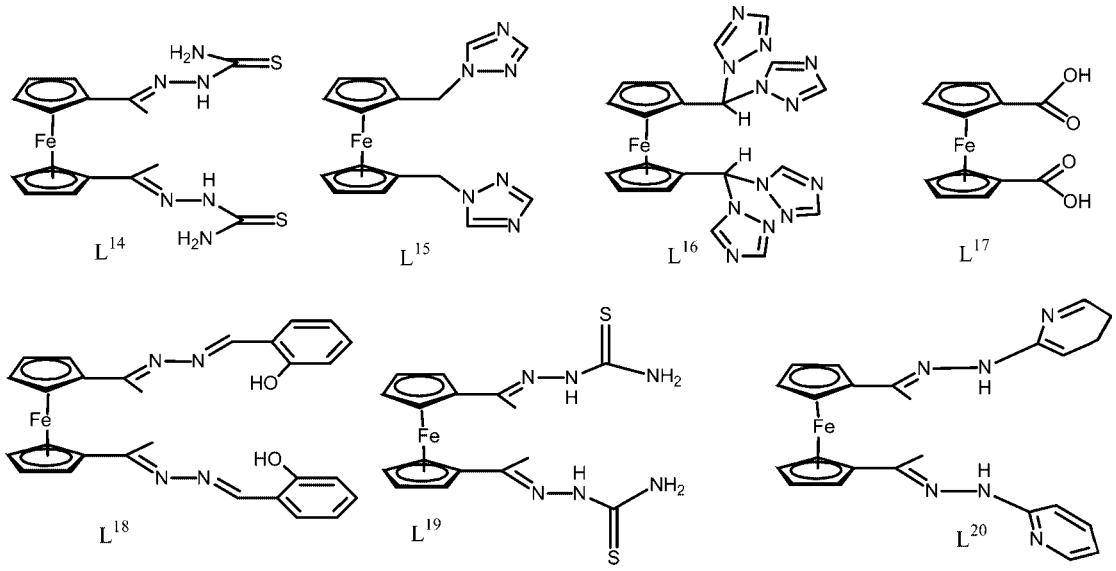

Figure 5. Ferrocene-containing ligands exhibiting a conformationally chiral bridging mode.[19,20,29,30,32]

the chiralities are determined by the helicands themselves rather than the metal centers.[14]

Another evidence to support the above hypothesis comes from the assembly of enantiopure double helicates derived from conformationally chiral ligand L^7. Generally, enantiomerically pure chiral ligands only introduce a second source of chirality into the helicates, forming diastereomers according to the screw turn and the arrangement of the ligands. However, in the resulting triple helicate $Zn_2L^7{}_3$, the configurations of the stereogenic metal centers are completely controlled by the atropisomeric chiral configuration of the binaphthyl groups, and the discrete dinuclear complex adopts an overall D_3 symmetric *P* configuration with both of the two octahedral metal centers exhibiting the Δ configuration.[15] In fact, a lot of homochiral discrete polynuclear complexes and infinite coordination polymers were constructed by introducing the binaphthyl group as the stereogenic resource of conformational chirality (Figure 4).[16–18]

Two-armed, multidentate, ferrocene-containing compounds are another sort of ligands that could efficiently translate chirality from one transition metal center to the others (Figure 5).[19,20] Generally, the 1,1′-substituted ferrocene derivatives exhibit a planar chirality. When they act as bridging ligands to coordinate to metal centers in the formation of the helicates, atropisomeric chirality of the ligand is generated and replicated with the bridged metal centers being homochiral (Figure 6).

In terms of the structural requirements of bridging ligands for chirality translation between metal centers, the principle obtained from the dinuclear species − *that the chirality transformation between the metal centers occurs only when the bridging mode of the ligands exhibit conformational chiralities* − should be valid to explain the formation of some complicated helicates besides the dinuclear helicates.[21] For example, in the trinuclear Cu^I complex derived from ligand L^3 and a variety of other circular helicates,[22–24] the nonplanar bridging modes of these ligands

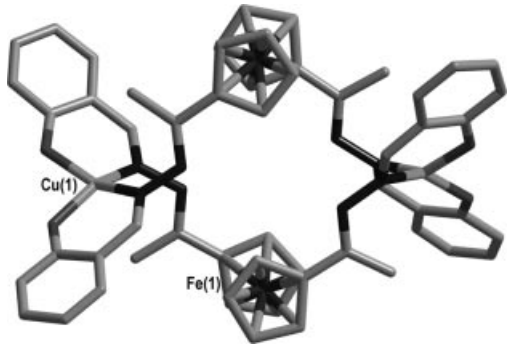

Figure 6. Molecular structure of the copper–ferrocene helicate $Cu_2L^{18}{}_2$.[20]

are likely to facilitate the chirality transfer, which results in homochiral metal centers. Whereas in the metallocycles derived from the ligands containing carboxhydrazone units, the planar bridging conformation causes the formation of achiral species, despite the presence of a similar –N–N– bond within the backbone of the ligands.[25]

Recent developments in the design and assembly of helical species have spanned to the construction of supramolecular architectures by hydrogen bonding and coordination bonding. As shown in Figure 7, two ligands L^{21} coordinate

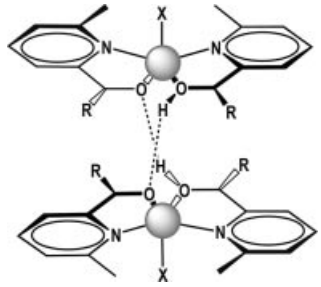

Figure 7. Hydrogen-bond-linked dinuclear helicates $Co_2L^{21a}{}_2X_2$, L^{21a},R = H; L^{21b}, R = CH_3, X = Cl, Br, NO_3.[26,27]

to a cobalt(II) atom in a bis(bidentate) fashion by the pyridyl and alcohol donor groups.[26] Two chelating units are twisted through the O–H···O hydrogen bond, achieving a new conformational chirality, which is transmitted from one cobalt center to another by hydrogen bonds between the alcohol oxygen atoms. Interestingly, when the alcohol carbon atom is stereogenic, the chirality at this point could control the absolute configurations of the metal centers and the helicity sense of the overall structure.

3. Aggregation of Oligonuclear Helicates – Chirality Translation in Supramolecular Assemblies

Whereas the basic requirements for the design of a discrete helicate from achiral components have been well-established, the design and control of the formation of homochiral superstructures that are based on helical units still remain a substantial challenge. Assembling small molecular units into complicated aggregations in a controlled fashion is one target of sophisticated supramolecular chemistry.[27] Especially, the assembly of helical units into a homochiral array is of great interest in this case.

Investigation into the superstructures assembled from helicate building blocks reveals that the functional groups attached to the ligands of helicates are able to carry weak interactions to favor the extension of the homochiralities. In principle, if the interactions between helicates are substantially strong and directional without mirror symmetric elements, the local or whole homochiral assembly might be achieved.[28] As shown in Figure 8, the twisted bridging mode of diacetylferrocene thiosemicarbazone L^{19} leads to dinuclear complexes that crystallize in a helical fashion.[29] The imino nitrogen atoms of the thiosemicarbazone moieties attached in the double helicates act as H-bond acceptors paired up with the corresponding amino nitrogen atoms of the thiosemicarbazone group on a parallel neighboring helix through hydrogen bonds. Only the helicates with the same chirality can be connected to each other into an infinite chain such that all the zinc ions in the infinite chiral chain have the same chirality. It is likely that the chirality of the helicates is translated through the discriminative bridges. The same structure is also found in an analogous Co^{II} compound.[30] Weak additional coordination interactions could also be utilized to construct helical chains.[31] In the ferrocene-containing double helicate $CuL^{20}{}_2Cl_2$, the copper center is coordinated by two pyridylimine groups with the fifth coordination site occupied by a chloride ion.[32] In the crystal, a chloride anion bridges two homochiral double helicates featuring a one-dimensional polymer. Each chain exhibits a crystallographic 2_1 helix with the double helicates in the chain being a single enantiomer.

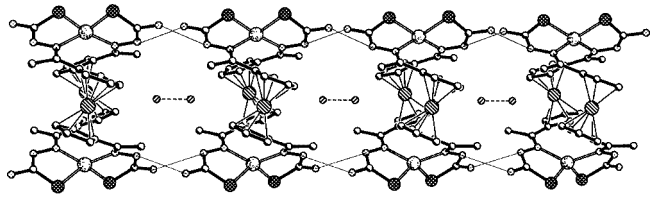

Figure 8. The hydrogen-bonding one-dimensional tube from ferrocenyl-based $Zn_2L^{19}{}_2$ dinuclear helicate with water molecules included.[29]

By introducing multiaromatic rings into the dinuclear helicates, homochiral assemblies and even 3D homochiral conglomerates could be obtained through π–π stacking interactions. Reaction of potentially atropisomeric chiral ligands L^{22} and L^{23} with Ag^{I} generate the silver double helicates $[Ag_2L^{22}{}_2]^{2+}$ and $[Ag_2L^{23}{}_2]^{2+}$, respectively.[33] The symmetry-related helicates are connected together through face-to-face stacking interactions between the pyridine and benzene rings to form an infinite chain around a 3_2 screw axis (Figure 9). Owing to the twofold symmetry of the dinuclear helicates, these screws align in parallel and maintain the helical chirality, featuring a homochiral 3D structure with the spontaneous resolution occurring. On the basis of solid CD measurements of the 20 crystals of the latter upon crystallization (Figure 10), the *ee* value of 60% clearly reveals the appearance of a chiral selectivity in the bulk crystals. From

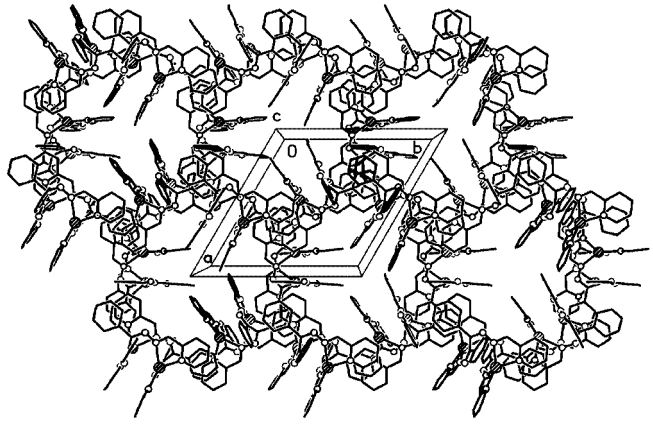

Figure 9. Infinite helical chain for $Ag_2L^{23}{}_2$ with *P* helicate through π–π stacking interactions and the 3D network stabilized by the homochiral interactions.[33]

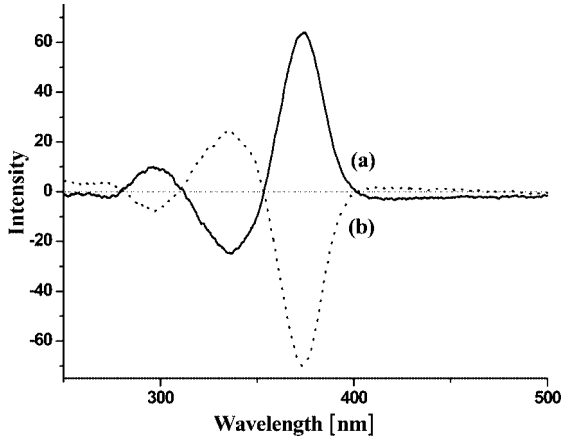

Figure 10. Solid-state CD spectra exhibiting the significant Cotton effect of the crystals of compound $Ag_2L^{23}{}_2$ consisting of *P* (a) and *M* (b) configurations of helicates.[33]

further investigations of the crystals in 50 independent crystallizations, it was found that the intensities of the CD signals show a bimodal probability distribution. Such an occurrence of bulk crystal chirality, namely spontaneous resolution, accidentally through a chiral autocatalytic resolution process in the absence of molecular chirality is much more haphazard.

High-dimensional homochiral structures could also be assembled by the helical fragments and adducts as initial components. Chen et al. reported a 2D network built from hydrogen bonds between the connecting water clusters and the helicates.[34] The initial fragment for the assembly is a binuclear Cd^{II} helicate with two spiral-like *N*,*N*′-bis(picolinamide)azine ligands (L^2) coordinated to the two Cd^{II} centers. The chiral binuclear helicates are assembled into homochiral layers by water tapes. However, owing to the lack of strong interlayer chiral interactions, the layers are alternatively stacked in a heterochiral fashion to yield the final racemic crystal. Hahn and coworkers reported a triple-stranded helical complex $Na(PNP)_3[Ti_2(L^{25})_3]$ [PNP = bis(triphenylphosphoranylidene)ammonium], where the Na^+ ions act as bridges between the $[Ti_2(L^{25})_3]^{4-}$ helicates, leading to the infinite homochiral chains in the crystal lattice.[35] Both metal centers of $[Ti_2(L^{25})_3]^{4-}$ in the crystal are formed with the same configuration, but crystallization in the $P\bar{1}$ acentric space group indicates that the opposite enantiomer must have also formed.

Another interesting example of the aggregation of helical species was reported by Matsumoto et al. He described a fascinating model for the assembly of the homochiral structure.[36,37] The initial building block is a mononuclear CuL^{26} complex containing two imidazole groups. This species could be described as a mononuclear helicate with either Δ (clockwise) or Λ (anticlockwise) enantiomorph (Figure 11) owing to the spiral arrangement of the ligands around the copper(II) ion. In the presence of an equimolar ratio of base, one of the two imidazole groups loses a proton and functions as a hydrogen-bond acceptor to connect with the neighboring protonated imidazole as a donor. For this to occur, the hydrogen bond between the imidazole group and the deprotonated imidazolate group in the two neighboring molecules is asymmetric, and the helicates are linked into a one-dimensional helical chain with the chirality of the initial unit being translated from one to the other, and then extending to the whole helical chain.[36] Similarly, the cobalt(III) complex with achiral tripodal-type ligands consisting of three imidazole groups induces the chiralities of the *C* and *A* enantiomers,[37] The hemideprotonated species $[Co(H_{1.5}L^{27})]^{1.5+}$ functions as a self-complementary chiral building block, generating equal numbers of protonated and deprotonated molecules by an acid–base reaction to form an extended 2D homochiral layer consisting of hexanuclear structures with trigonal void units (Figure 12).

To further develop such a synthetic strategy, an interesting mononuclear helicate Mn^{II} compound was synthesized.[38] The thiosemicarbazone metal complex $MnL^{28}{}_2$ adopts either a Δ or a Λ enantiomorph, depending on the arrangement of the two thiosemicarbazone ligands in which

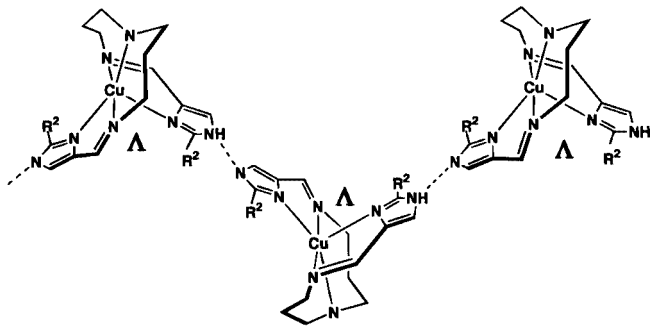

Figure 11. 1D helical chain formed from hydrogen bonds between the imidazole and imidazolate groups of adjacent mononuclear CuL^{26} units (R^2 = Me).[36]

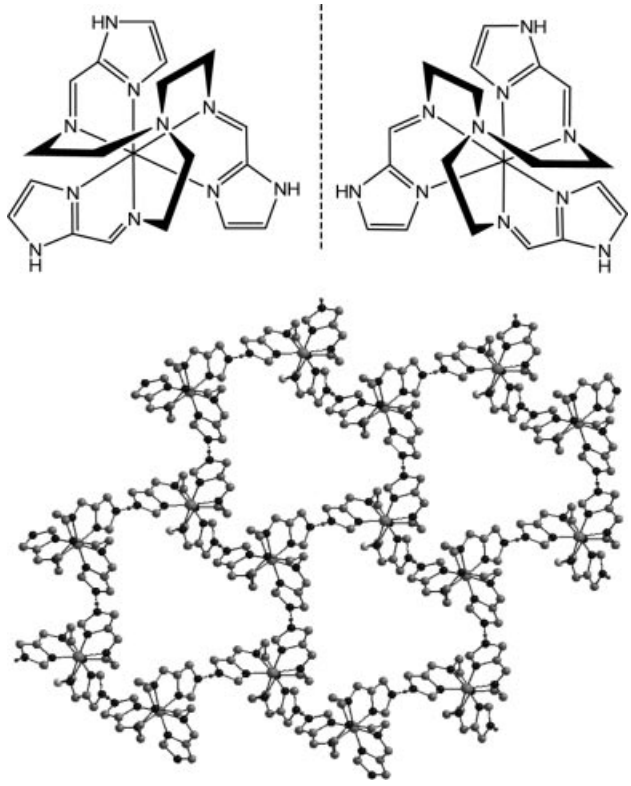

Figure 12. Structures of *C* (clockwise) and *A* (anticlockwise) mononuclear CoL^{27} enantiomers (top), and the top view of the 2D homochiral sheet in which the same enantiomers are linked by the intermolecular imidazole–imidazolate hydrogen bonds (bottom).[37]

the amine groups act as the proton donors and the pyrazine groups as acceptors. The neutral complex functions as chiral building blocks to be assembled into 2D layers through the pyrazine–amino hydrogen bonds (Figure 13). The head-to-tail fashion suggests that the hydrogen bonds that link the neighboring mononuclear units are chirally discriminative and maintains the metal coordinative spheres to exhibit the same absolute configuration. The chirality is then preserved and extended into the whole 2D sheet. Furthermore, the homochiral layers develop parallel to the *ab* plane and stack along the *c* direction through π–π interactions between the neighboring delocalization skeletons of the ligands. Adjacent sheets are related by 4_1 screw axes and

stack in an ABAB fashion (A and B represent layers with different orientations but with the same chirality, respectively), resulting in a homochiral porous 3D network.

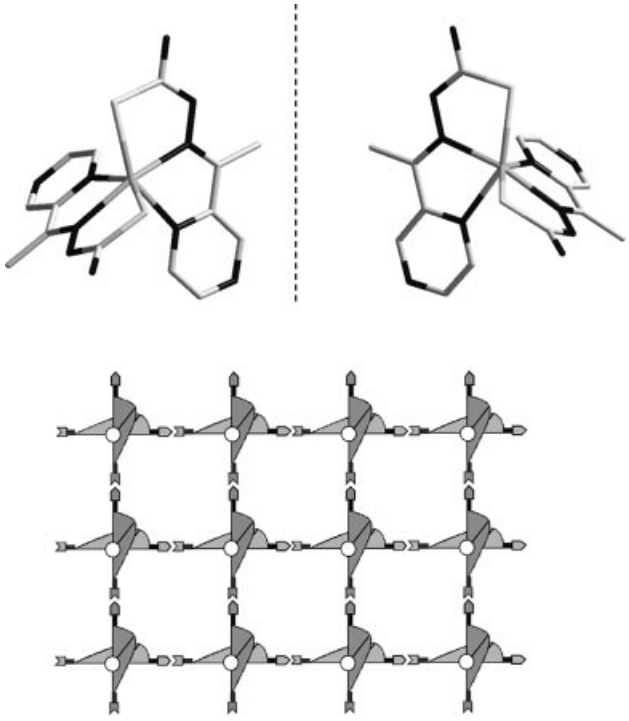

Figure 13. Structures of the Δ and Λ mononuclear Mn helicate enantiomorphs (top), and the carton scheme of the hydrogen bonding homochiral discriminating MnL^{28}_2 (bottom).[38]

4. One-Dimensional Helical Coordination Polymers – Precursors of Chiral Crystals

One-dimensional helicates are intermediates between the discrete molecular helicates and the solid-state helicity (chiral crystals) in the homochiral aggregations from achiral building blocks. Obviously, the construction of chiral solids from one-dimensional metallohelical chains would be more efficient than that from the oligohelicates. As mentioned above, the simple way to ensure the chirality extension within the infinite chain is to use the ligands as bridges that exhibit atropisomeric chirality. For example, assembling silver(I) or copper(I)[22] with helicand L^4 facilitates an infinite monohelicate with each metal atom bound to two bis(bidentate) ligands in a distorted tetrahedral geometry, and the ligands chelate and bridge the two metal centers by turns.[10a] Thus, the obstacle that limits the possibility to obtain a chiral solid from one-dimensional helicates hinges on how the chirality of the building fragments can be extended by chiral discriminative interactions.

An interesting example reported by Aoyama et al.[39] is chiral adduct $L^{29}{\cdot}Cd(NO_3)_2{\cdot}H_2O{\cdot}EtOH$, which was prepared from achiral 5-(9-anthracenyl)pyrimidine (L^{29}) but crystallizes in a chiral space group $P2_1$. The chirality of this compound arises from the twist of the two pyrimidine rings in a helical array of the pyrimidine/Cd^{2+} coordination polymer, in which the anthracene substituents are arranged in C_2 chirality across the chain (Figure 14). The helices are stabilized by intrastrand water–nitrate and ethanol–nitrate hydrogen bonds. The ligand has one extra free proton, which is used to connect the neighboring helix chains with the *same* chirality (helicity) by interstrand water–nitrate hydrogen bonds. Thus, the chirality translation through H-bonds occurs inside the layer and then is preserved on both sides of the resulting sheet across the helices. The sheets are then assembled through herringbone-type packing of the anthracene moieties into the actual 3D structure. Crystals of this adduct exhibit significant CD signals that are consistent with the absolute helicity *P* or *M* with a positive or negative Cotton effect, respectively. All the crystals recovered from one operation of crystallization show the same CD sign with the same chirality (helicity). It is reasonable that the chirality of the crystals is essentially governed by the chirality that happened to the first-separating nucleus serving as the seed for the subsequent crystal growth.

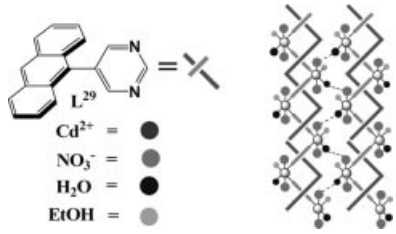

Figure 14. Crystal structure of $L^{29}{\cdot}Cd(NO_3)_2{\cdot}H_2O{\cdot}EtOH$: front view of two neighboring helices hydrogen bonded to form a sheet and its schematic explanations.[39]

Because the direction of the interhelicate donor–acceptor interactions between the chiral helicates is controlled by spatial affects and intrinsic characters of the interactions themselves, these interactions are likely to be characteristically chiral and run through inheriting the original chirality of the helicates they linked. Thus, the strategy to connect helical chains in a homochiral fashion rests on the potential chiral interactions, despite that some of these interactions are quite weak. As shown in Figure 15, a helical chain is also formed through the coordination of potential atropisomeric chiral ligand L^{30} to the Zn^{II} ions. Neighboring chains are bonded together through π–π interactions between the phenyl groups and the cyclopentadienone units.[40] These supramolecular interactions of exclusively achiral building blocks contribute to the helical chirality of the coordination polymers that arise from spontaneous chiral resolution. The bunches of needle crystals show pronounced (and partially opposite) Cotton effects in their CD spectra, suggesting that one kind of enantiomer is in local excess and even dominant.

C–H···X interactions also have the potential to act as directional interactions in the formation of helical chains and the homochiral aggregation of helicates.[41] With the use of an achiral α,α,′-bis(pyrazolyl)-*m*-xylene ligand (L^{31}), Mukherjee and coworkers identified two different handed solids of Zn^{II} coordination polymers.[42] As shown in Figure 16, the chiral pseudotetrahedral coordination environ-

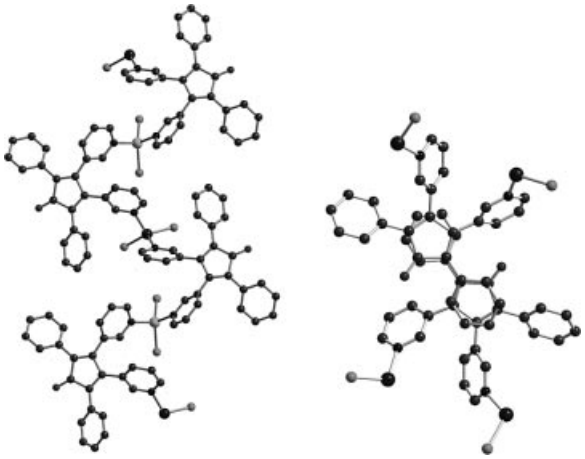

Figure 15. Multiaromatic ring ligand L^{30} (left) and π–π interactions leading to homochiral interactions between helical chains $(ZnCl_2L^{30})_\infty$.[40]

ment around the Zn centers and the twisted conformation of the bidentate ligands bring about the formation of helical chains with the positions of the chlorine atoms fixed. The adjacent parallel helices are held together along the *b* axis primarily by directional C–H···Cl interactions and secondarily by weak π–π interactions between the phenyl rings, leading to the formation of the homochiral 2D sheet. The sheets are again stitched together through the chiral intermolecular C–H···Cl interactions to generate the chiral channels.

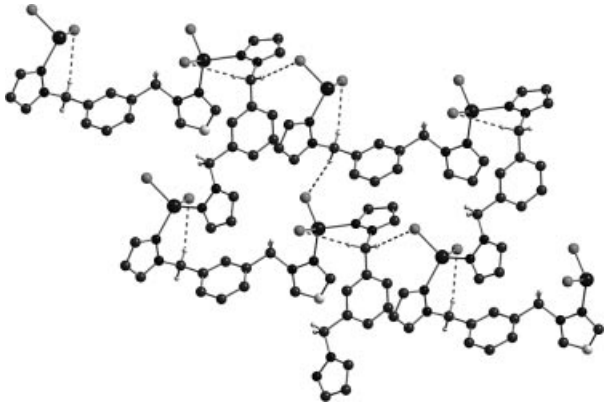

Figure 16. View of the 2D helical sheet $(L^{31}ZnCl_2)_\infty$ formed through C–H···Cl interactions.[42]

The N-positional isomer 2-pyridinyl-3-pyridinylmethanone (L^{32}) is another simple ligand that was investigated in terms of chirality transfer.[43,44] Reaction of ligand L^{32} with $Ag(CF_3SO_3)$ in different solvents lead to the generation of a pair of different helical conformational polymorphs. In the racemic crystal A, the ligand winds latitudinally around the helical axis of 2_1. In the chiral crystal B, the ligand spans longitudinally around a 4_1helical axis (Figure 17). Spontaneous resolution occurs in the assembly from the helical chains to a homochiral conglomerate $\{[AgL^{32}](CF_3SO_3)\}_\infty$. It seems that the rotation of the pyridyl rings causes the presence of atropisomeric chirality, and the metal centers are bridged to form the homochiral helical chains directly.[44]

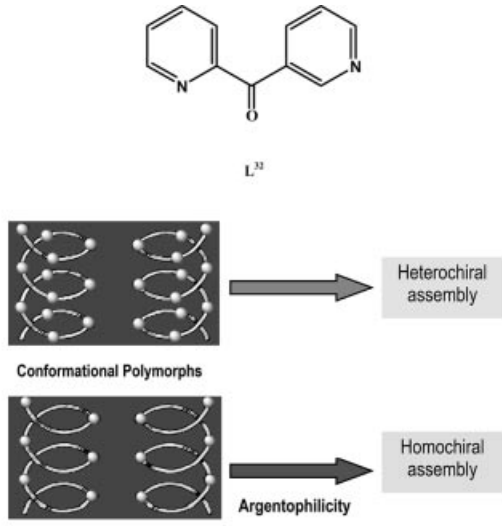

Figure 17. Two kinds of bridging conformations of L^{32} in its coordination complexes. Heterochiral (A, top) and homochiral (B, bottom) assembly of different conformational polymorphs AgL^{32} helical chains by argentophilic interactions.[43,44]

5. Homochiral Frameworks – From Achiral Components to Chiral Crystals

Chiral coordination polymers, which possess chiral functionalities such as enantioselective absorption and catalysis, are of great interest. The generation of chiral coordination polymers from achiral ligands without any chiral auxiliary through spontaneous resolution not only provides an easy method for the preparation of chiral functional materials, but also helps the understanding of the chirality origin of life.

Discovered as early as 1846 by Louis Pasteur, spontaneous resolution is still a relatively scarce phenomenon and cannot be predicted a priori because the laws of physics determining the processes are not yet fully understood. The formation of three-dimensional crystal conglomerates is not very frequent (and is even less predictable), reflecting the tremendous preference (more than 90%) for compounds to crystallize in centrosymmetric space groups. However, if there are substantially strong, selective, and directional enough interactions, such as coordination bonds, between neighboring chiral units, the chirality would be able to extend to higher dimensionality, and hence spontaneous resolution would be more likely to occur. Usually, in the preparation of homochiral coordination polymers by spontaneous resolution, two steps are achieved: the generation of the chiral units from the achiral components, and the chirally discriminative interactions may arise from additional intermolecular interactions. Of course, it is quite difficult to isolate the chiral units, always helical chains, from the well-connected network in some case.

One simple way to construct a homochiral 3D framework is to use the ligands that not only have an atropisomerically chiral bridging mode but also several additional chelating units – some chelators attribute to the formation of helical units, and the others contribute to the extension of the chirality to the whole crystal. Ligand L^{24}, *N*,*N*′-bis[1-(pyrazine-2-yl)ethylidene]benzil dihydrazone (Figure 18), falls well into the category of conformational chiral bridging models.[45] As shown in Figure 19, its silver complex comprises a chiral infinite 4_1 monohelical chain through the two pyrazine–imine bidentate chelating sites. Each ligand adopts a twisted chiral conformation and spans two silver ions to transmit the chirality from one silver center to the other. The metal centers with the same chirality are coordinated by the coupled ligands, leading to the replication of the conformational chirality from one ligand to the other. Such a helical fashion provides an opportunity to modulate the positions and the directions of the additional groups associated with the pyrazine nitrogen atom for interhelicate coordination bonding. Two pyrazine nitrogen atoms from different helical chains coordinate to one silver atom Ag(2) and connect the helical chains together to form a three-dimensional helical network, in which all the fourfold helices are homochiral. Therefore, it is revealed that the chirality of the silver(I) is transmitted through the discriminative helical linkage, or alternatively, the chirality of the helical chain is transmitted through the discriminative bridged units. However, owing to the presence of large voids, the second network with the opposite chirality interpenetrates the former one. The two enantiomeric frames are centrosymmetrically relative, forming a three-dimensional enmeshed "racemate".

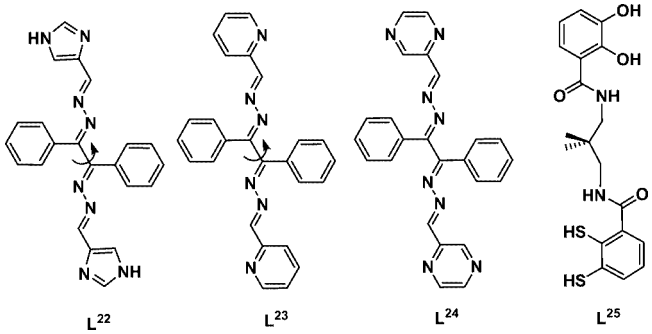

Figure 18. Benzil-based and -related ligands exhibiting a conformationally chiral bridging mode.[33,35,45]

Multicarboxylates with two or more carboxylates connected to aromatic rings are another kind of ligand for the construction of high-dimensional frameworks (Figure 20).[46–50] These species with conformationally chiral coordination modes were also used for homochiral assembly in which the versatile coordination modes of the carboxylate donors make the networks quite complicated.[51] Ligands containing biphenyl groups with more than two carboxylate groups might induce all the metal centers in the network to exhibit the same absolute configuration. 2,2′,3,3′-Oxydiphthalic acid (L^{33}) is one such ligand, which was used to build various homochiral 3D features based on

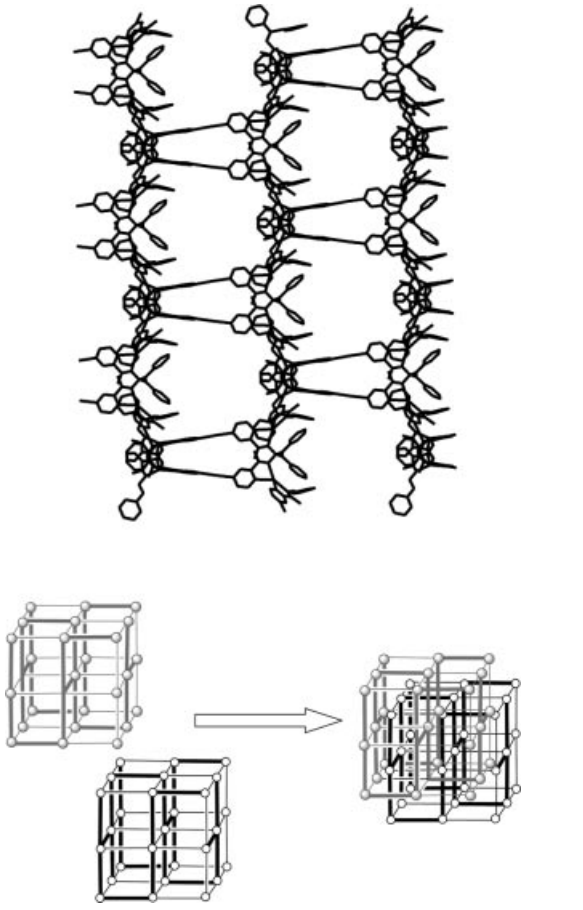

Figure 19. A view of the double interpenetrating nets of AgL^{24} enantiomeric forms of the chiral 3D networks.[45]

helical chains with a suitably bridged bipyridine coligand.[52,53] For example, in the Zn^{II} complex,[52] two kinds of Zn ions are bridged by 2,3- and 2′,3′-carboxylate groups, respectively, to form two similar helical chains from which the chiral puckered herringbones are formed by aligning these helices in parallel (Figure 21). Adjacent layers are interrelated by the 2_1-screw axis and stack in a slipped *AAA*

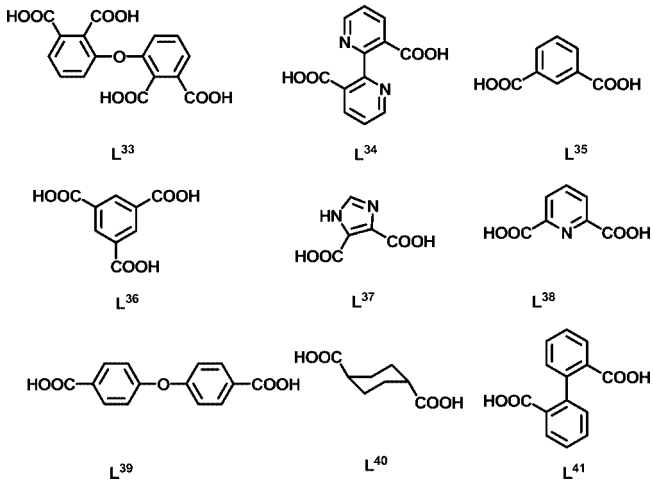

Figure 20. Symmetrical multicarboxylate ligands.[46–50,52,53]

fashion through hydrogen bonds, resulting in a 3D homochiral network. The Cd complex also has two kinds of homochiral helices and chiral 2D sheets, and different from that of the Zn^{II} complex, the chiral layers are parallel and stack through interlayer interactions of coordination bonds (Cd–O) to give a 3D chiral network.

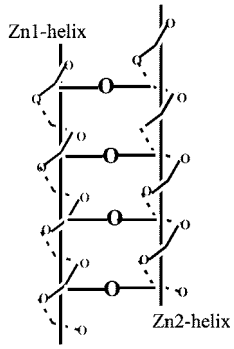

Figure 21. Zn(bpy)L^{33} complexes with homochiral 3D structure assembled from helical chain building units.[52]

Of course, the additional coordinated sites might come from short auxiliary ligands, so that the direction of these interactions could be controlled by the spatial affects of the chiral building units.[54,55] Yan et al. used the simple bis(didentate) pyridylimine ligand containing a –N–N– bond to build a 2D manganese–azido framework.[9] The chirality of the structure unit is induced by the twisted chiral conformation of the coordinated diazine ligands (Figure 2). The constraint of the diazine ligands in the twisted chiral conformation imparts chirality to the triple linkage that consists of two end-on azido bridges plus a –N–N– bridge. This chiral linkage equipped with two chelate sites is chirally discriminative and requires that the two metal coordination spheres have the same absolute configuration. The chirality is preserved when the dimers are interlinked into the 2D network by the homochiral interdimer interactions that arise from the unique bridging topology of the single EE azido bridges. As a result, two kinds of crystals are obtained in the same batch by evaporating the solution of this compound and separating the crystals manually. In both crystals, the homochiral layers extend parallel to the *ab* plane and stack along the *c* direction. In one of these two kinds of crystals, adjacent layers are related by 3_1 screw axes and stack in an *ABCABC* fashion (*A*, *B*, and *C* represent layers with different orientations but with the same chirality), resulting in a homochiral crystal.

Poeppelmeier et al. reported another interesting complex Zn(pyrazine)(H_2O) (MoO_2F_4),[56] where the *cis*-$MoO_2F_4^{2-}$ anions in the complex are ordered and coordinated to *trans*-$[Zn(pyrazine)_2(H_2O)_2]^{2+}$ cations in an alternating fashion, forming a 3_1 inorganic helical chain. It is found that when the large organic cations associated with the coordinated donors pack orderly in the solid, the negatively charged $MoO_2F_4^{2-}$ anions are fixed in a special arrangement to fit the helical formation with the two bridged fluoride sites positioned oppositely to the *cis* O atoms. Considering more than six helices interleaved through the Zn–pyrazine–Zn bridges, it is likely that the presence of a short enough linear pyrizine bridging ligand could give rise to the helices packing without introducing any inversion center among them. As illustrated in Figure 22, helices with the same handedness share identical spatial and translational orientations along the Zn–N bridges. When two helices with opposite handedness are bonded together, there are no matching sites for any other helices of either handedness.

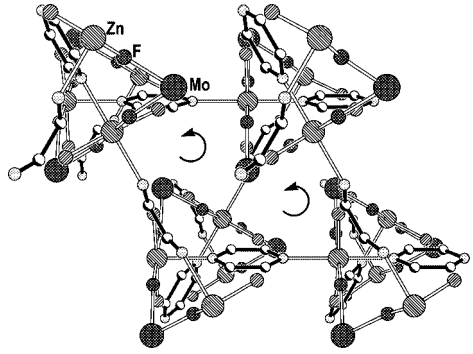

Figure 22. Helix with possible interaction packs with other helices that have the same handedness in compound Zn(pyrazine)(H_2O)-(MoO_2F_4).[56]

Another way to construct homochiral 3D frameworks is by using the unsymmetrical ligands as effective connectors to form the polymeric chiral helicates (Figure 23).[57] Lin and his coworkers pointed out that the steric interactions in *cis*-pyridylethenylbenzoate (L^{42}) would cause the pyridyl and phenyl groups to be significantly deviated from coplanarity.[58] Such a "skewing" of coordination sites of L^{42} should favor the formation of a helical structure. Hong and coworkers used 4-sulfanylmethyl-4′-phenyl carboxylate pyridine (L^{43})[59] to construct a homochiral Zn^{II} coordination network. As shown in Figure 24, each zinc(II) atom is located in a distorted tetrahedral environment. The chirality transmitting model could be described as that in the former example, in which two kinds of homochiral helices are alternatively assembled along the crystallographic *b* axis. One type of helix is formed by hydroxy-bridging Zn^{II} atoms, and the other is constructed by L^{43}-bridging Zn^{II} centers. These distinct homochiral helices are arranged orderly with the zinc(II) atoms acting as hinges, and the novel two-dimensional layers in the *bc* plane stack along the crystallographic *a* axis in an interlocking fashion. The chirality of the [Zn–spcp] helicate should also arise from the sp^3 configurations of the C and S atoms in the $–CH_2S–$ spacer, which forces the ligand to be nonlinear and results in the formation of the twisty helical conformation. Because the compound crystallizes in an asymmetric space group $P2_1$, only one kind of tubular helix is involved in the crystal structure.

Another interesting ligand is 2,5-pyridinedicarboxylate L^{45}. Its unsymmetricial coordinated mode and the short separation could force the helices to pack together without the introduction of any inversion center.[60] Hong et al. illustrated the dimensional extension of chirality in the helicates based on $\{[NH_2(CH_3)_2]Fe^{III}(L^{45})_2\}_n$. In this complex, the Fe^{III} coordinates to L^{45} in a *cis* mode, forming 2_1 helical

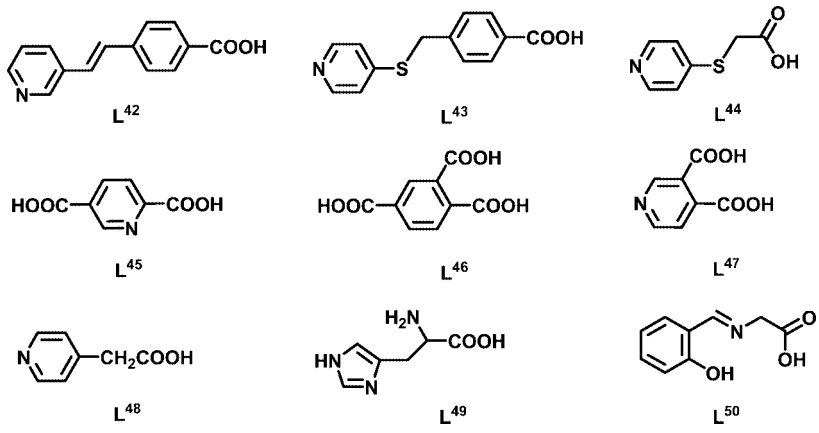

Figure 23. Unsymmetrical ligands.[57–61]

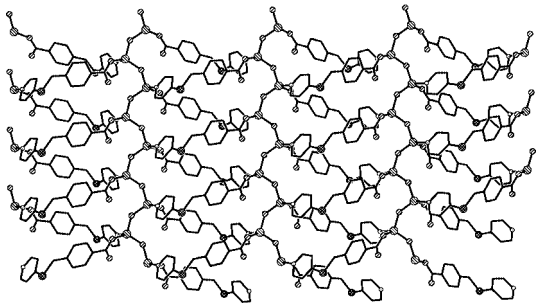

Figure 24. A view of the two types of homochiral helices in the ZnL^{43} complex.[59]

chains that are arranged parallel or perpendicular to each other with the metal atoms as the connective nodes. This kind of interaction of the helical chains is directional enough to force the 3D network to be homochiral (space group $P4_32_12$), namely the overall structure being chiral. Qiu et al. synthesized the compound $Co(L^{45})(H_2O)_2{\cdot}H_2O$, which crystallized in a space group $P2_12_12_1$.[61] In this compound, there are two types of twofold screw axes along the crystallographic *b* axis, and the helices are interconnected to each other through the cobalt centers to produce an interesting two-dimensional layered structure (Figure 25). Furthermore, the interlayer hydrogen bonds corresponding to the homochiral sheets are directional and strong enough to further pack the 2D undulating layers into a 3D homochiral supramolecular framework. It is notable that the resulting crystals are not racemic as verified by the observation of strong signals in the vibrational circular dichroism (VCD) spectra. The enantiomeric excess might be ascribable to the initial crystals formed as seeds for the handedness of the bulk product, in which the particular handedness of the bulk sample is dependent on what random handedness was formed in the initial crystals.

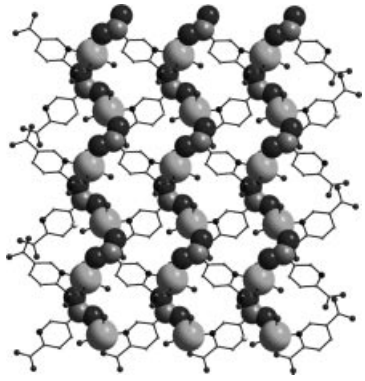

Figure 25. The 2D structure including the right-handed helical chains of –C–O–Co– (the space-filling view) and the left-handed helical chains of –PDC–Co– (the cylindrical view).

6. Conclusions

The rational design and construction of chiral materials from achiral sources requires fundamental understanding of the chirality origination and translation. Helicates obtained by self-assembly possess fascinating structures and could act as excellent model systems for studying the extended supramolecular chirality developed from the conformational chirality in classical coordination complexes. In these processes, the coordination bond has become a very useful tool for the construction of large, well-organized, chiral architectures and further chiral aggregations, in the presence of various noncovalent interactions, such as hydrogen bonding, π–π stacking interactions, and van der Waals interactions. Though the structural control and molecular programming in the chiral assembly by using helicates as building intermediates with conformational chiral bridging modes have been significantly explored and improved, the use of achiral ligands to provide self-organized chiral supramolecular species through spontaneous resolution is still in its infancy. The construction and chiral aggregation of helicates will probably suffer from the competition of other fascinating metal-containing achiral assemblies, but they will keep a dominant place if their promising potential applications as molecular and supramolecular functional devices are confirmed and developed. We have no doubt that academic and aesthetic interests will lead to further development in the formation and aggregation of new chiral crystals with helical features. We do think that the enormous potential applications of helical complexes will make it become a considerably attractive field in the near future.

Acknowledgments

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