

# Molecular Tectonics: From Simple Tectons to Complex Molecular Networks

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Received July 13, 2004

## ABSTRACT

Molecular networks in the crystalline phase are infinite periodic molecular assemblies formed under self-assembly conditions between self-complementary or complementary tectons. These millimeter-size structures may be regarded as hypermolecules formed by supramolecular synthesis using reversible intertecton interactions. Molecular tectonics, based on molecular recognition events and their iteration, is the approach dealing with design and preparation of molecular networks in the solid state. In this Account, an overview of the rational behind this approach is presented. A variety of molecular networks based on van der Waals interactions and hydrogen and coordination bonding possessing diverse connectivity and topology are discussed.

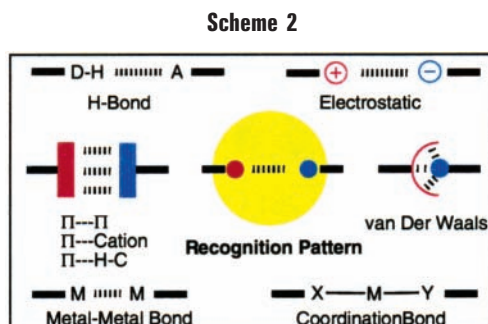
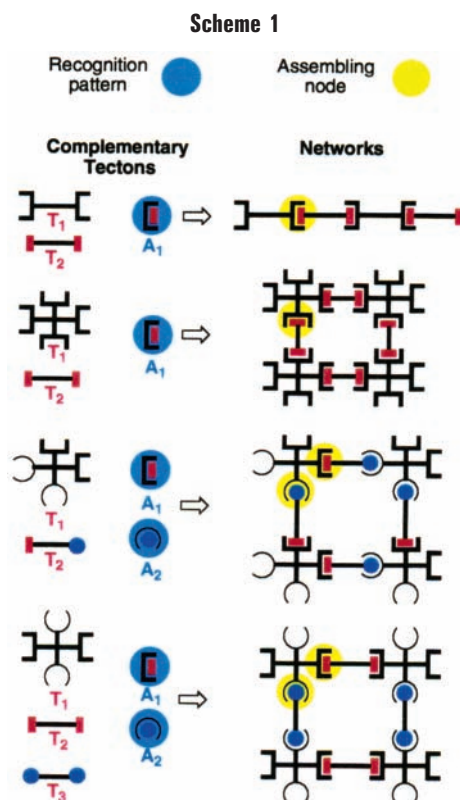
## Introduction

A crystal is by definition a compact and periodic system for which all the components are in close contact. Due to the periodic nature of the crystalline phase, a crystal is essentially a 3-D network. However, by considering the crystal as a supramolecular architecture,<sup>1,2</sup> one may identify specific intermolecular interactions between components composing the crystal.<sup>3</sup> These interactions are recognition patterns appearing during the crystallization event. Thus, by considering the recognition patterns as structural nodes of the architecture, one may describe the formation of molecular networks as resulting from translations of the nodes into one (1-D), two (2-D), or three directions (3-D) of space (Scheme 1).

Molecular tectonics<sup>4,5</sup> deals with the design and generation of molecular networks. This strategy is based on tectons,<sup>6</sup> which are active building units bearing recognition information and thus capable of recognizing each other. Since the formation of networks takes place under self-assembly conditions, only reversible processes may be used for the recognition events. Indeed, the use of

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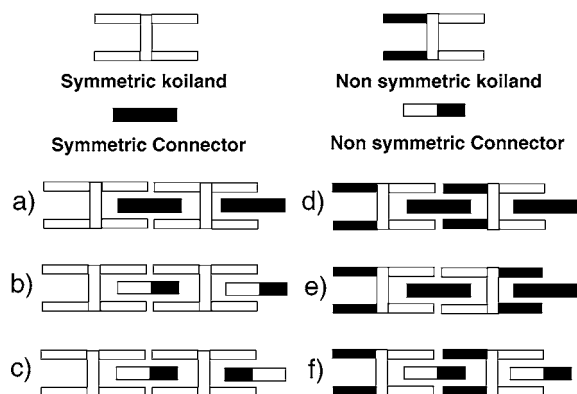


reversible processes allows the system to self-repair. In other words, the system composed of complementary tectons finds its own way to the most stable situation under given conditions (temperature, pressure, concentration, solvent, etc.). The recognition event may be set up through a variety of reversible attractive intermolecular interactions such as van der Waals, electrostatic,  $\pi$ - $\pi$ , H-bonding, and coordination bonding (Scheme 2).

Here we present some selected examples of strategies and networks following an increasing order of energy of interaction.

## Inclusion Networks: An Interplay between Concave and Convex Tectons

Inclusion processes between concave and convex units lead to molecular complexes in solution, in the solid state, or in both. Many receptors possessing a cavity have been designed to bind substrates through inclusion processes. On the other hand, the formation of clathrates in the solid state has been also extensively explored. We have ex-



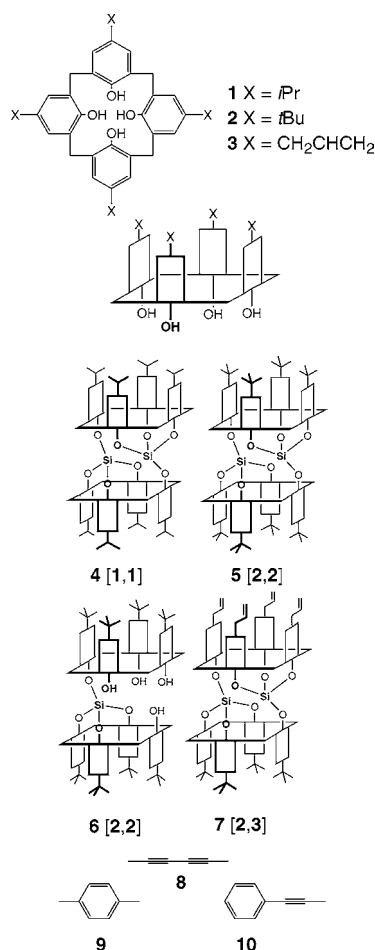
**FIGURE 1.** Schematic representations of 1-D inclusion networks based on interconnection of koilands and connectors.

tended the concept of inclusion in solution and clathrate formation in the solid state to the design of inclusion networks called koilates.<sup>7</sup> The design of koilates is based on the use of koilands (from Greek *koilos*, hollow),<sup>8</sup> which are multicavity tectons possessing at least two cavities arranged in a divergent fashion, and connectors capable of being included within the cavities of the koilands and thus connecting consecutive units by inclusion processes. van der Waals interactions are the driving forces for the formation of koilates. It is interesting to note that recognizing a network in a molecular crystal is a matter of translation of the recognition pattern. For inclusion networks exclusively based on van der Waals interaction, spotting a network is not trivial since the packing of all components is ensured by the same type of interactions. However, by consideration of the inclusion between the koiland and the connector as a specific recognition pattern, this difficulty may be overcome.

For the design of koilates, we have explored a variety of possibilities in terms of geometry and dimensionality.<sup>9</sup> For the purpose of demonstration, here we shall restrict ourselves to 1-D koilates based on two-component systems, that is, a combination of koilands possessing two divergent cavities and linear connectors. For 1-D koilates, as for any 1-D networks, two possibilities (directional or nondirectional) may be envisaged (Figure 1). A combination of centrosymmetric koilands and connectors will lead to nondirectional koilates due to the translation of centers of symmetry (Figure 1a). To impose the directionality, one may envisage a combination of nonsymmetric koilands, connectors, or both (Figure 1b–f). When centrosymmetric koilands and noncentrosymmetric connectors are combined, either directional (Figure 1b) or nondirectional (Figure 1c) koilates may be generated. Similarly, when noncentrosymmetric koilands and symmetric connectors are used, directional (Figure 1d) or nondirectional (Figure 1e) koilates may be obtained. Finally, the most promising strategy, based on specific recognition between koilands and connectors, is a combination of noncentrosymmetric koilands and connectors (Figure 1f).

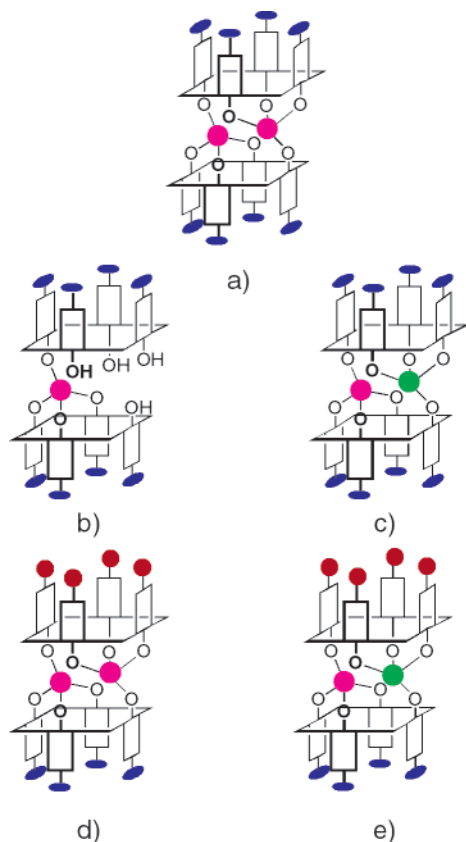
**Design of Koilands.** Calix[4]arene derivatives<sup>10</sup> are appropriate candidates for the design of koilands since these compounds accommodate in the solid state a variety of neutral guests molecules in their cavity (Scheme 3).

**Scheme 3**



Indeed, these compounds offer a preorganized and tunable hydrophobic pocket, as well as four hydroxy groups for further functionalization. However, the calix[4]arene backbone presents conformational flexibility. Among the four possible conformations, only the cone conformation is of interest for the design of koilands, which is based on double fusion of two units by two Si atoms.<sup>8</sup> Furthermore, calix[4]arenes offer the possibility of controlling both the entrance and the depth of the cavity by the nature of the substituents X. Although a large number of calix[4]arenes have been used for the synthesis of koilands, here, we shall focus only on three of them (1–3) (Scheme 3).

**Centric and Noncentric Koilands: (Figure 2).** Centrosymmetric koilands (Figure 2a) may be generated upon double fusion of two identical calix[4]arene derivatives by two identical fusing elements such as silicon atom (see koilands 4 and 5 in Scheme 3). The design of nonsymmetric koilands may be based on electronic, geometric, or both electronic and geometric differentiation of the two cavities (Figure 2b–e). Electronic differentiation may be achieved using a single silicon atom to connect two calix units (Figure 2b). Indeed, in that case, one of the two calix units is triply coordinated to a Si atom, whereas the other one is coordinated by a single bond to the Si atom. Another possibility may be based on two different fusing atoms (same oxidation state IV) such as Si and Ti or Ge (Figure 2c). Although all three cases have been investi-

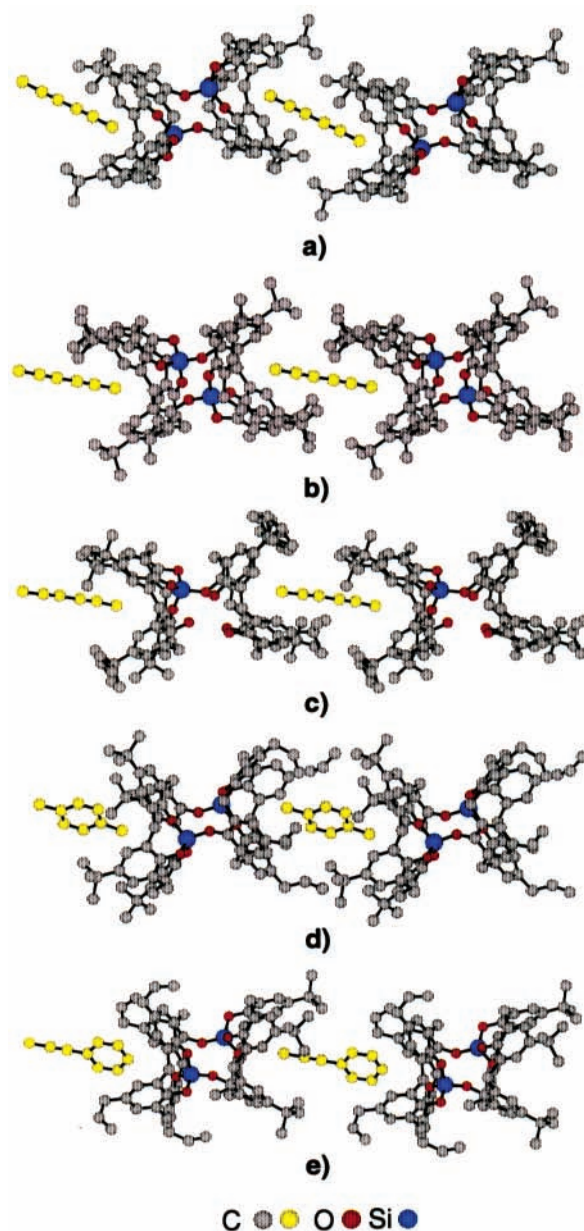


**FIGURE 2.** Schematic representation of centrosymmetric and noncentrosymmetric koilands.

gated, here we only present the case of koiland **6**.<sup>11</sup> Geometric differentiation may be accomplished, while keeping the same fusing element such as Si, by connecting two different calix units. Here we only describe the behavior of the geometrically differentiated koilands **7**.<sup>12</sup> The third possibility consisting in fusing two different calix derivatives by two different atoms has not been yet exploited.

**Nondirectional and Directional Koilates.** Relevant examples of koilates using koilands **4–7** and connectors **8–10** are given in Figure 3. The formation of nondirectional koilates in the crystalline phase was demonstrated by combining the centric koilands **4** (Figure 3a)<sup>13</sup> or **5** (Figure 3b)<sup>14</sup> with **8**, a rod-type molecule possessing both the requested linear geometry and distance between its two terminal CH<sub>3</sub> groups. As expected, linear koilates are formed through the interconnection of consecutive koilands by the connector molecules. Each connector bridges two consecutive koilands **8** by penetrating deeply their cavities through its terminal CH<sub>3</sub> groups generating thus 8–12 van der Waals contacts.

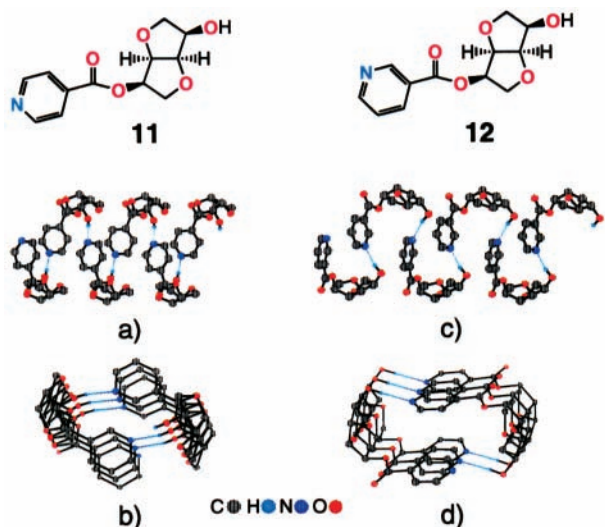
Since **8** is the most appropriate connector for **5**, the same connector was used to generate directional koilate with **6** (Figure 3c).<sup>15</sup> The connectivity between **6** and **8** is roughly the same as the one described above. Due to the noncentrosymmetric nature of **6**, the network generated is directional. The packing of koilates within the crystal is parallel. However, due to the opposite orientation of linear arrays, a nondirectional arrangement is obtained.



**FIGURE 3.** Portions of structures of koilates (1-D inclusion networks) formed between koilands **4** (a), **5** (b), and **6** (c) and the connector **8** and koiland **7** with connectors **9** (d) and **10** (e).

To deal with the geometrically differentiated koiland **7**, the formation of directional koilates was studied using **9** as a centrosymmetric and **10** as a noncentrosymmetric connector.<sup>16</sup> For a combination of **7** and **9** (Figure 3d), a directional koilate formed by bridging of consecutive koilands **7** by **9** was obtained. Interestingly, since **9** is centric, the noncentric nature of the network is due to nonsymmetrical arrangement of consecutive koilands **7**. Unfortunately, again, the directional linear koilates are packed in antiparallel fashion.

The final example deals with the combination of the noncentric **7** and the noncentric connector **10** (Figure 3e). As in the previous case discussed above, again a directional koilate is observed. And again, the 1-D inclusion networks are positioned in a parallel fashion but with opposite orientation.



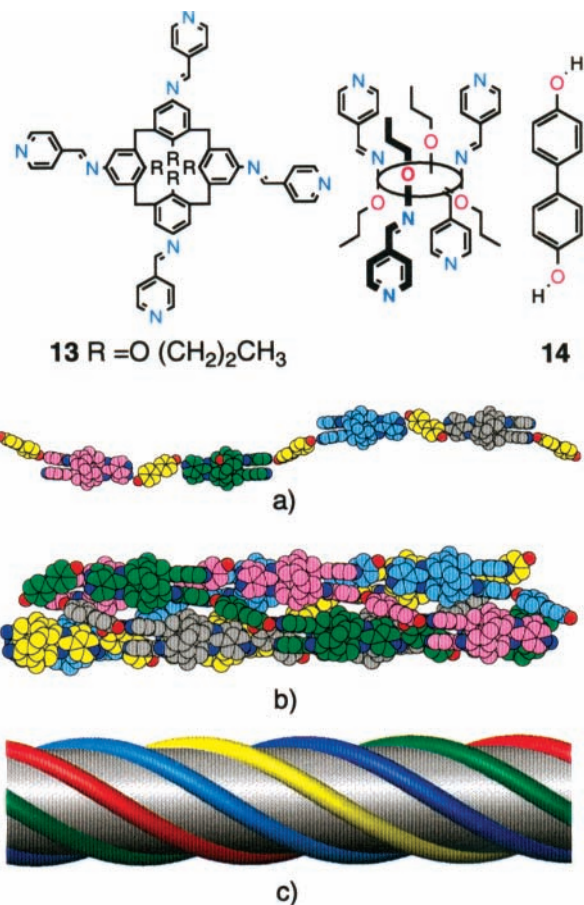
**FIGURE 4.** Portions of the structure of enantiomerically pure 1-D helical networks formed upon self-bridging of **11** (a,b) or **12** (c,d).

### H-Bonded Networks: Combining Electrostatic Interactions and H-Bonding

H-bonding is one of the most used interactions for the design of molecular networks.<sup>17,18</sup> The hydrogen bond (DH...A) forms between two electronegative atoms, D (donor) and A (acceptor), and is defined by the nature of D and A, the distance between them, and the DHA angle. For design of H-bonded networks, one may use different modes of H-bonding. The monohapto mode, although synthetically easier to achieve, due to the large angular (DHA) distribution<sup>19</sup> is not always a viable mode because often it does not allow a fine control of geometrical features of the recognition pattern and thus the prediction of the connectivity and the overall topology of the network. However, by restricting the number of possible geometrical arrangements through the use of the di- or trihapto mode of H-bonding, one may control, to a certain extent, and thus predict the connectivity pattern between tectons.

**Neutral 1-D Helical H-Bonded Networks.** For single-stranded 1-D networks, one may obtain linear, stair-type, or helical geometries. The design of helical H-bonded networks is a subject of current investigations. Although few cases of enantiomerically pure H-bonded helical networks have been published,<sup>20</sup> the majority of examples reported deal with achiral or racemic mixtures of tectons, which leads to the formation of racemates.

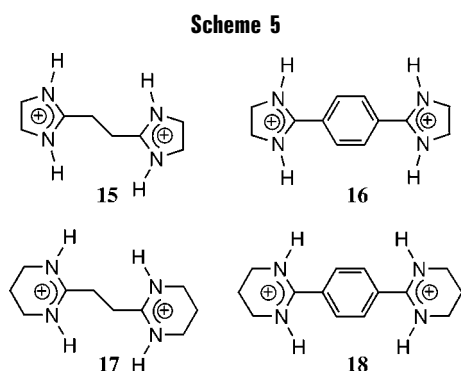
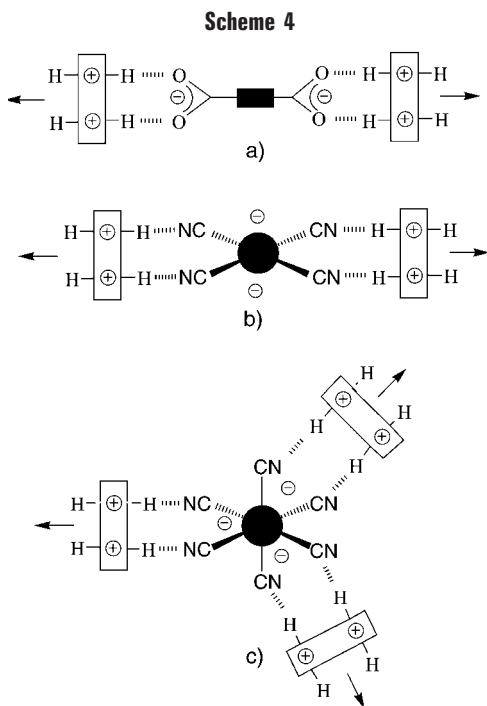
Molecular networks may be generated using either a self-complementary tecton (single-component system) or two or more complementary tectons (multicomponent system). Let us focus here on the first possibility. Neutral tectons **11** and **12** (Figure 4) are based on the optically active isomannide backbone bearing both H-bond donor (OH) and acceptor (pyridine) sites. Because of the stereochemistry of the isomannide unit, in both cases the pyridine and the OH groups are divergently oriented toward the concave face of the bicyclic unit. The difference between enantiomerically pure tectons **11** and **12** results from the orientation of the nitrogen atom of the pyridine



**FIGURE 5.** A portions of the structure of the single-stranded helical network formed between **13** and **14** (a), the braid generated by five helical strands (b), and its schematic representation (c).

ring.<sup>21</sup> Due to their self-complementarity and enantiomerically pure nature, both **11** (Figure 4a,b) and **12** (Figure 4c,d) lead to the formation of single-stranded H-bonded helical networks. The mutual interconnection of consecutive tectons indeed takes place through H-bonding between the OH and pyridine groups. For both helical networks, the P helicity is imposed by the predefined stereochemistry of isomannide. For both cases, the helical strands are packed in parallel mode. The difference between the two helical structures results from the location of the nitrogen atom on the pyridine ring inducing thus different pitches.

The second possibility deals with the formation of helical arrangements using a two-component system based on two complementary tectons. The tecton **13**, possessing four H-bond acceptor sites of the pyridine type occupying the apices of a pseudo-tetrahedron, was combined with the linear connector **14** possessing two H-bond donor sites of the phenolic OH type (Figure 5).<sup>22</sup> The H-bond acceptor **13** and donor **14** form a single-stranded helical network by mutual bridging (Figure 5a). Rather interestingly and unexpectedly, probably for best compaction reasons, five helical strands of the same handedness are assembled into a quintuple helical braid (Figure 5b,c). Finally, the quintuple helices are packed in a parallel mode. Three levels may be used to describe this rather complex system: the formation of a single-stranded

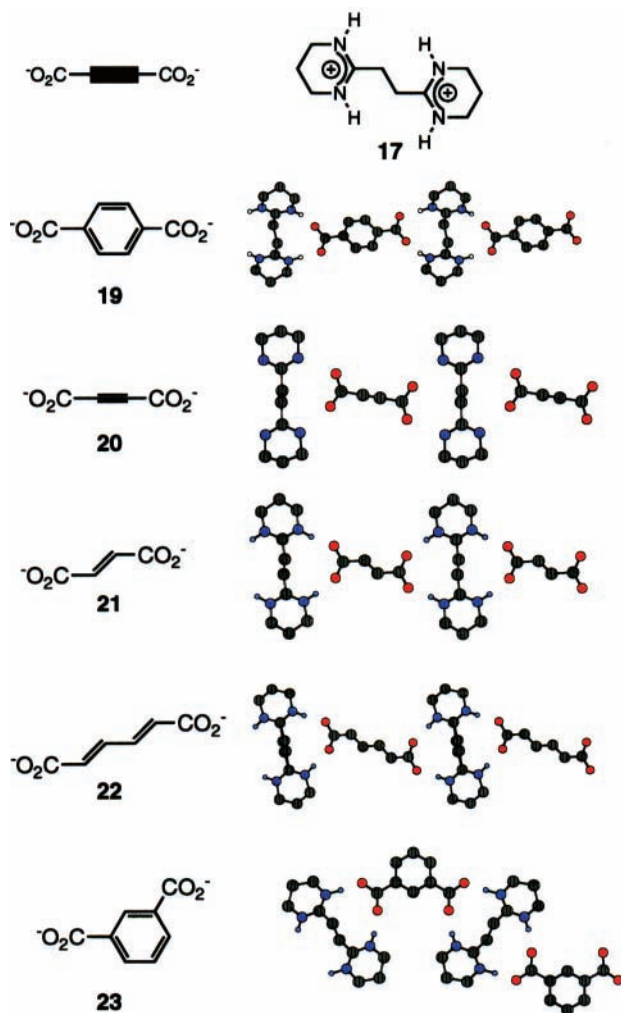


H-bonded helical network, the formation of the quintuple helical braided network, and the lateral association of braided networks leading to the crystal.

**Charge-Assisted H-Bonded Networks.** The majority of reported H-bonded molecular networks are based on nonionic hydrogen bonds.<sup>17</sup> To increase the robustness of the recognition pattern between H-bond donors and acceptors, one may combine directional hydrogen bonds with strong but less directional ionic interactions (Scheme 4).<sup>18,23</sup>

Bisamidinium dications such as **15–18** (Scheme 5) are interesting building blocks for the design of charge-assisted H-bonded networks. Indeed, these dications, due to the presence of four acidic N–H protons oriented in a divergent fashion, may act as tetra-H-bond donors in the presence of H-bond acceptors such as carboxylates, tetracyanometalates, and hexacyanometalates. By tuning the distance between the acidic hydrogens on the same side of these units, one may induce the recognition of the above-mentioned anions by a dihapto mode of interaction (Scheme 4).

**H-Bonded Networks Based on Recognition of Carboxylates.** The formation of 1-D H-bonded networks

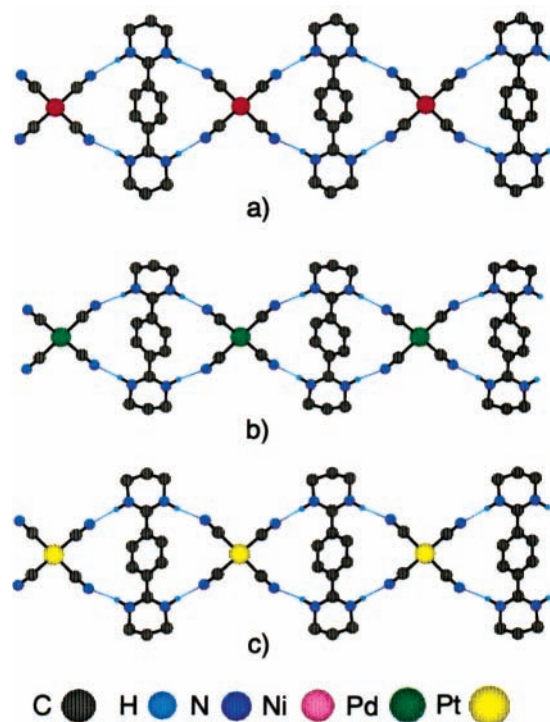


**FIGURE 6.** Portions of structures of the 1-D networks formed through dihapto mode of H-bonding between **17** and dianions **19–23**.

based on dicarboxylates was demonstrated using dicationic tectons such as **17** (Figure 6).<sup>18,24,25</sup> Due to the proper spacing of the two cyclic amidinium moieties ((CH<sub>2</sub>)<sub>2</sub>), **17** recognizes on each of its faces the carboxylate moiety by a dihapto mode of H-bonding (Scheme 4). This mode of recognition was also established between **17** and monocarboxylate for the formation of discrete exo-bi-nuclear complexes.

As expected, the formation of a variety of 1-D networks between **17** and different dicarboxylates such as **19–23** was demonstrated (Figure 6). In all cases, the common features of the networks are as follows: **17** adopts a centrosymmetric conformation; all four acidic protons are localized on **17**; the neutral 1-D networks are formed through the mutual interconnection of dicationic and dianionic tectons. With other combinations of cationic and anionic tectons, other 1-D, as well as 2-D and 3-D, networks have been also obtained.<sup>25</sup>

**H-Bonded Networks Based on Recognition of Tetracyanometalate.** The bisamidinium **18** has been designed to generate H-bonded networks with [M(CN)<sub>4</sub>]<sup>2-</sup>.<sup>26</sup> Indeed, the distance between the two nitrogen atoms located on the same side of **18** is optimum for the binding of square-



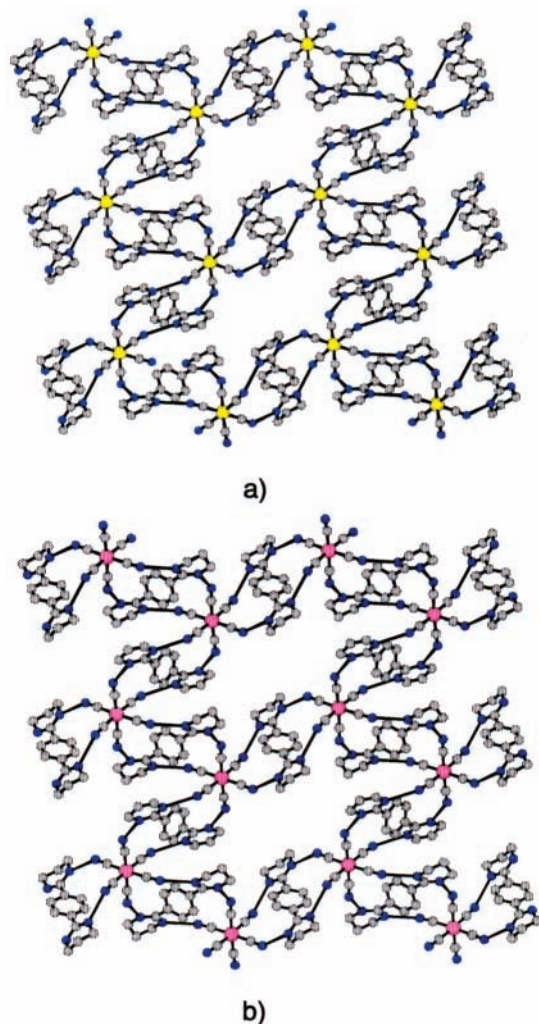
**FIGURE 7.** Portions of structures of 1-D networks formed between square-planar  $[M(CN)_4]^{2-}$  dianions and **18**.

planar  $[M(CN)_4]^{2-}$  anions by a dihapto mode. The latter mode of recognition may be regarded as the organization of the second coordination sphere around the transition metal (Scheme 4).<sup>27,28</sup>

The combination of **18** with  $[M(CN)_4]^{2-}$  ( $M = Pd, Pt$ , or  $Ni$ ) leads, as predicted, to almost identical 1-D networks (Figure 7).<sup>27,28</sup> These 1-D neutral networks are generated by H-bonds in the dihapto mode between consecutive cationic and anionic tectons and are packed in a parallel fashion in the crystalline phase. Interestingly, all three networks obtained are isostructural. The same type of approach was used by others by combining  $[MCl_4]^{2-}$  anions with protonated bispyridine derivatives.<sup>29</sup>

**H-Bonded Networks Based on Recognition of Hexacyanometalate.** Since the distance between CN groups in syn localization in  $[M(CN)_6]^{3-}$  anions is almost the same as the one in  $[M(CN)_4]^{2-}$ , a similar mode of recognition may be expected with dicationic tectons such as **18** (Scheme 4). However, for charge neutrality reasons, an **18**/ $[M(CN)_6]^{3-}$  ratio of  $3/2$  is expected. Due to the octahedral geometry around the metal center, the interconnection of  $[M(CN)_6]^{3-}$  complexes by **18** leads to a neutral 2-D network.

A combination of **18** with  $[Fe(CN)_6]^{3-}$  (Figure 8a) or  $[Co(CN)_6]^{3-}$  (Figure 8b) leads indeed to the formation of the expected 2-D networks.<sup>27</sup> These are formed by interconnection of dicationic and dianionic units through dihapto mode. The geometrical features of both the organic tecton **18** and the anionic  $[M(CN)_6]^{3-}$  complex are almost identical. In both cases, the packing of the neutral 2-D networks leads to channels that are filled with seven



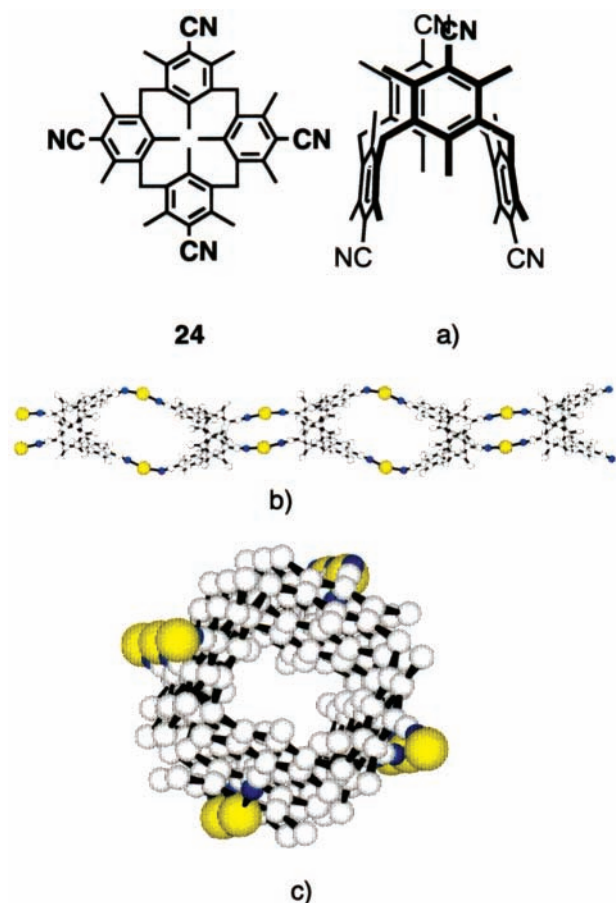
**FIGURE 8.** Portions of structures of 2-D networks formed between **18** and  $[Fe(CN)_6]^{3-}$  (a) and  $[Co(CN)_6]^{3-}$  (b) anions.

water molecules. The latter, in both cases, form H-bonded 1-D networks composed of hexagons interconnected by tetragons.

It is worth noting that due to the dihapto or chelate mode of H-bonding between **18** and  $[M(CN)_6]^{3-}$ , supramolecular chirality taking place within the second coordination sphere around the metal is generated. By analogy with  $\Delta$  and  $\Lambda$  type chirality defined for octahedral complexes surrounded by two or three chelating ligands, the supramolecular chirality of the type  $\Delta'$  and  $\Lambda'$  occurring within the second coordination sphere is defined as resulting from noncovalent reversible interactions through a chelate mode of H-bonding. Since **18** is achiral, both  $\Delta'$  and  $\Lambda'$  enantiomers are present in the 2-D network thus leading to achiral crystals. Again, as in the case of  $[M(CN)_4]^{2-}$ , both networks are isostructural.

## Coordination Networks: An Interplay between Organic and Metallic Tectons

Coordination networks are infinite metallo-organic architectures resulting from mutual bridging between organic and metallic tectons. The design of this type of network with predefined dimension (1-, 2-, or 3-D) is based on the

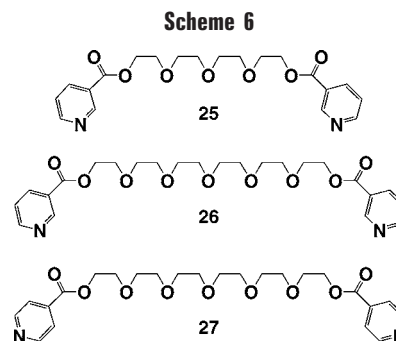


**FIGURE 9.** Tecton **24** adopting the alternate conformation (a) leads in the presence of  $\text{Ag}^+$  to a tubular network (b, c).

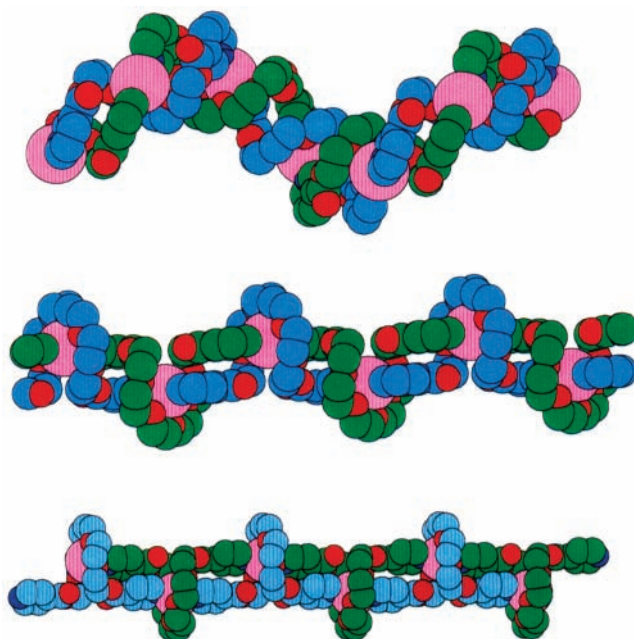
interplay between both electronic and geometric requirements of the organic and the metallic tectons. Because the combination of organic and metallic tectons offers endless structural possibilities and, furthermore, because metal centers may present a variety of physical properties (redox, optical, magnetic), the formation of coordination networks or polymers is a subject of intensive investigations.<sup>30</sup> Although, we have reported many examples of 1-, 2-,<sup>31</sup> and 3-D<sup>32</sup> coordination networks, here we shall only describe design principles dealing with the formation of 1-D networks.

**Tubular Coordination Networks.** Infinite tubular architectures are 1-D networks. This type of assembly may be obtained under self-assembly conditions using reversible coordination bonding (Figure 9).<sup>33</sup>

The tecton **24** was designed because it adopts the 1,3-alternate conformation presenting thus four nitrile groups located below and above the main plane of the macrocycle in an alternate fashion (Figure 9a). As predicted, the combination of **24** with  $\text{Ag}^+$  leads to the formation of a cationic tubular structure through bridging of consecutive tectons **24** by  $\text{Ag}^+$  cations adopting a linear coordination geometry. (Figure 9b,c). The cationic networks are packed in a parallel mode. The tubular networks are interconnected in a dihapto mode by strong metal- $\pi$  interactions between  $\text{Ag}^+$  cation and the aromatic moiety belonging to the next tubular strand. The tubular network is not empty but occupied by solvent molecules.



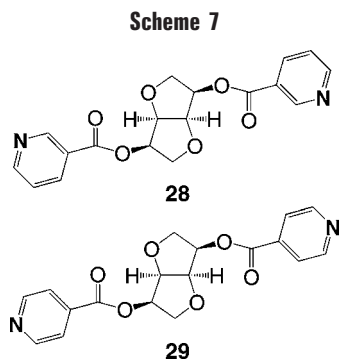
**Helical Coordination Networks.** The formation of helical networks has been a subject of intensive investigations.<sup>34</sup> Tectons **25**–**27** are bis-monodentate ligands based on two coordinating pyridine units interconnected by the oligo(ethylene glycol) moieties (Scheme 6). The combination of **25**–**27** with  $\text{Ag}^+$  leads to the formation of double-stranded intertwined networks (Figure 10).<sup>35,36</sup> The bridg-



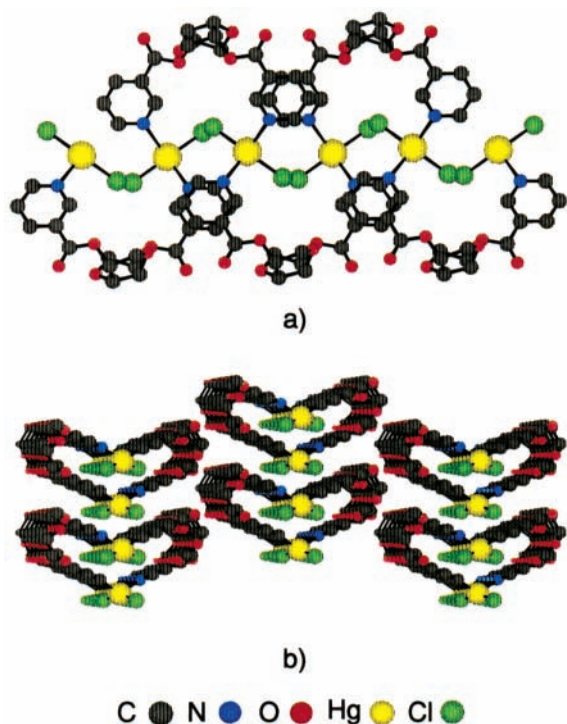
**FIGURE 10.** Portions of structures of double-stranded helical networks formed between  $\text{Ag}^+$  and **25** (a), **26** (b), and **27** (c).

ing of consecutive organic tectons by silver cations leads to the formation of a helical polycationic network. Interestingly but unpredicted, adjacent linear networks are interwoven. The driving force for the formation of these assemblies is related to the loop-type disposition (pseudo-crown ether) of the oligo(ethylene glycol) units allowing interactions between silver cations belonging to one strand and ether oxygen atoms of the other strand. It was demonstrated that the pitch of the helical arrangement could be controlled by the length of the oligo(ethylene glycol) spacer and by the orientation of the nitrogen atom of the pyridine ring.

The three examples of helical assemblies mentioned above deal with achiral tectons. Consequently, in all three cases, racemates have been obtained. This is indeed the case for the majority of helical coordination networks

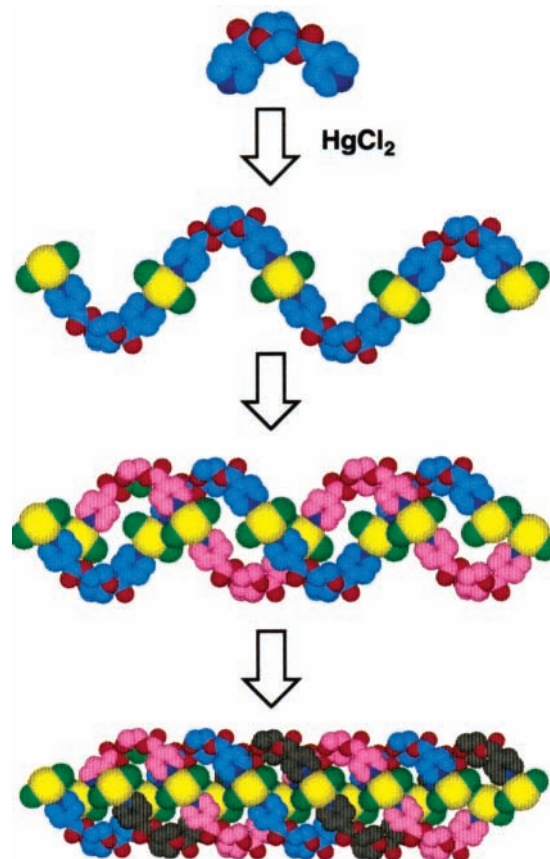


reported. To generate optically pure helical strands, we used enantiomerically pure tectons such as **28** and **29** (Scheme 7).<sup>37</sup> Both tectons are based on isomannide backbone and bear two pyridine units as neutral coordination sites. The difference between the two tectons results from the orientation of the N atom of the pyridine ring. A combination of **28** with  $\text{HgCl}_2$  leads to the formation of a single-stranded helical coordination network with P helicity. The latter is imposed by the stereochemistry of isomannide.<sup>38</sup> The helical arrangement is obtained upon bridging of consecutive tectons **28** by mercury cations (Figure 11a). It is interesting to note that the helical networks are packed in the syn-parallel fashion thus generating polarity (Figure 11b).

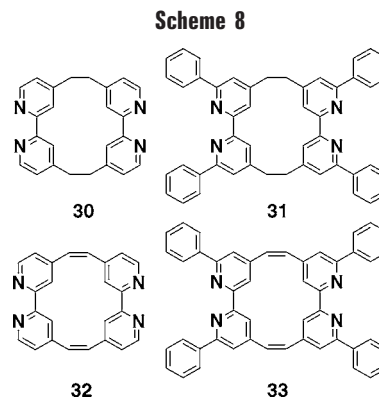


**FIGURE 11.** Portions of the structure of the single-stranded helical networks formed between  $\text{HgCl}_2$  and **28** (a) and the syn-parallel packing of 1-D networks affording a polar crystal.

A combination of **29** and  $\text{HgCl}_2$  leads again to the formation of an enantiomerically pure helical strand with P helicity. Again, the network is generated by bridging of consecutive tectons **29** by mercury cations (Figure 12). Interestingly but unexpectedly, because of interstrand



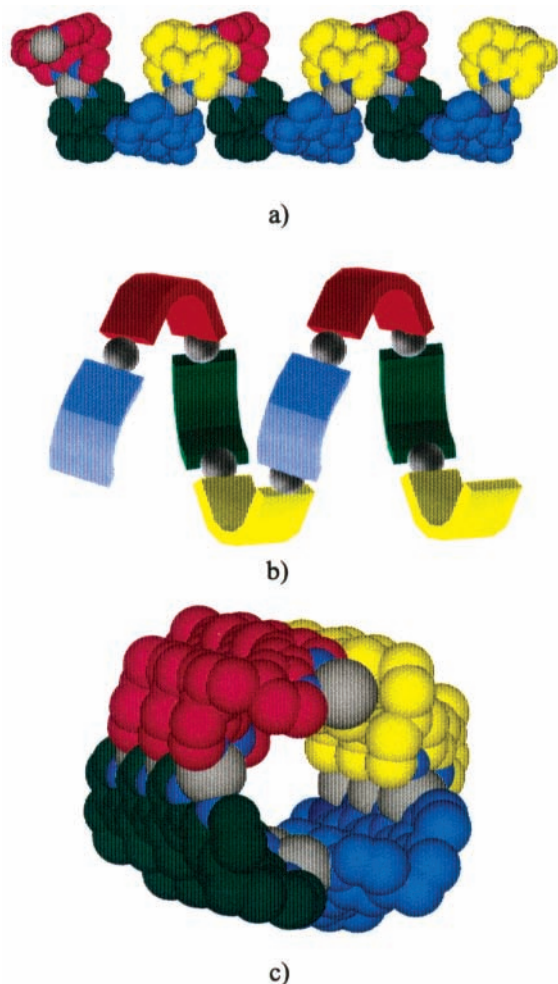
**FIGURE 12.** Generation of the triple-stranded helical networks formed between  $\text{HgCl}_2$  and **29**.



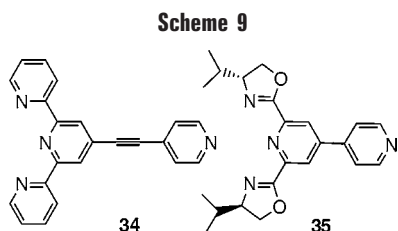
interactions, a triple-stranded helical arrangement is observed. The latter is not cylindrical but rather flat. The triple-stranded helices are arranged in a parallel fashion.<sup>38</sup>

The formation of helical strand based on another combination using the exo-bischelate tectons **30–33** (Scheme 8) and again silver cation was also demonstrated.<sup>39</sup> These macrocyclic ligands, because of the spacer groups connecting the two 2,2'-bipyridine units at positions 4 and 4', adopt a roof-type conformation. For that reason, when **31** is interconnected by cations such as silver adopting the tetrahedral coordination geometry, a single-stranded helical network is formed (Figure 13). Because of the achiral nature of the organic tecton, both P and M helices are present in the crystal, affording thus a racemate.



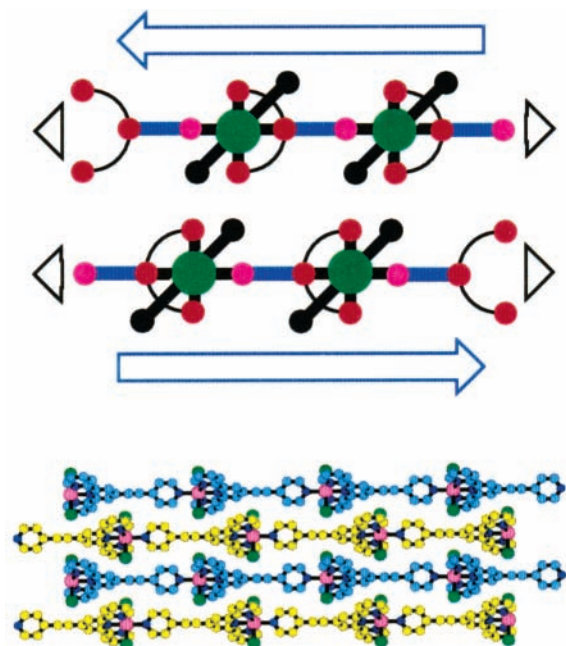


**FIGURE 13.** Portions of the structure of the single-stranded helical networks formed between  $\text{Ag}^+$  and **31** (a), its schematic representation (b), and a lateral view (c). Phenyl groups are not represented for clarity.



**Directional 1-D Coordination Networks.** The design of directional networks is an important issue for the exploitation of directional physical properties. Here, we shall focus only on 1-D networks. The strategy investigated was to combine dissymmetric organic tectons bearing monodentate and tridentate coordination poles such as **34** and **35** (Scheme 9) with a transition metal complex ( $\text{CoCl}_2$ ) adopting an octahedral coordination geometry and offering four coordination sites in square arrangement.<sup>40</sup> Indeed for such a strategy, interestingly, the mutual binding between the organic and metallic tectons leads to a neutral directional 1-D network (Figure 14).

For directional 1-D networks, two packing arrangements (syn-parallel and anti-parallel) may be envisaged. In the case of the achiral **34**, as expected, the centro-



**FIGURE 14.** Schematic representation of two directional 1-D networks packed in an anti-parallel fashion (top) and a portion of the structure of the neutral network formed between  $\text{CoCl}_2$  and **34** (bottom). Carbon atoms belonging to consecutive strands are differentiated by color.

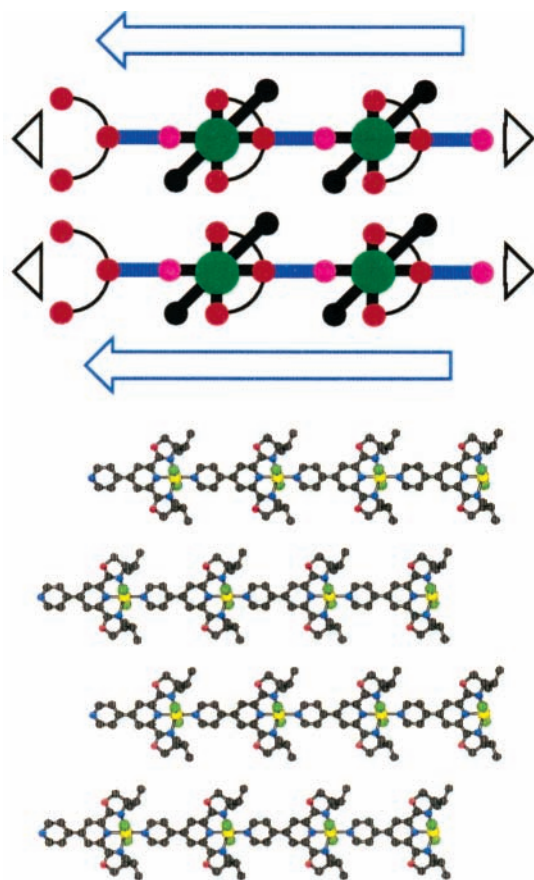
symmetric packing is observed leading thus to an apolar arrangement.

To investigate the possibility of avoiding the anti-parallel packing, the introduction of chirality within the backbone of the organic tecton was explored. Thus, the neutral acentric and *c2*-chiral tecton **35** was designed. The latter is based on two coordination poles composed of a pyridine unit connected at the 4-position to a pyridine bearing at the 2- and 6-positions two optically active oxazoline moieties.<sup>41</sup>

Upon combination of the chiral tecton **35** with  $\text{CoCl}_2$ , a chiral and directional 1-D network is obtained. As stated above, the directionality of the network is due to the acentric nature of **35**. In marked contrast with the case mentioned above, here, a syn-parallel arrangement of the chiral 1-D networks is observed. This packing mode leads to a polar solid (Figure 15).

## Summary and Outlook

In this Account, we have tried to demonstrate that molecular tectonics is a viable approach for the design and generation of molecular networks in the crystalline phase. Indeed, by designing programmed and active molecular tectons capable of mutual interactions (molecular recognition) and allowing the translation of the recognition event (iteration), one may predict, in some cases, the connectivity pattern between tectons and thus the geometry, topology, and directionality of molecular networks. An important issue here is the reliability of the prediction. The latter is the consequence of the quality of the design of the tectons. This, obviously, depends on the nature and thus the energy associated with interactions



**FIGURE 15.** Schematic representation of two directional 1-D networks packed in a syn-parallel fashion (top) and a portion of the structure of the neutral network formed between  $\text{CoCl}_2$  and **35** (bottom) showing the polar arrangement. H atoms are not represented for clarity.

used, the number of components, and the structural flexibility of tectons. Our experience showed that, as one may expect, using strong interactions such as a combination of charge/charge electrostatic interactions and the dihapto mode of H-bonding or coordination bonds based on the polyhapto mode of coordination, the reliability in the prediction of the network is ca. 60–70%. This may be further increased by using tectons with rather restricted conformational space (rigid structures). In our opinion, today this domain is in its infancy and thus not fully explored and mastered. More systematic investigations are needed before reaching the maturity. Now about the interesting, recurrent, and strongly under discussion question on the relationship between this approach and crystal engineering.<sup>3</sup> In other terms, are crystal structures predictable?<sup>42,43</sup> In our opinion, the response is **NO**. With our present level of knowledge and understanding, we are not capable of predicting the crystal structure of a set of tectons: in particular, the adopted conformation by flexible tectons, the presence of solvent molecules, polymorphs, etc. However, as stated by Dunitz,<sup>1</sup> by considering a crystal as a “supermolecule *par excellence*”, using concepts and principles developed in supramolecular chemistry,<sup>2</sup> one may, through the control of molecular recognition events, predict some of the connectivity

patterns between tectons and thus the formation of molecular networks. After many years of investigations by several research groups, today one may design molecular networks in the crystalline phase with an acceptable degree of precision. So far the description of molecular networks is based on geometrical features. Recently, we have analyzed network formation using extensive energy analysis.<sup>44</sup> This type of analysis must be pursued and shall allow a more precise description. A further important issue is obviously to use this knowledge for the design of molecular networks with predicted properties. In other terms, the molecular tectonics approach must extend structural networks to functional networks. This aspect is of prime importance in terms of applications and remains a challenge.

*This Account summarizes ca. 15 years of investigations. Many thanks to all my co-workers, students, and visiting Professors for their invaluable discussions and hard work. I am also grateful to the Université Louis Pasteur, Institut Universitaire de France, the CNRS, and the French Ministry of Education and Research for financial support.*

## References

- (1) Dunitz, J. D. Phase transitions in molecular crystals from a chemical viewpoint. *Pure Appl. Chem.* **1991**, *63*, 177–185.
- (2) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
- (3) Desiraju, G. D. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1999.
- (4) Mann, S. Molecular tectonics in biomineralization and biomimetic materials chemistry. *Nature* **1993**, *365*, 499–505.
- (5) Hosseini, M. W. Reflection on molecular tectonics. *CrystEngComm* **2004**, *6*, 318–322.
- (6) Simard, M.; Su, D.; Wuest, J. D. Use of Hydrogen Bonds to Control Molecular Aggregation. Self-Assembly of Three-Dimensional Networks with Large Chambers. *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698.
- (7) Hosseini, M. W.; De Cian, A. Molecular Tectonics: An Approach to Organic Networks. *Chem. Commun.* **1998**, 727–733.
- (8) Delaigue, X.; Hosseini, M. W.; De Cian, A.; Fischer, J.; Leize, E.; Kieffer, S.; Van Dorsseleer, A. Multicavitand I: Synthesis and X-ray Crystal Structure of a Fused bis-*p-tert*-butylcalix[4]arene by two Silicon Atoms. *Tetrahedron Lett.* **1993**, *34*, 3285–3288.
- (9) Martz, J.; Graf, E.; Decian, A.; Hosseini, M. W. Molecular tectonics: molecular networks based on inclusion processes. In *Crystal design: structure and function*; Desiraju, G. R., Ed.; Perspectives in Supramolecular Chemistry, Vol. 7; Wiley: Chichester, U.K., 2003; pp 177–209.
- (10) Gutsche, C. D. Calixarenes. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1989.
- (11) Delaigue, X.; Hosseini, M. W.; Leize, E.; Kieffer, S.; van Dorsseleer, A. Multicavitands II: Synthesis of a Non Centrosymmetric Hollow Molecular Unit (Koiland) Based On Fusion of Two *p-tert*-butylcalix[4]arenes by Both Silicon and Titanium Atoms. *Tetrahedron Lett.* **1993**, *34*, 7561–7564.
- (12) Hajek, F.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. Multicavitands V: Synthesis and X-ray Analysis of Unsymmetrical Linear Koilands Based on the Double Fusion of two Different Calix[4]arenes by two Silicon Atoms. *Tetrahedron Lett.* **1997**, *38*, 4555–4558.
- (13) Martz, J.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. Molecular tectonics X: design, synthesis and structural analysis of a molecular network based on inclusion processes in the crystalline phase. *J. Mater. Chem.* **1998**, *8*, 2331–2333.
- (14) Hajek, F.; Graf, E.; Hosseini, M. W.; Delaigue, X.; De Cian, A.; Fischer, J. Molecular Tectonics I: The First Synthesis and X-ray Analysis of a Linear Koilate Obtained by Self-Assembly of Linear Koilands and Hexadiyne. *Tetrahedron Lett.* **1996**, *37*, 1401–1404.
- (15) Martz, J.; Graf, E.; Hosseini, M. W.; De Cian, A., manuscript in preparation.

- (16) Martz, J.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. Directional 1-D Inclusion Networks: self-assembly of unsymmetrical Koilands into Directional koilates in the crystalline phase. *J. Chem. Soc., Dalton Trans.* **2000**, 3791–3796.
- (17) Etter, M. C. Encoding and Decoding Hydrogen-Bond Patterns of Organic Compound. *Acc. Chem. Res.* **1990**, *23*, 120–126. Aakerøy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397–407. Subramanian, S.; Zaworotko, M. J. Exploitation of the hydrogen bond: recent developments in the context of crystal engineering. *Coord. Chem. Rev.* **1994**, *137*, 357–401. Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311–2327. Lawrence, D. S.; Jiang, T.; Levett, M. Self-Assembling Supramolecular Complexes. *Chem. Rev.* **1995**, *95*, 2229–2260. Stoddart, J. F.; Philip, D. Self-Assembly in Natural and Unnatural Systems. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154–1196. Fredericks, J. R.; Hamilton, A. D. In *Templating, self-assembly, and self-organization*; Sauvage, J. P., Hosseini, M. W., Vol. Eds.; Comprehensive Supramolecular Chemistry, Vol. 9; Atwood, J. L., Davis, J. E., Macnicco, D. D., Vögtle, F., Eds.; Elsevier: Oxford, U.K., 1996, pp 565–594. Braga, D.; Grepioni, F. Intermolecular Interactions in non Organic Crystal Engineering. *Acc. Chem. Res.* **2000**, *33*, 601–608.
- (18) Hosseini, M. W. Molecular tectonics: from molecular recognition of anions to molecular networks. *Coord. Chem. Rev.* **2003**, *240*, 157–166.
- (19) Taylor, R.; Kennard, O. Hydrogen-Bond Geometry in Organic Crystals. *Acc. Chem. Res.* **1984**, *17*, 320–326.
- (20) Saladino, R.; Hanessian S. In *Crystal Design: Structure and Function*; Desiraju, G. R., Ed.; Perspectives in Supramolecular Chemistry, Vol. 7; Wiley: Chichester, U.K., 2003; pp 77 ff.
- (21) Grosshans, P.; Jouaiti, A.; Bulach, V.; Planeix, J.-M.; Hosseini, M. W.; Nicoud, J.-F. Molecular tectonics: Design of enantiomerically pure single-stranded helical H-bonded molecular networks. *CrystEngComm* **2003**, *5*, 414–416.
- (22) Jaunky, W.; Hosseini, M. W.; Planeix, J.-M.; De Cian, A.; Kyrtsakas, N.; Fischer, J. Molecular Braids: Quilted Helical Hydrogen Bonded Molecular Network. *Chem. Commun.* **1999**, 2313–2314.
- (23) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. Metric Engineering of Soft Molecular Host Frameworks. *Acc. Chem. Res.* **2001**, *34*, 107–118.
- (24) Hosseini, M. W.; Ruppert, R.; Schaeffer, P.; De Cian, A.; Kyrtsakas, N.; Fischer, J. A molecular Approach to the Solid State Synthesis: Prediction and Synthesis of self-assembled Infinite Rods. *Chem. Commun.* **1994**, 2135–2136. Félix, O.; Hosseini, M. W.; De Cian, A.; Fischer, J. Molecular Tectonics V: Molecular Recognition in the Formation of Molecular Networks Based on Hydrogen Bonding and Electrostatic Interactions. *Tetrahedron Lett.* **1997**, *38*, 1933–1936. Félix, O.; Hosseini, M. W.; De Cian, A.; Fischer, J. Molecular Tectonics IV: Molecular Networks Based on Hydrogen Bonding and Electrostatic Interactions. *Tetrahedron Lett.* **1997**, *38*, 1755–1758.
- (25) Hosseini, M. W.; Brand, G.; Schaeffer, P.; Ruppert, R.; De Cian, A.; Fischer, J. A molecular Approach to Solid Structures II: Prediction and Synthesis of Sheets Through Assembly of Complementary Molecular Units. *Tetrahedron Lett.* **1996**, *37*, 1405–1408. Félix, O.; Hosseini, M. W.; De Cian, A.; Fischer, J. Molecular Tectonics III: The Simultaneous Use of H–Bonding and Charge–Charge Interactions For the Self-Assembly of Fumaric Acid and Cyclic Bisamidinium Into One- and Two- Dimensional Molecular Networks. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 102–104. Félix, O.; Hosseini, M. W.; De Cian, A.; Fischer, J. Crystal engineering of 2-D hydrogen bonded molecular networks based on the self-assembly of anionic and cationic modules. *Chem. Commun.* **2000**, 281–282.
- (26) Félix, O.; Hosseini, M. W.; De Cian, A.; Fischer, J. A Molecular Approach to Organic Solids: Synthesis of Phenyl Di- and Tri-Carboxamidines. *New J. Chem.* **1997**, *21*, 285–288.
- (27) Ferlay, S.; Félix, O.; Hosseini, M. W.; Planeix, J.-M.; Kyrtsakas, N. Second sphere supramolecular chirality: racemic hybrid H-bonded 2-D molecular networks. *Chem. Commun.* **2002**, 702–703. Ferlay, S.; Hosseini, M. W. Crystalline Molecular Alloys. *Chem. Commun.* **2004**, 787–788.
- (28) Ferlay, S.; Bulach, V.; Félix, O.; W. Hosseini, M.; Planeix' J.-M.; Kyrtsakas, N. Molecular tectonics and supramolecular chirality: rational design of hybrid 1-D and 2-D H-bonded molecular networks based on bisamidinium dication and metal cyanide anions. *CrystEngComm* **2002**, *4*, 447–453.
- (29) Lewis, G. R.; Orpen, A. G. A Metal Containing synthon for crystal engineering: synthesis of the hydrogen bond ribbon polymer [4,4'-H<sub>2</sub>bipy] [MCl<sub>4</sub>] (M = Pd, Pt). *Chem. Commun.* **1998**, 1873–1874.
- (30) Batten, S. R.; Robson, R. Interpenetrating Nets: Ordered Periodic Entanglement. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. Inorganic Crystal Engineering using Self-Assembly of Tailored Building-Blocks. *Coord. Chem. Rev.* **1999**, *183*, 117–138. Hosseini, M. W. An Approach to the Crystal Engineering of Coordination Networks. In *Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., Grepioni, F., Orpen, G., Serie c, Eds.; NATO ASI Series 538; Kluwer: Dordrecht, Netherlands, 1999; pp 181–208. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. Modular Chemistry: Secondary Building Blocks as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **2001**, *34*, 319–330. Moulton, B.; Zaworotko, M. J. From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids. *Chem. Rev.* **2001**, *101*, 1629–1658.
- (31) Akdas, H.; Graf, E.; Hosseini, M. W.; De Cian, A.; Harrowfield, J. McB. Design, synthesis and structural investigation of a 2-D coordination network based on the self-assembly of the tetracarboxylate derivative of tetrakis[4]arene and silver cation. *Chem. Commun.* **2000**, 2219–2220. Zimmer, B.; Bulach, V.; Hosseini, M. W.; De Cian, A.; Kyrtsakas, N. 1- and 2-D coordination networks based on porphyrin and copper: an example of supramolecular isomerism. *Eur. J. Inorg. Chem.* **2002**, 3079–3082. Grosshans, P.; Jouaiti, A.; Hosseini, M. W.; Kyrtsakas, N. Gradual increase in the dimensionality of cobalt and mercury coordination networks based on conformation of tetradentate tectons. *New J. Chem.* **2003**, *27*, 793–797.
- (32) Klein, C.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. Design and structural analysis of interpenetrated 3-D coordination networks by self-assembly processes using tetrapyridinocyclophane and silver cations. *New J. Chem.* **2001**, *25*, 207–209. Ferlay, S.; Koenig, S.; Hosseini, M. W.; Pansanel, J.; De Cian, A.; Kyrtsakas, N. Design of 3-D coordination networks: topology and metrics. *Chem. Commun.* **2002**, 218–219.
- (33) Klein, C.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. Metallatubulane: Synthesis and Structural Analysis of an Infinite Tubular Coordination Network Formed by the Self-Assembly of a Tetracyanocyclophane and Silver Cations. *Chem. Commun.* **2000**, 239–240.
- (34) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. Towards the Construction of Functional Solid-State Supramolecular Metal Complexes Containing Cooper(I) and Silver (I). *Adv. Inorg. Chem.* **1999**, *46*, 173–303.
- (35) Schmaltz, B.; Jouaiti, A.; Hosseini, M. W.; De Cian, A. Double stranded interwound infinite linear silver coordination network. *Chem. Commun.* **2001**, 1242–1243.
- (36) Jouaiti, A.; Hosseini, M. W.; Kyrtsakas, N. Molecular tectonics: infinite cationic double stranded helical coordination networks. *Chem. Commun.* **2003**, 473–474.
- (37) Grosshans, P.; Jouaiti, A.; Bulach, V.; Planeix, J.-M.; Hosseini, M. W.; Nicoud, J.-F. Molecular tectonics: from enantiomerically pure sugars to enantiomerically pure triple stranded helical coordination network. *Chem. Commun.* **2003**, 1336–1337.
- (38) Grosshans, P.; Jouaiti, A.; Bulach, V.; Planeix, J.-M.; Hosseini, M. W.; Nicoud, J.-F. Molecular tectonics: Design and structural analysis of enantiomerically pure tectons and helical coordination networks. *C. R. Chim.* **2004**, *7*, 189–196.
- (39) Kaes, C.; Hosseini, M. W.; Rickard, C. E. F.; Skelton, B. W.; White, A. H. Synthesis and Structural Analysis of a Helical Coordination Polymer Formed by the Self-assembly of a 2,2'-bipyridine based Exoditopic Macrocyclic Ligand and Silver Cations. *Angew. Chem., Int. Ed.* **1998**, *37*, 920–922.
- (40) Jouaiti, A.; Hosseini, M. W.; De Cian, A. Design, synthesis and structural investigation of a 1-D directional coordination network based on the self-assembly of an unsymmetrical mono-tridentate ligand and cobalt cation. *Chem. Commun.* **2000**, 1863–1864.
- (41) Jouaiti, A.; Hosseini, M. W.; Kyrtsakas, N. Noncentrosymmetric packing of 1-D coordination networks based on chirality. *Chem. Commun.* **2002**, 1898–1899.
- (42) Gavezzotti, A. Are Crystal Structures Predictable? *Acc. Chem. Res.* **1994**, *27*, 309–314.
- (43) Dunitz, J. D. Are crystal structures predictable? *Chem. Commun.* **2003**, 545–548.
- (44) Henry, M.; Hosseini, M. W. Molecular tectonics: geometry and energy based analysis of coordination networks. *New J. Chem.* **2004**, *28*, 897–906.