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Molecular tectonics: from molecular recognition of anions to molecular networks

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Contents

Abstract

One may apply concepts developed in the context of molecular recognition of anions by synthetic receptors in solution to the design of molecular tectons capable of generating molecular networks with anionic species in the crystalline phase. With respect to that, bis-cyclic amidinium dications are interesting tectons because they offer two positive charges allowing strong electrostatic charge–charge interactions with anions and four acidic protons divergently oriented and capable of forming two sets of two H-bond chelates. The latter characteristic is of interest for the generation of supramolecular chirality taking place within the second coordination sphere around anionic metal complexes adopting an octahedral coordination geometry.
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Keywords: Recognition; Anion; Amidinium; Supramolecular; Network; Chirality; Tecton

1. Introduction

Crystals are defined by the chemical nature of their molecular components and their interactions with respect to each other in the solid state. Whereas molecular chemistry deals with the design and the synthesis of individual units composing the crystal, their assembly through intermolecular interactions is governed by concepts developed in the area of supramolecular chemistry [1].

Although single crystals are formed by translation of the unit cell into all three directions of space, nevertheless, by analysing more deeply the intermolecular interactions and geometrical motives within a crystalline material one may spot some particular recognition pattern leading to molecular networks. In marked contrast with discrete molecules, molecular networks which posses translational symmetry, are defined as chemical assemblies for which specific interaction patterns or assembling cores are repeated through space. In other terms, the assembling core which is based on

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molecular recognition processes between the components composing the crystal, become structural nodes of the network. The dimensionality of a molecular network depends on the number of translations operating at the level of the assembling cores. Thus, 1-D or α-networks are formed when a single translation takes place. Similarly, β- (2-D) and γ-networks (3-D) are defined when two or three translations, respectively of the same or different assembling cores are present (Fig. 1) [2]. Although, in principle molecular networks may be obtained in any type of media such as solution, gel or solid state, the crystalline phase has been extensively used because it allows accurate structural studies using X-ray diffraction techniques on single crystal.

Molecular tectonics [3] is an approach dealing with the design and formation, under self-assembly conditions [4], of molecular networks using structurally defined and energetically programmed molecular tectons. A tecton is an active molecular construction unit or building block bearing recognition sites [5]. Thus, molecular networks may be seen as molecular assemblies formed between complementary molecular tectons capable of mutual interactions through one or several recognition patterns or assembling cores [6].

For a decade now, the design and formation of molecular networks in the crystalline phase has been a subject of intense investigation [7–11]. Owing to our limited knowledge of all subtle intermolecular interactions governing the formation of the crystalline phases, a complete understanding of the packing of molecular entities is currently unreachable [12]. However, with our current ability to master some of the intermolecular interactions, by using proper molecular tectons, one may design molecular networks with predicted structures. Dealing with energetic aspects of the recognition pattern, in principle, any type of reversible intermolecular interactions may be used.

2. From molecular recognition to molecular networks

The construction of molecular networks in the crystalline phase may be achieved through self-assembly processes engaging either a self-complementary or several complementary tectons (Fig. 2). Although the simplest design would be based on a mono component system composed of a unique self-complementary tecton bearing properly located and oriented complementary interaction sites, in practice often such a system produces insoluble powders difficult to be structurally characterised. A more viable strategy may be based on the use of a poly component system composed of several complementary tectons. For poly component systems, both thermodynamic and kinetic parameters leading to the formation of the crystalline material may be monitored, and thus, the structure of the network may be investigated in some cases by X-ray crystallography. However, when increasing the number of components, the formation of molecular networks with predicted connectivity and dimensionality requires a rather strict design of the tectons.

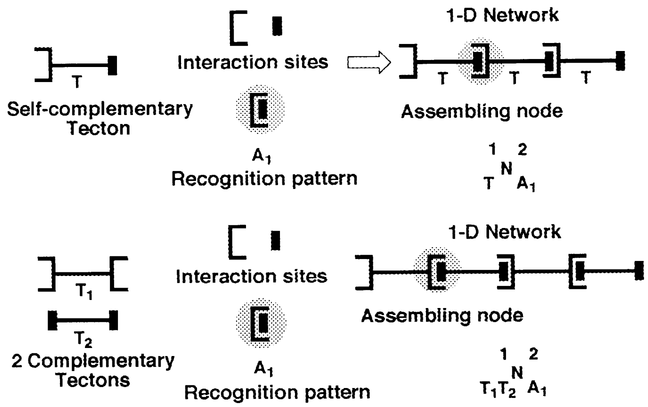


Fig. 2. Schematic representations of 1-D molecular networks based on a single self-complementary tecton (top) and on two complementary tectons (bottom).

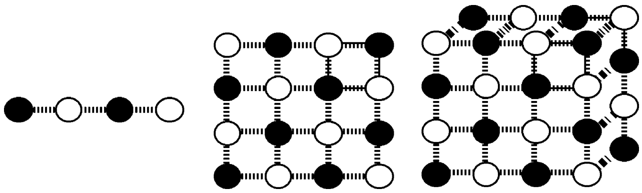


Fig. 1. Schematic representation of 1- (left), 2- (middle) and 3-D (right) networks formed upon translation of recognition patterns into 1, 2 and 3 directions of space, respectively.

Dealing with energetic aspects of the recognition pattern, although in principle, any type of reversible intermolecular interactions may be used, the majority of molecular networks reported so far are either based on hydrogen bonding [13–19] or on coordination bonds [20–24]. Recently, it was also demonstrated that inclusion processes based on van der Waals interactions may be used as a design principle for the construction of inclusion molecular networks in the solid state [25].

In the present contribution, we shall give a short and nonexhaustive review mainly focused on the design and formation of molecular networks engaging anionic tectons.

Anions are in principle H-bond acceptors. Thus, it seems obvious to use H-bonding for the design of molecular networks engaging anionic entities. Many examples of anion receptor molecules of the polyammonium or polyguanidinium types capable of recognising anions through H-bonding and electrostatic interactions were reported some two decades ago [26–29].

Dealing with hydrogen bonding, using a monohapto (DH···A) mode of interaction, *i.e.* a single hydrogen bond between a donor (D) and an acceptor (A), due to

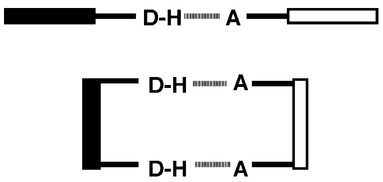


Fig. 3. Schematic representation of H-bonding between a donor and an acceptor in monohapto (top) and dihapto (bottom) mode.

the large angular (DHA) distribution [30], it seems difficult to control and thus to predict the overall topology of the molecular network. However, by restricting the number of possible geometrical arrangements through the use of di- or tri-hapto mode of H-bonding, one may control, to a certain extent, and thus predict the connectivity pattern between tectons in molecular networks (Fig. 3). This design principle is widely used in nature. Indeed, the dihapto mode of interactions between aminoacids such as arginine and aspartate residues in proteins or di- and tri-hapto modes of H-bonding between nucleic acids in DNA and RNA are common features of the biological world.

3. Molecular networks based on recognition of carboxylates anions

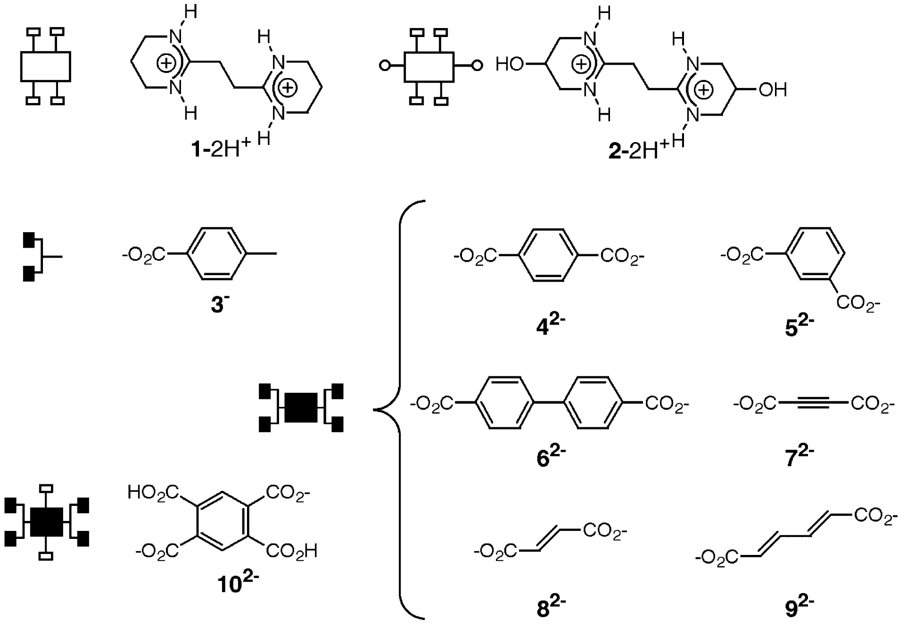
Although the majority of reported molecular networks are mainly based on nonionic hydrogen bonds [13–19,31], the simultaneous use of directional hydrogen bonds and strong but less directional ionic interactions has been also reported [32–51].

Bis-amidinium dications such as **1**-$2H^+$ and **2**-$2H^+$ (Scheme 1) are interesting building blocks for the design of hydrogen bonded molecular networks engaging carboxylate anions [39–49]. Indeed, the **1**-$2H^+$ and **2**-$2H^+$ dications, due to the presence of four acidic N–H protons oriented in a divergent fashion, may act as a tetra- and hexa-H-bond donors, respectively. Furthermore, due to the proper spacing of the two cyclic amidinium moieties ($(CH_2)_2$), compounds **1**-$2H^+$ and **2**-$2H^+$ interact with two carboxylate units by a dihapto mode of recognition on each side of the module (Fig. 4a).

Indeed, it has been demonstrated that in the presence of the mono carboxylate anion $\mathbf{3}^-$, acting as stopper, **1**-$2H^+$ forms a discrete exobinuclear complex (Fig. 5) [43].

3.1. 1-D molecular networks

As may be expected from the observations mentioned above, when using dicarboxylate dianions such as $\mathbf{4}^{2-}$–$\mathbf{9}^{2-}$ acting as connecting tectons, the same dicationic compound **1**-$2H^+$ leads to 1-D H-bonded molecular networks (Fig. 4b). All networks presented have been observed in the crystalline phase by X-ray diffraction methods on single crystals (Fig. 6). In all cases, the common features of the networks are: the neutral 1-D H-bonded networks are formed through the mutual interconnection of dicationic and dianionic tectons. The dicationic tecton **1**-$2H^+$ adopts a centrosymmetric conformation. Both six-member cycles adopt a half-chair conformation. The ethylene chain connecting the two cyclic amidinium units are in trans conformation and fully extended. The two planes containing the amidinium groups are parallel but not coplanar. All four acidic protons are localised on **1**. The N–N distance between two nitrogen atoms located on the



Scheme 1.

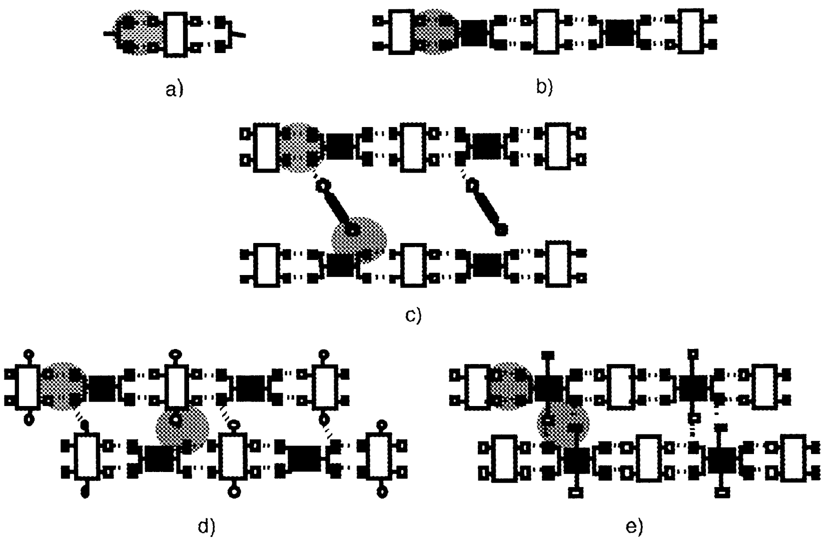


Fig. 4. Schematic representation of a discrete neutral exo-binuclear complex (a), neutral 1-D network formed between the dicationic and dianionic tectons through dihapto mode of H-bonding (b), and of 2-D networks based on interconnection of neutral 1-D networks by a third neutral tecton (c), or interconnection of neutral 1-D networks by extra H-donor sites located on dicationic tectons (d), or interconnection of neutral 1-D networks by extra H-donor sites located on dianionic tectons (e). The grey circles represent the assembling cores which by translation generate the molecular networks.

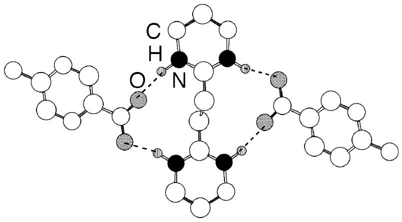


Fig. 5. X-ray structure of (**1**-2H$^+$, 2 × **3**$^-$) complex. For the sake of clarity only hydrogen atoms involved in H-bonding are represented.

same face of the tecton is around 5 Å thus allowing the recognition of carboxylate groups through a strong dihapto mode of H-bonding with an average N···O distance of ca. 2.8 Å. The recognition by the dication **1**-2H$^+$ of the carboxylate moieties of the dianionic tecton takes place on each side of the tecton. The recognition pattern defining the assembling core is translated into one direction of space leading thus to a 1-D network.

3.2. 2-D molecular networks

The enhancement of the dimensionality of the above mentioned network from 1- to 2-D, requires the interconnection of the 1-D networks. This may be achieved using different design strategies. The most obvious one consists in increasing the number of components (Fig. 4c). This has been indeed achieved using a three components system based on the dication **1**-2H$^+$, fumarate dianion **8**$^{2-}$ and fumaric acid **8**-2H$^+$ (Fig. 7a) [44].

As shown above, the 1/1 co-crystals formed between **1**-2H$^+$ and **8**$^{2-}$ dianion were exclusively composed of 1-D networks. However, when 1 equivalent of the free amidine **1** was allowed to react with 2 equivalents of fumaric acid **8**-2H$^+$, the co-crystals formed were composed of 2-D networks.

The simultaneous presence of fumarate **8**$^{2-}$ and fumaric acid **8**-2H$^+$ may be explained in terms of differences in the pK_a values between **1** and fumaric acid **8**-2H$^+$. Indeed, **1** and **8**-2H$^+$ being a di-base and a di-acid, respectively, upon transfer of two protons from the acid to the base, the bis-amidinium **1**-2H$^+$ and the dianionic **8**$^{2-}$ are generated. Since a twofold excess of fumaric acid **8**-2H$^+$ was used, the excess of acid remains unchanged and thus may participate to the formation of 2-D network as a ditopic H-bond donor. The 2-D network may be described as the interconnection of 1-D networks composed of dicationic and dianionic tectons by fumaric acid molecules. The 1-D network is analogous to the one obtained for the 1/1 ratio of **1**-2H$^+$ and **8**$^{2-}$ described above. The assembling core leading to the 1-D network by translation is of the same type as the one observed for the 1/1 co-crystals. Whereas, the conformation of both components **1**-2H$^+$ and **8**$^{2-}$ are almost identical to the one obtained for the 1/1 co-crystal, the hydrogen-bonding pattern connecting the cationic and anionic units and thus defining the assembling core was less symmetrical in the case of 1/2 co-crystals. The interconnection of 1-D networks is ensured by a second assembling core based on strong H-bonds between fumarate dianions **8**$^{2-}$ and fumaric acid **8**-2H$^+$. The 2-D network thus obtained may be described either as neutral 1-D networks composed of **1**-2H$^+$ and **8**$^{2-}$ tectons interconnected by neutral fumaric acids **8**-2H$^+$, or as anionic 1-D networks, based on

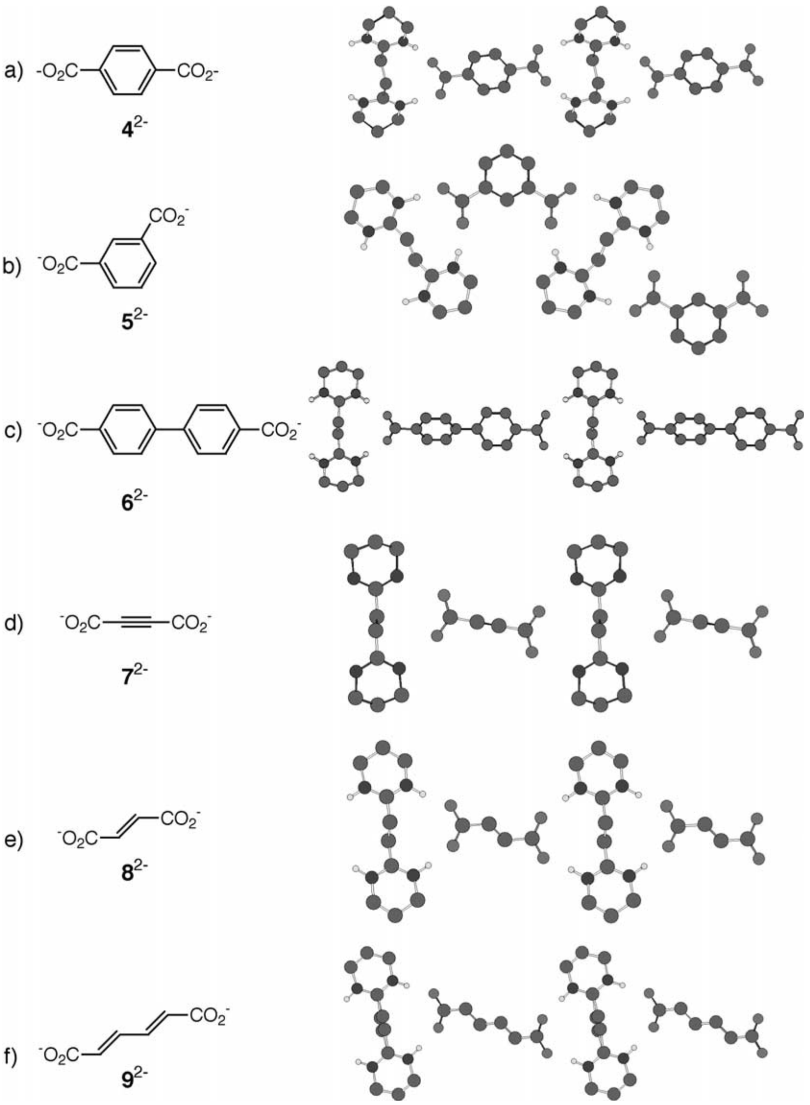


Fig. 6. Portions of X-ray structure of the α-networks formed between **1**-2H$^+$ and dicarboxylate dianions **4**$^{2-}$–**9**$^{2-}$. For the sake of clarity all other hydrogen atoms expect those involved in H-bonding are not represented.

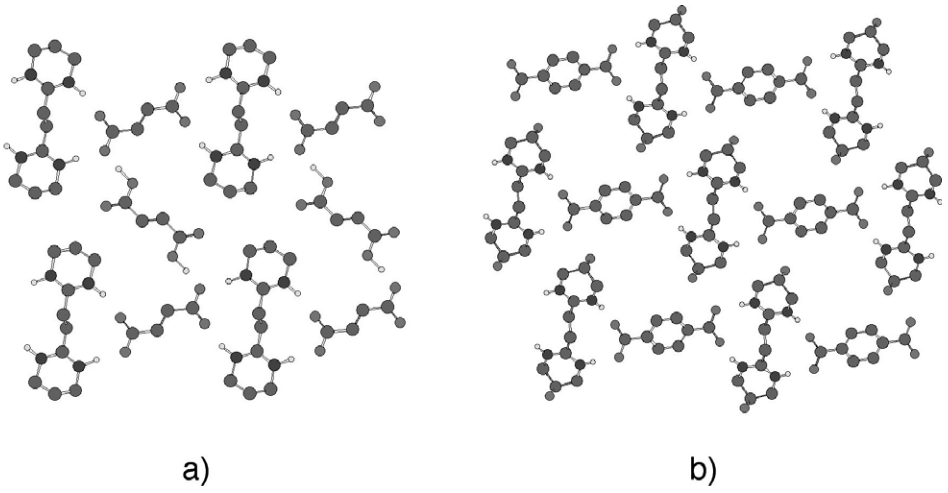


Fig. 7. Portions of the X-ray structure of 2-D networks formed between **1**-2H$^+$, fumarate **8**$^{2-}$ and fumaric acid **8**-2H$^+$ (a) and **2**-2H$^+$ and **4**$^{2-}$ (b). For the sake of clarity all other hydrogen atoms expect those involved in H-bonding are not represented.

hydrogen bonding between fumarate **8**$^{2-}$ and fumaric acids **8**-2H^{+}, interconnected by the dicationic **1**-2H^{+} units.

While using a two-component system based on dicationic and dianionic tectons, another possibility to generate 2-D networks may be based on the increase in the number of interaction sites (H-bond donors) from four to six within the dicationic tecton (Fig. 4d). This has been also achieved using the dicationic tecton **2**-2H^{+} and terephthalate dianion **4**$^{2-}$ (Fig. 7b) [46]. The neutral 2-D network obtained is exclusively composed of **2**-2H^{+} and **4**$^{2-}$ and formed through mutual interconnection of cationic and anionic tectons. Again, as in the case of **1**-2H^{+}, in the centrosymmetric **2**-2H^{+} unit, because of the fully extended trans conformation of the ethylene chains, the two planes containing the amidinium groups are almost parallel but not coplanar. The two six-member cycles adopt a half-chair conformation with the OH groups in axial positions. Again, all four acidic protons are localised on **2** allowing the recognition of carboxylate groups through a dihapto mode of H-bonding. The 2-D network may be described as the interconnection of neutral 1-D network, formed by a dihapto mode of H-bonding between **2**-2H^{+} dication and **4**$^{2-}$ dianions, through strong H-bonds between the OH groups and carboxylate moieties.

A further possibility, while using the dicationic tecton **1**-2H^{+}, may be based on the enhancement of the number of interaction sites within the dianionic tecton (Fig. 4e). This strategy was probed using pyromellitic acid **10**. The latter offers the following interesting features: depending on the number of deprotonated carboxylic units, compound **10** may behave as mono-, di-, tri- or even tetra-anionic tecton in the solid state [52]. Due to the rather strong basicity (pK_a over 10) of the tecton **1**, the equimolar mixture of **1** and **10** leads to a double proton transfer process from the tetra-acid **10** to the di-base **1** leading thus to (**1**-2H^{+}, **10**$^{2-}$) salt. Depending on the location of the two carboxylates moieties with respect to carboxylic units (Fig. 8), **10**$^{2-}$ may behave as an analogue of orthophthalate dianion (the two CO_2^- units located at 1 and 2 positions), or as an analogue of terephthalate dianion **4**$^{2-}$ (the two CO_2^- units located at 1 and 4 positions) or finally as an analogue of isophthalate dianion **5**$^{2-}$ (the two CO_2^- units located at 1 and 3 positions).

The formation of 2-D H-bonded molecular networks based on the use of **1**-2H^{+} and **10**$^{2-}$ was demonstrated by X-ray diffraction on a single-crystal (Fig. 9) [48]. The co-crystal is exclusively composed of **1** and **10** units. All four acidic protons are localised on **1** thus leading to the dicationic tecton **1**-2H^{+}. The recognition by the dication **1**-2H^{+} of the carboxylate moieties of the dianionic tecton **10**$^{2-}$ takes place on each side of the tecton through two strong H-bonds. The latter recognition pattern defines one of the two assembling cores. The dianion **10**$^{2-}$ behaves as an analogue of terephthalate, with the two carboxylate moieties located at positions 1 and 4 of the aromatic ring. The dicationic **1**-2H^{+} and dianionic **10**$^{2-}$ tectons form a neutral 1-D network through a single translation of the assembling core defined by the recognition pattern between the carboxylate moiety of **10**$^{2-}$ and two NH^{+} hydrogen bond donor sites of **1**-2H^{+} (Fig. 9 (left)). These 1-D networks are further interconnected into a 2-D network (Fig. 9 (right)) through another mode of hydrogen bonding of the type OH···O^{-} between the two carboxylic groups and carboxylates moieties of **10**$^{2-}$ already engaged in H-bonds with the amidinium units. The latter recognition pattern leads to the second assembling core. As in the case of co-crystals of **1**-2H^{+} and fumarate **8**$^{2-}$ and fumaric acid **8**-2H^{+}, the 2-D network may either be regarded as neutral 1-D networks, formed between the cationic and anionic tectons, interconnected through the second assembling core by formation of OH···O^{-} H-bonds or alternatively, as anionic 1-D networks, formed through OH···O^{-} H-bonds between **10**$^{2-}$ tectons, interconnected by the cationic tectons **1**-2H^{+} through strong H-bonds of the type O^{-}···HN^{+}.

Based on tecton **1**-2H^{+}, a further strategy for the formation of 2-D H-bonded molecular network was developed using anionic tectons bearing a sp^{3} centre instead of sp^{2} hybridised carboxylate group. In particular, 2-D networks were obtained using pyrophosphate [42].

4. Design of tectons for metal cyanide complexes

The molecular recognition of anionic transition metal complexes by macrocyclic polyammonium receptor

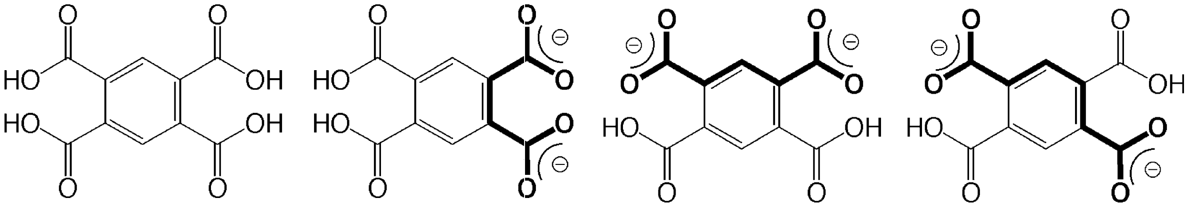


Fig. 8. Different possible locations of two carboxylate groups for the dianion of pyrromellitate **10**$^{2-}$.

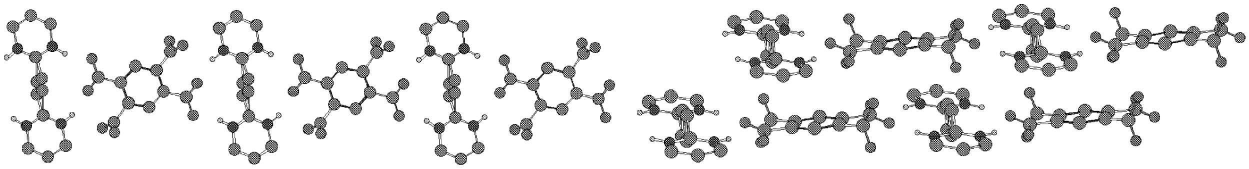
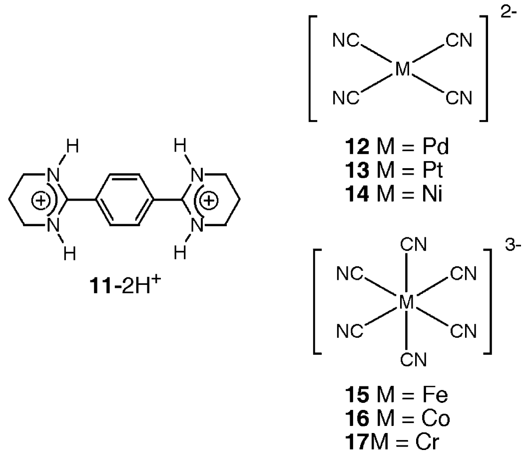


Fig. 9. Portions of the X-ray structure of 2-D networks formed between **1**-2H$^+$, pyrromellitate **10**$^{2-}$. The 2-D networks are obtained upon interconnection of 1-D networks obtained upon mutual H-bonding between the dicationic tecton **1**-2H$^+$ and dianionic tecton **10**$^{2-}$ (left) by carboxylic groups of **10**$^{2-}$ (right). For the sake of clarity, only hydrogen atoms involved in H-bonding are represented.



Scheme 2.

molecules using interactions within the second coordination sphere around the metal centre was demonstrated through the formation of discrete complexes [52–56]. On the other hand, diprotonated 4,4′-bipyridine [57] was used as a H-bond donor unit in the formation of discrete complexes with CoCl_4^{2-} and molecular networks with $[\mathrm{MCl}_4]^{2-}$ (M = Pd, Pt, Mn, Cd) [58–61]. Based on 4,4′-bis-piperidinium derivatives [62], the same strategy was also applied for the generation of infinite networks using $[\mathrm{PtCl}_4]^{2-}$.

The bis-amidinium **11**-2H$^+$ (Scheme 2) is an analogue of tectons **1**-2H$^+$ and **2**-2H$^+$ and should lead to the formation of H-bonded molecular networks based on both strong electrostatic charge–charge interaction and strong and directional hydrogen bonds. The tecton **11**-2H$^+$, a tetra-H-bond donor dicationic unit bearing four acidic divergently oriented protons forming two sets of two H-bond donors and located on both sides of the tecton was designed for the generation of H-bonded in the presence of metal tetra- and hexa-cyanides. Dealing with the localisation of the protons, owing the difference in pK_a values between $[\mathrm{M(CN)}_4]^{2-}$ or $[\mathrm{M(CN)}_6]^{n-}$ anions and unprotonated **11**, the acidic protons should be localised on the nitrogen atoms of **11**. The connection of the two amidinium units by a phenyl group was motivated by geometrical requirements for the recognition of metal tetra- and hexa-cyanides. Indeed, the use of phenyl group as the spacer reduces the conformational space of the tecton and imposes an appropriate inter amidinium distance for the recognition of metal tetra- and hexacyanides anions. As revealed by an X-ray study [45] on the dichloride salt of **11**-2H$^+$, the 7.01 Å separation between the nitrogen atoms located on the same side of **11**-2H$^+$ is optimum for the binding of square planar $[\mathrm{M(CN)}_4]^{2-}$ and octahedral $[\mathrm{M(CN)}_6]^{n-}$ anions by a dihapto mode of hydrogen bonding.

4.1. A metal tetracyanide

As stated above, **11**-2H$^+$ was designed as a dicationic and complementary tecton for the formation of 1-D H-bonded networks with $\mathrm{M(CN)}_4^{2-}$ (Fig. 10). For a combination of **11**-2H$^+$ and $\mathrm{M(CN)}_4^{2-}$, due to the possibility of obtaining a neutral network, one would expect a 1/1 stoichiometry and the formation of a 1-D network. In other terms, for such a network each dication **11**-2H$^+$ should be surrounded by two dianions and conversely, each dianion $\mathrm{M(CN)}_4^{2-}$ should be in interactions with two dications through a dihapto mode of H-bonding.

The predicted networks were indeed observed for $[\mathrm{Pd(CN)}_4]^{2-}$ (**12**), $[\mathrm{Pt(CN)}_4]^{2-}$ (**13**) and $[\mathrm{Ni(CN)}_4]^{2-}$ (**14**). In all three cases, X-ray diffraction on single crystals (Fig. 11) [51] revealed that the three crystalline materials obtained are isostructural (triclinic system, space group $P\bar{1}$). In all three cases, the crystal was exclusively composed of one dication **11**-2H$^+$ and one dianion $[\mathrm{M(CN)}_4]^{2-}$. The 1-D networks formed through interconnection of dicationic and dianionic tectons by strong H-bonds were packed in a parallel fashion. In all cases, the coordination geometry around the metal in the oxidation state II was a slightly distorted square with CMC angle varying between ca. 88 and 92°. The rather strong nature of the H-bonds formed was evidenced by the N–N average distance of ca. 2.95 Å.

4.2. A metal hexacyanide

Since the distance between CN groups in syn localisation in $[\mathrm{M(CN)}_6]^{3-}$ anions is almost the same as the one in $[\mathrm{M(CN)}_4]^{2-}$, one would expect similar interactions with the dicationic tecton **11**-2H$^+$. However, for charge

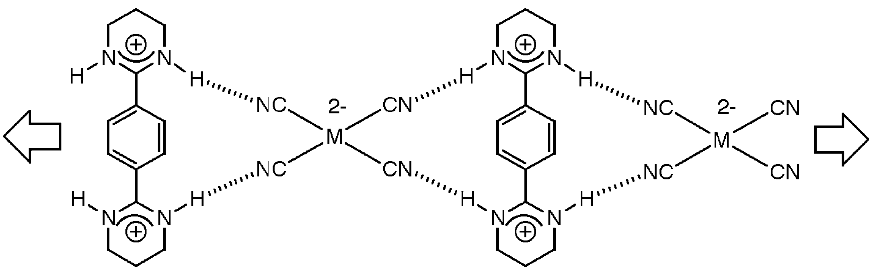


Fig. 10. Representation of a neutral 1-D H-bonded network formed between a square planar $M(CN)_4^{2-}$ dianion and **11**-2H$^+$. The interconnection between the dicationic and dianionic tectons is ensured by strong H-bonds through a dihapto mode of interaction.

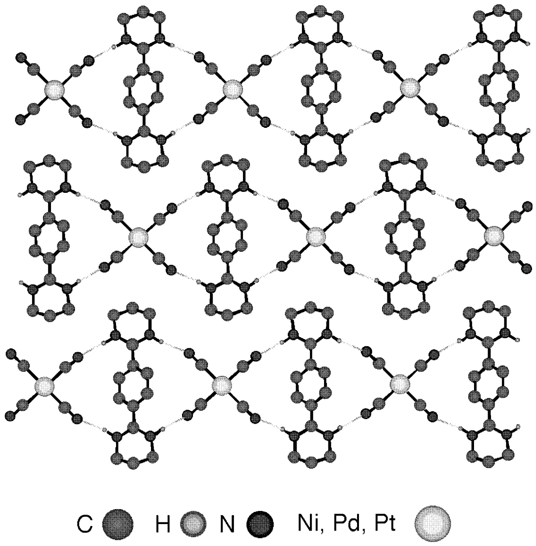


Fig. 11. A portion of the crystal structure of the 1-D network formed between square planar $M(CN)_4^{2-}$ (M = Pd, Pt and Ni) dianion and **11**-2H$^+$. The 1-D networks are packed in a parallel fashion. Only H atoms involved in H-bonds are represented for clarity.

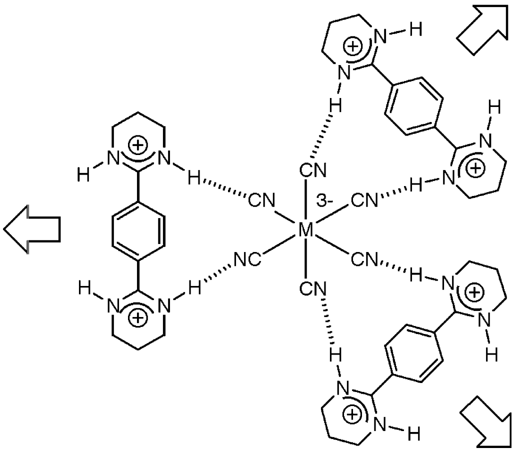


Fig. 12. Representation of a neutral 2-D H-bonded network formed between an octahedral $M(CN)_6^{3-}$ complex and **11**-2H$^+$. The interconnection between the dicationic and dianionic units takes place through strong H-bonds with a dihapto mode of interaction.

neutrality reasons, one may expect a **11**-2H$^+$/$[M(CN)_6]^{3-}$ ratio of 3/2. Furthermore, due to the octahedral geometry around the metal centre, the interconnection of the anionic $[M(CN)_6]^{3-}$ complexes by the cationic unit **11**-2H$^+$ through a dihapto mode of H-bonding, a neutral 2-D network may be expected (Fig. 12).

The 2-D networks were observed by X-ray diffraction studies on a single crystal for $[Fe(CN)_6]^{3-}$ (**15**) [50], $[Co(CN)_6]^{3-}$ (**16**) [50] and $[Cr(CN)_6]^{3-}$ (**17**) [51]. In all three cases, crystals were composed of three dication **11**-2H$^+$ and two dianion $[M(CN)_6]^{3-}$ and water molecules (Fig. 13). The geometrical features of both the organic tecton **11**-2H$^+$ and the anionic complex were almost identical. The 2-D networks are formed by interconnection of dicationic and dianionic units through dihapto mode of H-bonding (N···N distance varying between ca. 2.8 and 3.0 Å) and may be regarded as either $M(CN)_6^{3-}$ tectons interconnected by **11**-2H$^+$ or conversely as **11**-2H$^+$ units interconnected by $M(CN)_6^{3-}$.

The packing of the neutral 2-D networks leads to channels which are filled with seven water molecules in the case of $[M(CN)_6]^{3-}$ (M = Fe and Co) [50] (Fig. 13) and six water molecules in the case of $[Cr(CN)_6]^{3-}$ [51]. The water molecules in all three cases form H-bonded 1-D networks composed of hexagons interconnected by tetragons with an average O···O distance of ca. 2.85 Å.

Due to the dihapto or chelate mode of H-bonding between **11**-2H$^+$ and the octahedral $[M(CN)_6]^{3-}$ anion, a supramolecular chirality taking place within the second coordination sphere around the metal is generated (Fig. 14). By analogy with Δ and Λ type chirality defined for octahedral complexes surrounded by two or three chelating ligands, the supramolecular chirality of the type Δ′ and Λ′ occurring within the second coordination sphere is defined as resulting from non-covalent reversible interactions through a chelate mode of H-bonding between the dicationic **11**-2H$^+$ and octahedral $[M(CN)_6]^{3-}$ complex. Since **11**-2H$^+$ is achiral, both Δ′ and Λ′ enantiomers are present in the 2-D network and the resulting crystal is achiral.

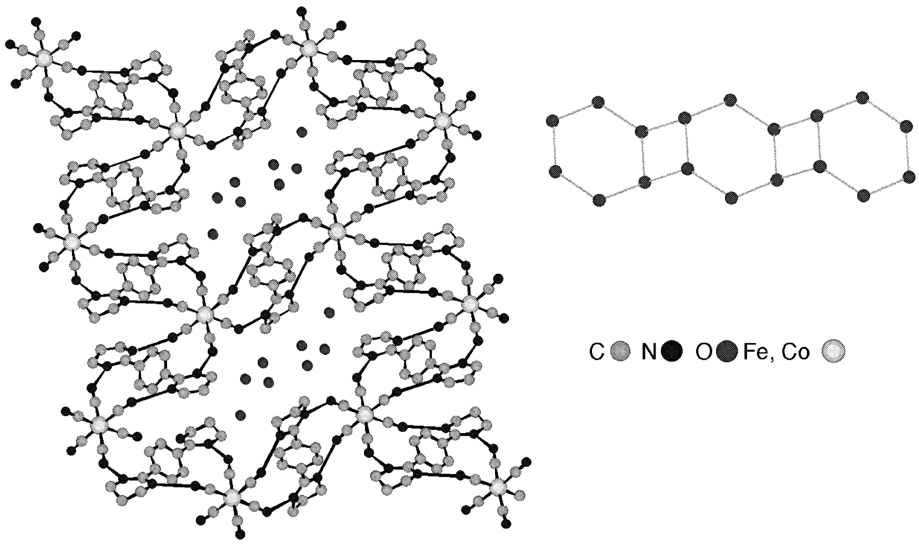


Fig. 13. A portion of the X-ray structure of the 2-D H-bonded network obtained upon self-assembly of **11**-2H$^+$ and Fe(CN)$_6^{3-}$ (**15**) and Co(CN)$_6^{3-}$ (**16**) anions (left) showing the inclusion of water molecules and a view of the H-bonded water polymer (right). Except those involved in H-bonds between **11**-2H$^+$ and M(CN)$_6^{3-}$ anion, other H atoms are omitted for clarity.

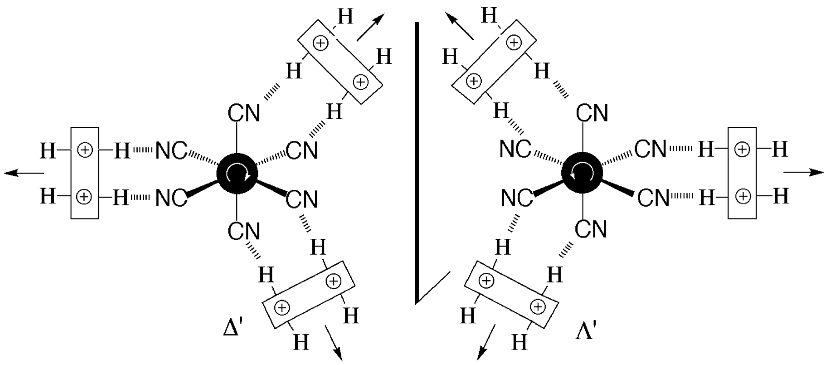


Fig. 14. Schematic representation of the supramolecular chirality of the Δ′ and Λ′ type obtained upon binding within the second coordination sphere of octahedral M(CN)$_6^{3-}$ anion by dicationic tecton **11**-2H$^+$ capable of forming a dihapto or chelate mode of H-bonding.

5. Conclusion

In conclusion, using concepts developed in the field of molecular recognition of anions in solution, cationic molecular tectons capable of forming H-bonded molecular networks in the crystalline phase by iteration of the recognition pattern were designed. The formation of networks with a variety of dicarboxylate dianions was demonstrated in the solid state by X-ray diffraction methods on single crystals. The same design principle was further used for the recognition of metal cyanide complexes and generation of 1-D and 2-D hybrid molecular networks based on both H-bonding and charge–charge electrostatic interactions. Furthermore, taking advantage of the formation of two H-bonds in a dihapto or chelate mode, a supramolecular chirality taking place within the second coordination sphere of metals adopting octahedral coordination was demonstrated. The latter point may be of a wider significance, in particular in the area of chiral transformations and is currently under investigation.

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