

# Crystal engineering of 2-D hydrogen bonded molecular networks based on the self-assembly of anionic and cationic modules†

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Using a self-assembly strategy based on both H-bonding and ionic interactions, a molecular module composed of two cyclic amidinium units and that bears two additional OH groups, thus possessing a total of six H-bond donor sites, was used to engineer 2-D crystalline molecular networks in the presence of carboxylate anions.

Molecular networks, formed in the crystalline phase by the self-assembly<sup>1</sup> of structurally defined and energetically programmed molecular modules,<sup>2</sup> are molecular assemblies possessing translational symmetry of one or several assembling cores.<sup>3</sup> The latter may be regarded as a series of interaction patterns between complementary molecular building blocks comprising the solid. In principle, any type or combination of intermolecular interactions such as H-bond,<sup>4</sup> van der Waals interactions<sup>1</sup> or coordination-bonds<sup>5</sup> may be used to design the assembling core. In the present contribution, we focus on the formation of molecular networks based on H-bonds. The dimensionality of molecular networks (1-, 2- or 3-D) is defined by the number of translations (1, 2, or 3 respectively) of the assembling cores.<sup>3</sup> Although, one dimensional networks have become more commonplace,<sup>4,6</sup> the formation of 2-7 and 3-D-networks<sup>8</sup> is still a matter of active research interest.

Here we report the formation of  $\beta$ -networks using the tecton  $2\text{-}2\text{H}^+$  and mono- ( $3^-$ ) and di-carboxylate ( $4^{2-}$ ) anions.

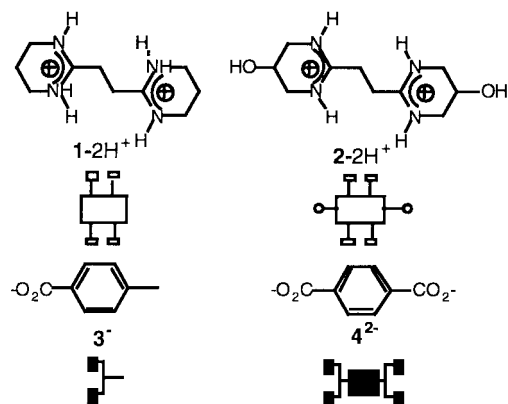
Molecular networks may be generated through self-assembly processes using either a monocomponent system based on a single self complementary module or a polycomponent system composed of several complementary units. Although the former case is ideal in terms of atom economy, in practice, such a system often leads to amorphous powders and thus eludes structural investigations. On the other hand, using polycomponent systems, for which both thermodynamic and kinetic parameters may be monitored, the structure of the network may be investigated by X-ray crystallography in some cases.

Although the majority of reported molecular networks are mainly based on nonionic hydrogen bonding,<sup>3</sup> the simultaneous use of directional hydrogen bonds and strong but less directional ionic interactions has been also reported.<sup>4e,6</sup> It has been

shown that bis-amidinium dications such as  $1\text{-}2\text{H}^+$ <sup>6</sup> (Scheme 1) are interesting building blocks for the crystal engineering of hydrogen bonded molecular networks. Indeed, the  $1\text{-}2\text{H}^+$  dication, owing to the presence of four acidic NH protons oriented in a divergent fashion, acts as a tetra H-bond donor.<sup>6</sup> Furthermore, owing to the appropriate spacing of the two cyclic amidinium moieties by an ethylene spacer, compound  $1\text{-}2\text{H}^+$  was shown to interact with two carboxylate units by a dihapto mode of recognition on each side of the module (Fig. 1). It has been shown that in the presence of the monoanion  $3^-$  acting as stopper,  $1\text{-}2\text{H}^+$  forms a discrete exobinuclear complex [Fig. 1(a)], and in the presence of dicarboxylates, such as iso- or terephthalate  $4^{2-}$  acting as connectors, the same compound leads to 1-D networks [Fig. 1(b)].

The enhancement of the dimensionality of the above mentioned network from 1- to 2-D, requires interconnection of the 1-D networks. This may be achieved using different design strategies. The most obvious one would consist of increasing the number of components. This has indeed been achieved using a three-component system based on the dication  $1\text{-}2\text{H}^+$ , fumarate dianion and fumaric acid.<sup>6d</sup> On the other hand, while using a two-component system, another possibility would be to increase the number of interaction sites within the dianionic module. This may be achieved by using a  $\text{sp}^3$  centre such as in pyrophosphate instead of  $\text{sp}^2$  carboxylate units.<sup>6c</sup> Finally, one may introduce additional H-bond donor sites within the cationic partner [Fig 1(c)].

The design of the bisamidinium  $2\text{-}2\text{H}^+$  is based on a combination of NH and OH groups as H-bond donors. The quadruple H-bond donor module  $1\text{-}2\text{H}^+$  may be transformed into a sextuple H-bond donor  $2\text{-}2\text{H}^+$  by introduction of two OH groups within its framework. Owing to the half-chair conformation adopted by both cyclic amidinium moieties, the OH group, by virtue of its axial positioning should be oriented below and above the main plane of the module and thus should allow the interconnection of consecutive 1-D networks through strong  $\text{OH}\cdots\text{O}^-$  hydrogen bonds. The synthesis of **2** was achieved following the reported procedure for the bisamidine **1**.<sup>9</sup> 1,3-Diamino-2-hydroxypropane was first transformed into its



Scheme 1

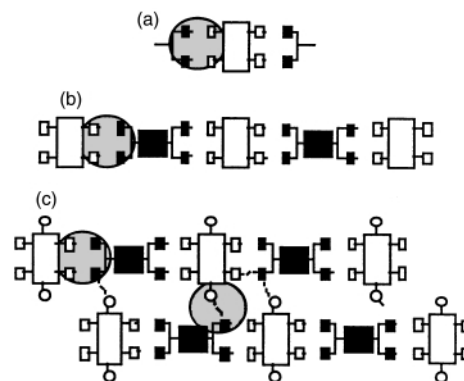
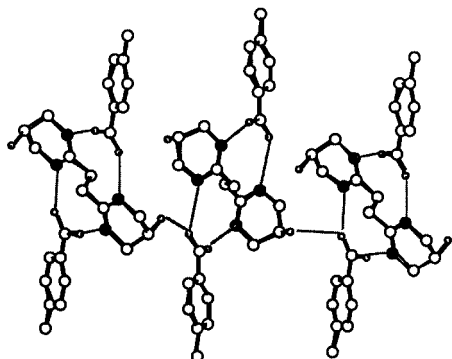


Fig. 1 Schematic representation of a discrete exo-binuclear complex (a), 1-D molecular network (b) based on the translation of a single assembling core (grey circle), and of a 2-D network based on the translation of two different assembling cores in two different spatial directions (c).

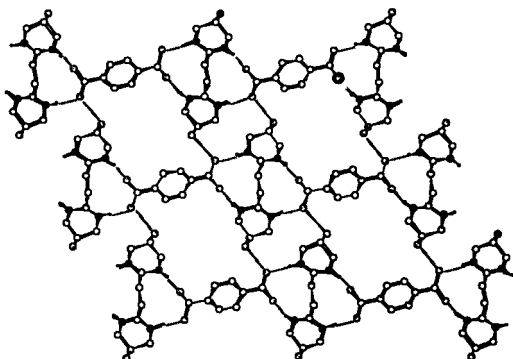
† Dedicated to the memory of Professor Olivier Kahn.

mono tosylate salt before it was treated with 0.5 equiv. of succinonitrile under argon for 1 h at 140 °C. Pure 2-2TsOH was isolated as a white crystalline solid in 78% yield upon crystallisation from EtOH–H<sub>2</sub>O.

Using the module 2-2H<sup>+</sup>, the formation of molecular networks in the crystalline phase was investigated using toluate 3<sup>-</sup> (Fig. 2) as well as terephthalate dianions 4<sup>2-</sup> (Fig. 3).



**Fig. 2** A portion of the X-ray structure of (2-2H<sup>+</sup>, 23<sup>-</sup>) co-crystals showing the formation of a 1-D network. In fact the co-crystal shows a 2-D network formed by H-bonds engaging the remaining OH groups.



**Fig. 3** A portion of the X-ray structure of (2-2H<sup>+</sup>, 4<sup>2-</sup>) co-crystals showing the formation of a 2-D hydrogen bonded network that is formed by the interconnection of 1-D networks formed by the amidinium and carboxylate moieties, through strong OH...O<sup>-</sup> hydrogen bonds.

Upon mixing the free base **2** with 2 equiv. of toluic acid or 1 equiv. terephthalic acid in EtOH, colourless single crystals were obtained. The formation of molecular networks in the above mentioned co-crystals was investigated by X-ray crystallography which revealed the following common features for both structures (Fig. 2 and 3)‡: (i) for the centrosymmetric 2-2H<sup>+</sup> unit, owing to the fully extended *trans* conformation of the ethylene chains, the two planes containing the amidinium groups are almost parallel but not coplanar; (ii) both six-member cycles adopt a half-chair conformation with the OH groups in axial positions, (iii) all four acidic protons are localised on **2** with an average N–H distance of ca. 1.01 Å; (iv) the N1...N3 and N2...N4 average distance is, as for 1-2H<sup>+</sup>,<sup>6a</sup>, close to 5.0 Å, thus allowing the recognition of carboxylate groups through a dihapto mode of H-bonding (Fig. 2); (v) the recognition of two carboxylate moieties by the dication 2-2H<sup>+</sup>, as for 1-2H<sup>+</sup>,<sup>6a</sup> takes place in a symmetric mode on each side of the module through two strong H-bonds with an average N...O distance of ca. 2.72 Å an NH...O distance of ca. 1.72 Å and an average N–H...O angle value of ca. 172°.

Interestingly, whereas for (1-2H<sup>+</sup>, 23<sup>-</sup>) co-crystals a 0-D solid composed of discrete units without any specific interactions between them was obtained<sup>10</sup> [Fig. 1(a)], for the (2-2H<sup>+</sup>, 23<sup>-</sup>) salt, owing to the presence of the OH groups, the neutral complexes are interconnected into a β-network through strong H-bonds of the OH...O type (average *d*<sub>OH...O</sub> distance of ca. 2.64

Å) between the hydroxy moieties of **2** and carboxylate extremities of the anion 3<sup>-</sup> (Fig. 3).

For the (2-2H<sup>+</sup>, 4<sup>2-</sup>) co-crystals, as predicted and previously observed for the amidinium 1-2H<sup>+</sup>,<sup>6a</sup> case, a 1-D network exclusively composed of 2-2H<sup>+</sup> dication and 4<sup>2-</sup> (Fig. 3) dianions interconnected through strong H-bonds was observed in the solid state. However, as for the (2-2H<sup>+</sup>, 23<sup>-</sup>) salt, for (2-2H<sup>+</sup>, 4<sup>2-</sup>) cocrystals, owing to the presence of the additional OH groups, the above mentioned 1-D networks were interconnected into a 2-D network through strong OH...O bonds with an average *d*<sub>OH...O</sub> distance of ca. 2.71 Å.

In conclusion, the dicationic molecular module 2-2H<sup>+</sup> that bears both NH and OH groups and is capable of acting as a sextuple H-bond donor was designed and synthesised. The module 2-2H<sup>+</sup>, which is capable of specifically recognising two carboxylate units through strong H-bonds and ionic interactions, was assembled into 2-D networks using the additional hydrogen bond donor OH sites to interconnect 1-D networks formed between the amidinium dications and dicarboxylates in the crystalline phase. The extension of concepts discussed above for the design of 3-D networks is currently in progress.

## Notes and references

‡ *Crystal data*: for (2-2H<sup>+</sup>, 23<sup>-</sup>): data were collected on a MACH3 Nonius diffractometer at 294 K using colorless crystals (0.30 × 0.20 × 0.10 mm). C<sub>10</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>·2C<sub>8</sub>H<sub>7</sub>O<sub>2</sub>, *M* = 498.58, triclinic, space group *P*1̄, *a* = 6.0754(6), *b* = 14.989(1), *c* = 14.979(1) Å, α = 68.09(2), β = 89.34(2), γ = 87.19(2)°, *U* = 1264.0(2) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 1.16 g cm<sup>-3</sup>, Mo-Kα graphite monochromated radiation, μ = 0.075 mm<sup>-1</sup>, *R*(*F*) = 0.071 using 1405 reflections with *I* > 3σ(*I*).

For (2-2H<sup>+</sup>, 4<sup>2-</sup>): data were collected on a Kappa CCD diffractometer at 173 K using colorless crystals (0.26 × 0.10 × 0.10 mm). C<sub>10</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>·C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>, *M* = 392.42, triclinic, space group *P*1̄, *a* = 5.0376(2), *b* = 9.5318(5), *c* = 10.5146(5) Å, α = 68.186(9), β = 81.393(9), γ = 75.452(9)°, *U* = 452.81(1) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 1.44 g cm<sup>-3</sup>, Mo-Kα graphite monochromated radiation, μ = 0.102 mm<sup>-1</sup>, *R*(*F*) = 0.048 using 1615 reflections with *I* > 3σ(*I*).

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