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Charge assisted chiral hybrid H-bonded molecular networks†

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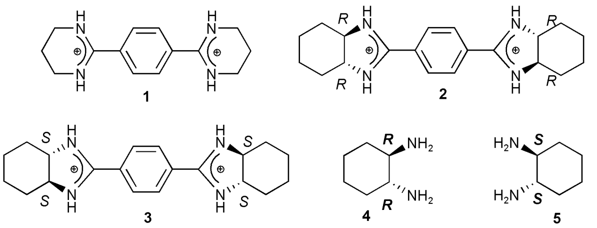
The co-crystallisation of $[Fe(CN)_5NO]^{2-}$ and cyclic achiral $\mathbf{1}^{2+}$ and chiral $\mathbf{2}^{2+}$ or $\mathbf{3}^{2+}$ bisamidinium tectons leads in the crystalline phase to the formation of 1-D H-bonded achiral and chiral molecular networks respectively. In all cases, the network is formed by mutual bridging of the anionic and cationic units through a chelate mode of H-bonding.

Molecular networks in the solid state are infinite architectures generated by translation into 1, 2 or 3 directions of space of recognition patterns formed between complementary tectons. The design and characterisation of H-bonded molecular networks have been thoroughly investigated over the last years.[1] Although the majority of H-bonded molecular networks reported to date are based on non-ionic H-bonds, examples of charge assisted H-bonded networks have also been reported.[2] Dealing with the latter case, bisamidinium dications have been shown to be interesting tectons for the design of H-bonded molecular networks combining both charge–charge electrostatic interactions and directional H-bonding.[3,4] In particular, using a bisamidinium dication, the formation of H-bonded networks with anionic transition metal cyanide complexes has been reported.[5] The same type of strategy was used with metal chloride anionic species and cationic organic units.[6]

Here we report on design and synthesis of two new optically pure tectons $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ and their self-assembly in the crystalline phase into infinite chiral neutral H-bonded 1-D molecular networks in the presence of $[Fe(CN)_5NO]^{2-}$ anion.

The design of the organic dicationic tectons $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ (Scheme 1) possessing four H-bond donor sites arranged in a divergent manner, is based on the interconnection of two cyclic amidinium moieties by a phenyl unit at the *para* positions. The choice of the latter was based on our previous study on the formation of H-bonded networks obtained upon combining the tecton $\mathbf{1}^{2+}$ and $[M(CN)_n]^{m-}$ ($n = 4$ or 6 and $m = 2$–4) anions.[5] Indeed, the phenyl spacer leads to a distance between the H-bond donor sites located on the same side of the tecton of *ca.* 7 Å which was found to be perfect for the recognition through a chelate-mode of H-bonding of anionic metal polycyanide complexes.[5] Furthermore, owing to the presence of recognition sites on both sides of the skeleton, tectons $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ were designed to generate H-bonded molecular networks in the crystalline phase through the translation of the recognition pattern generated upon chelation of two cyanide units by two H-bonds on the same face of the dicationic unit. While maintaining the same spacer, chirality was introduced within the backbone of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ by enantiomerically pure disubstituted 1, 2-cyclohexyl units (**2** : *R*, *R* and **3** *S*, *S*).



Scheme 1

Concerning the anionic partner, octahedral nitroprussiate $[Fe(CN)_5NO]^{2-}$ was chosen because it allows to study several issues related to supramolecular chirality (here, chirality taking place within the second coordination sphere around the metal centre). Due to the presence of five CN^- centres which may be engaged in H-bond patterns, depending on the dicationic tecton used, achiral or chiral architectures may be obtained (Fig. 1a). Indeed, if the double chelate mode of H-bonding occurs with four cyanide moieties occupying the corners of the square base of the octahedron, leading thus to an achiral (presence of symmetry plane) node of the network, an achiral network would be generated (Fig. 1b). On the other hand, if the two H-bond chelates are formed with non-coplanar four CN- groups, a supramolecularly chiral (Δ′ and Λ′) node must be generated (Fig. 1c and 1d). In the latter case, two possibilities may be envisaged. Either a homochiral situation for which consecutive nodes of the network are of the same supramolecular chirality (Δ′ or Λ′), or a heterochiral situation for which consecutive nodes of the network are of the opposite supramolecular chirality (Δ′ and Λ′)may be obtained. The aim of our study was to investigate these possibilities through the use of achiral tecton $\mathbf{1}^{2+}$ and chiral tectons $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$.

In the case of $\mathbf{1}^{2+}$, an X-ray diffraction study revealed the following features (Fig. 2) : the crystal‡ (triclinic, space group *P*1) is composed of $\mathbf{1}^{2+}$ dications, $[Fe(CN)_5NO]^{2-}$ dianions and H_2O molecules. The cationic and anionic components form a neutral 1-D network resulting from interconnection of the anionic units by the tecton $\mathbf{1}^{2+}$ through a dihapto mode of H-bonding (N–N distance varying between ca 2.87 and 2.92 Å). The chelate mode of H-bonding takes place on both sides of the tecton $\mathbf{1}^{2+}$ with two CN^- units located at the square base of the octahedron leading thus to an achiral unit. For the $\mathbf{1}^{2+}$ dication, the two cyclic amidinium units in half-chair conformation (CN distance of *ca.* 1.31 Å and CNC angle of *ca.* 121°) are almost parallel and tilted with respect to the phenyl ring (CCCN dihedral angles of *ca.* −41° and +40°). For the anionic

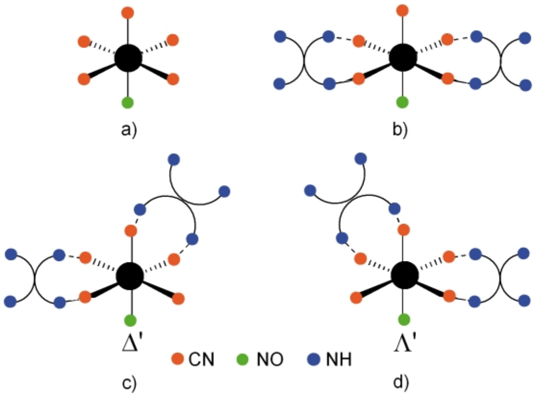


Fig. 1 Schematic representation of the octahedral complex $[Fe(CN)_5NO]^{2-}$ (a) and its double chelation by the dicationic tectons $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ through a dihapto mode of H-bonding.

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† Electronic supplementary information (ESI) available: synthetic details. See http://www.rsc.org/suppdata/cc/b3/b301467n/

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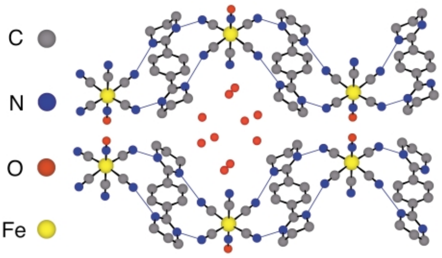

Fig. 2 A portion of two consecutive neutral achiral 1-D H-bonded networks obtained upon co-crystallisation of $\mathbf{1}^{2+}$ and $[Fe(CN)_5NO]^{2-}$. The water molecules occupy the channels with no H-bonding with the network. H atoms are omitted for clarity. For bond distances and angles see text.

$[Fe(CN)_5NO]^{2-}$ component of the network, the coordination geometry around Fe(II) is a distorted octahedral (CFeN angle of *ca*. 176°, CFeC *cis* and *trans* angles of 89° and 170° respectively). The average Fe–C and Fe–N distances are 1.93 and 1.66 Å respectively whereas the N–O distance is 1.13 Å. With each neutral 1-D networks the NO units are disposed in an alternate fashion. The 1-D networks are packed parallel to each other forming thus sheets and an unusual short distance of *ca.* 2.71 Å is observed between NO groups facing each other in consecutive networks. The packing of the 1-D networks in space leading to the formation of the solid generates channels which are filled with water molecules forming polymeric chains (O–O distance varying between 2.77 Å and 2.88 Å).

Both in the case of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ (Fig. 3), the crystal‡ (monoclinic, space group $P2_{1,}$) is exclusively composed of $\mathbf{2}^{2+}$ or $\mathbf{3}^{2+}$ dication and $[Fe(CN)_5NO]^{2-}$ dianion. Both crystals are isostructural with some minor differences in unit cell dimensions which may be due to slightly different conformations adopted by the organic components $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$. Because of the chirality of tectons $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, the cationic and anionic units form a neutral and chiral 1-D network resulting from their mutual interconnection through a dihapto mode of H-bonding between the H-bond donor sites of $\mathbf{2}^{2+}$ or $\mathbf{3}^{2+}$ dication located on the same side of the tecton and two CN^- groups of the dianion (N–N distance varying between *ca.* 2.89 and 2.96 Å). The chelate mode of H-bonding takes place on both sides of the tecton $\mathbf{2}^{2+}$ or $\mathbf{3}^{2+}$ with one CN^- unit located at the square base of the octahedron and the other occupying the apical position. Consequently, around each anionic metal complex a supramolecular chirality taking place within the second coordination sphere is generated. However, two consecutive centres are of the opposite chirality and thus, in terms of supramolecular chirality, a racemate is formed. For tectons $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, the two cyclic amidinium moieties (CN distance of *ca.* 1.31 Å and CNC angle of *ca.* 112°) are tilted with respect to the phenyl ring (CCCN dihedral angles of *ca.* −47° and +38°). The cyclohexyl groups adopt a chair conformation with the two substituents in equatorial positions (NCCN dihedral angles of *ca.* −31°). For the $[Fe(CN)_5NO]^{2-}$ anion, the coordination geometry around Fe(II), bond distances and angles are close to those observed for the network formed with tecton $\mathbf{1}^{2+}$ mentioned above. The 1-D networks are packed in a parallel fashion.

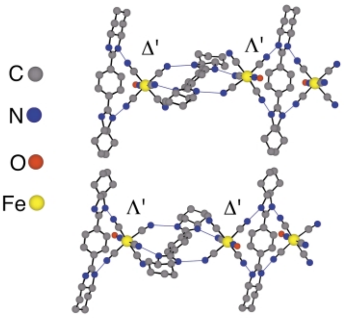

Fig. 3 Portions of neutral chiral 1-D H-bonded networks obtained upon co-crystallisation of chiral $\mathbf{2}^{2+}$ (top) and $\mathbf{3}^{2+}$ (bottom) tectons and $[Fe(CN)_5NO]^{2-}$. H atoms are omitted for clarity. For bond distances and angles see text.

In conclusion, the co-crystallisation of $[Fe(CN)_5NO]^{2-}$ in the presence of cyclic achiral $\mathbf{1}^{2+}$ and chiral $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ tectons leads in the solid state to the formation of 1-D H-bonded achiral and chiral molecular networks respectively. In all three cases, the network is formed by mutual bridging of the anionic and cationic units through a chelate mode of H-bonding taking place with the second coordination sphere of the metal centre. Whereas in the case of $\mathbf{1}^{2+}$, the chelation takes place with two CN^- groups located within the square base of the octahedron, in the case of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ the chelation occurs with one CN^- unit located at the square base of the octahedron and the other occupying the apical position. In the latter case an alternation of Δ′ and Λ′ supramolecular chirality occurring at the second sphere of Fe(II) is observed. With the aim of imposing supramolecular chirality, the use of other chiral tectons with more pronounced chirality is currently under investigation.

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Notes and references

‡ ($\mathbf{1}^{2+}$, $[Fe(CN)_5NO]^{2-})_n$: (slightly brownish, 173 K), $C_{14}H_{20}N_4{\cdot}C_5FeN_6O{\cdot}5H_2O$, M = 550.36, triclinic, a = 6.6651(1), b = 14.2444(3), c = 14.5059(4) Å, α = 84.574(5), β =_ 79.961(5), γ = 77.478(5), U = 1321.54(5) Å^3, Z = 2, space group $P1$, D_C = 1.38 g cm^{-3}, Mo-$K\alpha$, μ = 0.623 mm^{-1}, 3095 data with $I > 3\sigma(I)$, R = 0.047, Rw = 0.062; ($\mathbf{2}^{2+}$, $[Fe(CN)_5NO]^{2-})_n$: (slightly brownish, 173 K), $C_{20}H_{28}N_4{\cdot}C_5FeN_6O$ M = 540.42, monoclinic, a = 6.8450(2), b = 18.2841(4), c = 21.2222(6) Å, β = 79.038(5), U = 2636.0(1) Å^3, Z = 4, space group $P2_{1,}$ D_C = 1.36 g cm^{-3}, Mo-$K\alpha$, μ = 0.611 mm^{-1}, 3276 data with $I > 3\sigma(I)$, R = 0.035, Rw = 0.037; ($\mathbf{3}^{2+}$, $[Fe(CN)_5NO]^{2-})_n$: (slightly brownish, 173 K), $C_{20}H_{28}N_4{\cdot}C_5FeN_6O$ M = 540.42, monoclinic, a = 6.8414(2), b = 18.2099(5), c = 21.0634(6) Å, β = 79.290(5), U = 2602.9(1) Å^3, Z = 4, space group $P2_{1,}$ D_C = 1.38 g cm^{-3}, Mo–$K\alpha$, μ = 0.618 mm^{-1}, 3291 data with $I > 3\sigma(I)$, R = 0.045, Rw = 0.048. (Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMoleN package.[7] CCDC 203131–203133. See http://www.rsc.org/suppdata/cc/b3/b301467n/ for crystallographic data in .cif format.

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