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Crystalline molecular alloys†

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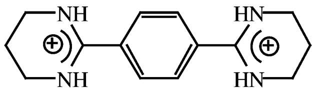
The dicationic tecton 1–2H$^+$ leads in the presence of anionic M(CN)$_6^{3-}$ complexes to two almost identical crystalline systems A (M = Fe) and B (M = Co) composed of 2-D H-bonded networks and water molecules. The epitaxial growth of B on A used as seed or A on B generates crystalline molecular alloys.

The design and characterisation of molecular networks in the crystalline phase are currently attracting much attention. The strategy called molecular tectonics[1] deals with the generation of these periodic architectures under self-assembly processes and is based on molecular recognition events[2] taking place between complementary tectons[3] in the solid state. Among various intermolecular interactions serving to connect tectons, H-bonding is one of the most used attractive forces.[4] A combination of H-bonding and charge–charge electrostatic interactions (charge assisted H-bonding) has been also employed to design molecular networks.[5,6] In particular, the dicationic tecton **1**-2H$^+$[7] (Scheme 1), particularly well suited to recognise cyanometallate complexes through H-bonding, was used to generate a variety of H-bonded networks.[8–10]

The formation of H-bonded molecular networks with polycyanometallates through dihapto or chelate H-bonding modes taking place within the second coordination sphere around the anionic metal complex has been demonstrated.[8–10] The H-bonding occurs between the acidic protons of **1**-2H$^+$ and nitrogen atoms of the cyanide ligands connected to the metal centre. The recognition of anionic metal complexes leading to discrete molecular complexes or infinite networks has been reported.[11,12] It has been demonstrated that a mixture of the dicationic tecton **1**-2H$^+$ and M(CN)$_6^{3-}$ (M = Fe, Co) in water leads to single crystals [(**1**-2H$^+$)$_3$–(Fe(CN)$_6^{3-}$)$_2$ ·8H$_2$O] (yellowish) : **A** and [(**1**-2H$^+$)$_3$–(Co(CN)$_6^{3-}$)$_2$·8H$_2$O] (colourless) : **B**. X-Ray diffraction studies on these crystals revealed in both cases the formation of similar 2-D H-bonded networks resulting from the interconnection of octahedral anionic units M(CN)$_6^{3-}$ by dicationic tectons **1**-2H$^+$ through a chelate mode of H-bonding (Fig. 1).[8] Furthermore, the two crystals **A** and **B**, are not only isostructural (triclinic, $P\bar{1}$ as the space group), but present almost identical metrics (a(Å) = 7.109 for **A** and 7.108 for **B**; b(Å) = 12.430 for **A** and 12.389 for **B**; c(Å) = 17.985 for **A** and 17.871 for **B**; α(deg) = 83.44 for **A** and 83.42 for **B**; β(deg) = 87.58 for **A** and 87.38 for **B**; γ(deg) = 84.05 for **A** and 84.10 for **B**). Indeed, only slight differences in cell parameters, in particular for b and c are observed.

We thought that one could take advantage of these observations to epitaxially grow crystals of **A** or **B** on seed crystals of **B** or **A**. To the best of our knowledge, this strategy has been used only recently by MacDonald *et al.*[13]



1$2H^{2+}$

Scheme 1

Here we report on the formation of two crystalline molecular alloys based on the use of the dicationic tecton **1**-2H$^+$ and iron or cobalt hexacyanometallate.

Since crystals **A** and **B** are yellowish and colourless respectively, the 3-D epitaxial growth process could be easily monitored by changes in colour at the surface of the seed crystal. Indeed, starting with **A**, the growth of **B** on **A** generates colourless surfaces (**A**-**B**) (Fig. 2 left), whereas starting with **B**, after epitaxial growth a yellow crystal was obtained (**B**-**A**) (Fig. 2 right).‡

The cutting of (**A**-**B**) composite crystal (Fig. 2) afforded yellowish and colourless single crystals which were analysed by X-ray diffraction. The study revealed that the yellow crystal corresponds to **A** and the colourless crystal to **B**. Furthermore, X-ray diffraction on the composite (**A**-**B**) crystal revealed that the two crystalline systems were oriented in the same space directions. However, some twinned reflection resulting from the slight difference in cell parameters between the crystalline systems of **A** and **B** were observed (Fig. 3).

A preliminary analysis by Scanning Electron Microscopy equipped with EDS for elemental analysis of both composite crystals (**A**-**B**) and (**B**-**A**) revealed that both systems were rather fragile (collapse of the crystal under the beam). However, in both cases no "discontinuity" was observed when scanning the composite crystal (**A**-**B**) from **A** toward **B** or when scanning the composite crystal (**B**-**A**) from **B** toward **A**. Furthermore, the analysis of the surface corresponding to **A** in (**A**-**B**) or in (**B**-**A**), indicated that Fe was the principal metallic element, whereas the analysis of the surface corresponding to **B** showed that Co was the principal metallic element. Unfortunately, owing to the lack of robustness of

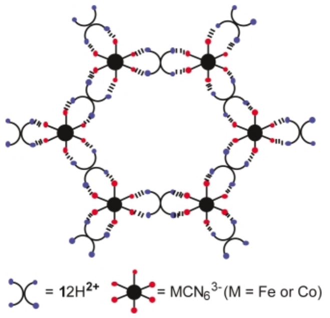


Fig. 1 Schematic representation of the 2-D H-bonded network formed between **1**-2H$^+$ and M(CN)$_6^{3-}$ (M = Fe, Co). The interconnection between the two components is achieved by a chelate mode of H-bonding and electrostatic interactions.

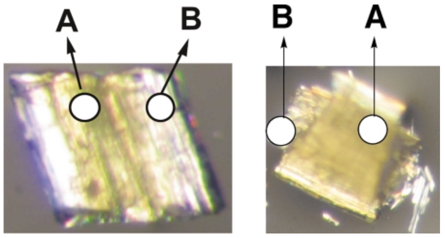


Fig. 2 Pictures of epitaxially grown composite (**A**-**B**) (left) and (**B**-**A**) (right) crystals (see text for definition of **A** and **B** and growth strategy).

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† Dedicated to J.-M. Lehn on the occasion of his 65th birthday.

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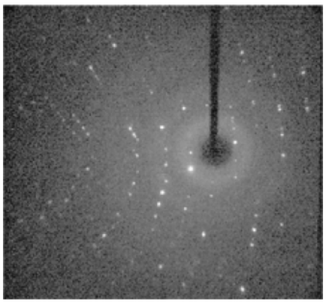

Fig. 3 A frame obtained by diffraction of X-ray by the composite (**A**-**B**) crystal showing that the two crystalline systems are oriented in same directions of space.

the composite crystals, it was not possible to establish the map of both Co and Fe elements.

This demonstration reported here offers the possibility of generating crystals of crystals. We propose the following description for this strategy. The seed crystal corresponds to the generation zero; the crystalline system grown on the seed crystal may be considered as generation one (Fig. 4). If the epitaxially grown crystal (generation one) is used as a seed crystal, the next crystalline system would correspond to generation two. We also propose to qualify these materials as crystalline molecular alloys. Indeed, i) in marked contrast with classical alloys which are composed of metallic atoms, in the present case, the components of the crystalline material (**A**-**B**) or (**B**-**A**) are molecules; ii) the material generated by the 3-D epitaxial growth being crystalline, it possesses periodicity and thus short and long range orders and iii) the crystal of composite crystal (**A**-**B**) or (**B**-**A**) possesses the dicationic tecton **1**-2H$^+$ as the common component and the two crystalline systems differ only by the nature of the metal centre ($Fe(CN)_6^{3-}$ for **A** and $Co(CN)_6^{3-}$ for **B**).

In conclusion, using the dicationic tecton **1**-2H$^+$ and $M(CN)_6^{3-}$ (M = Fe, Co) two crystalline molecular alloys based on the epitaxial growth of **B** on **A** used as seed or **A** on **B** used as a seed crystal were obtained and analysed by X-ray diffraction studies and preliminary by Scanning Electron Microscopy. The formation of higher generation of molecular alloys by step-by step epitaxial growth is currently under study. The use of other crystalline materials bearing paramagnetic centres is also under investigation.

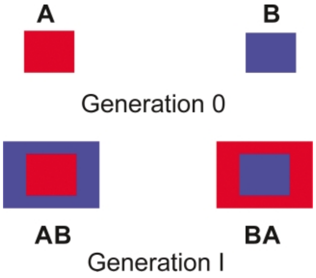

Fig. 4 Schematic representation of the strategy used to grow epitaxially crystalline molecular alloys (for definition of **A**, **B** and generations see text).

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Notes and references

‡ Single crystals of [(**1**-2H$^+$)$_3$($Fe(CN)_6^{3-}$)$_2$·8 H_2O] (yellowish) **A** and [(**1**-2H$^+$)$_3$($Co(CN)_6^{3-}$)$_2$·8 H_2O] (colourless) **B** were obtained as previously described.[8]

A yellow crystal of **A** (approximately 0.1 × 0.06 × 0.02 mm) was glued on a nylon wire before it was immersed in an aqueous solution (2 mL) containing $K_3Co(CN)_6$ (5 mM) and the ditosylate salt of **1**-2H$^+$ (7.5 mM). In addition to a few colourless crystals formed in solution corresponding to **B**, an epitaxial growth of colourless crystalline material on the seed crystal **A** was observed. The same procedure was repeated with colourless crystal **B** as seed and an aqueous solution containing K_3Fe(CN $_6$ (5 mM) and the ditosylate salt of **1**-2H$^+$ (7.5 mM). Again, in addition to yellowish crystals corresponding to **A** formed in solution, yellow crystalline material was grown on the faces of the colourless seed crystal **B**.

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