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Molecular Tectonics: control of crystalline sequences

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Following the molecular tectonics approach, the design and preparation of crystalline entities with controlled sequences were achieved by crystal welding processes based on *isostructural* and almost *isometric* coloured crystals. The strategy was based on stepwise 3D epitaxial growth.

Both for fundamental and applied sciences, the understanding and design of crystalline complex molecular systems with strict control of the short and long range orders both at the microscopic and macroscopic levels is of prime importance for developments of new solid state materials and devices. Hierarchical construction of crystalline species resulting from the interconnection of single crystals into networks of crystals leading to sequences of crystalline zones may be a powerful tool for the generating new crystalline task specific materials. This may be achieved by the molecular tectonics approach¹ for which molecular crystals are considered as supramolecular entities^{2,3} seen as periodic molecular networks⁴ composed of interconnected complementary tectons⁵ bearing within their framework specific geometric and recognition information. Beyond crystal engineering,⁶ engineering multi-zone single crystals such as core-shell crystals⁷⁻⁹ and welded crystals¹⁰ remain a challenge. For the molecular tectonics approach, four different categories of molecular crystals may be defined (Figure 1): crystal, a molecular architecture possessing periodicity both in position and in composition (Figure 1a); crystalline solid solution, a periodic assembly in position but random in composition (Figure 1b); a core-shell crystal composed of different interconnected crystalline zones each periodic in position and in composition (Figure 1c), this type of organization is obtained by stepwise hierarchical selfassembly processes and finally welded crystal, multi-zone architectures composed of at least

three domains periodic in position and in composition within each crystalline domain (Figure 1d). This type of architecture may be obtained by stepwise selfassembly strategy. It is worth noting that except for a molecular crystal, for a solid solution the tectons need to be similar. For the other two categories, obtained by 3D epitaxial growth processes, the crystalline domains must be *isostructural* and almost *isometric*.

Figure 1: Schematic representations (2D projection) of a portion of a) a crystal (periodic in position and in composition), b) a crystalline solid solution (periodic in position and random in composition), c) a core-shell crystal (periodic in position obtained by stepwise epitaxial growth) and d) a crystalline sequence (periodic in position displaying three crystalline zones). Red, blue and green spheres represent complementary tectons and the grey cylinder represents a recognition pattern connecting consecutive tectons.

In this contribution, we report on the extensive use of crystal welding in solution and under mild conditions using 3D

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epitaxial growth for the generation of a variety of crystalline materials displaying controlled and imposed sequences.

Among many possible attractive interactions that can be used for interconnecting consecutive tectons by selfassembly processes into periodic networks, directional H-bonding combined with charge-charge electrostatic interactions (charge-assisted H-bonding)¹¹ is particularly interesting.^{1c,12} Using such interactions, a variety of *isostructural* and almost *isometric* crystals has been generated by combining dicationic organic tectons and dianionic metallatectons as H-bond donors and acceptors respectively.¹² Furthermore, they were used to form core-shell crystals by 3D epitaxial growth processes.⁸ The same strategy was recently extended to the use of coordination bond using metallatectons and metal cations.⁹

Combinations of the dicationic H-bond donor organic tecton **1**²⁺ with tetraanionic complexes [ML₂]⁴⁻ (M = Mn, Fe, Co, Ni, Cu or Zn) as H-bond acceptor (Figure 2), were shown to lead to the formation of robust *isostructural* (monoclinic, C2/c, Z = 4) and almost *isometric* crystals **1**₂-ML₂ (see table S1, ESI).¹⁰ The latter are based on the formation of 3D H-bonded networks between H-bond donor and acceptor tectons.

Figure 2: Dicationic **1**²⁺ and tetraanionic [ML₂]⁴⁻ (Mn, Fe, Co, Ni, Cu or Zn) tectons used for the formation of *isostructural* and almost *isometric* crystals.

Interestingly, except for **1**₂-ZnL₂ which is colourless, depending on the nature of the divalent cation (M = Mn, Fe, Co, Ni, Cu) coloured rod type crystals are obtained (Figure 3).¹⁰ For the sake of clarity of description, **1**₂-ML₂ (M = Mn, Fe, Co, Ni, Cu or Zn) crystals will be designated as **A**, **B** or **C** in the following sections.

Figure 3: Photographs of *isostructural* and almost *isometric* coloured rod-type crystals **1**₂-ML₂ displaying absorption bands in the visible range.

In a preliminary investigation,¹⁰ using a series of rod-type *isostructural* and almost *isometric* coloured crystals (Figure 3), we have demonstrated that by 3D epitaxial growth, it is possible to generate, in solution and under mild conditions, core-shell crystals of the type **B**@**A**. Furthermore, two crystals **A** aligned and oriented along the fastest growth axis *c* (Figure 4a), may be welded in solution at room temperature into a welded single crystal **A-B-A** (Figure 4b). However, it must be noticed that since the welding process by 3D epitaxial growth takes place in solution, the growth phenomena operates at the two extremities of the welded crystal as well at the other two directions of space *a* and *b* (Figure 4b) leading thus to a welded core-shell crystal. Since the growth process is considerably faster along the *c* axis, by neglecting the growth along *a* and *b* axes, the welded crystal may be seen as a crystal displaying a palindromic **B-A-B-A-B** sequence composed of five crystalline zones (Figure 4c).

Figure 4: Schematic representation of two aligned crystals **A** along the fastest growth axis *c* (a), welding of two crystals **A** by a crystalline phase **B** (b) and simplified representation of the welded crystal along the *c* axis leading to the palindromic **B-A-B-A-B** sequence (c). Crystals **A** and **B** differ by the nature of M in the **1**₂-ML₂ unit (see figure 1).

The welding approach described above is rather versatile and may be further applied to the formation of strictly controlled sophisticated sequenced crystals. Indeed, instead of welding two identical crystals by a second crystalline phase (Figure 4), the approach may be extended to the welding of two different crystals **A** and **B** (Figure 5a) by a third crystalline domain **C** (Figure 5b) leading to a non-symmetric sequence **C-A-C-B-C** along the *c* axis (Figure 5c).

Figure 5: Schematic representation of aligned crystals **A** and **B** along the fastest growth axis *c* (a), welding of crystals **A** and **B** by a crystalline phase **C** (b) and simplified representation of the welded crystal along the *c* axis leading to the unsymmetrical **C-A-C-B-C** sequence (c). Crystals **A** and **B** differ by the nature of M in the **1**₂-ML₂ unit (see figure 1).

It is worth noting that crystals **1**₂-ML₂ (M = Mn, Fe, Co, Ni, Cu or Zn) possessing different colours, display a rod-type morphology with their extremities forming an angle with the fastest growth axis *c* (Figure 3). We used these two observations to align the crystals along the *c* axis and to orient them. The orientation was further confirmed by face indexation. These two issues are crucial for optimal epitaxial growth.

In a Petri dish, two different crystals 1_2-FeL_2 and 1_2-CoL_2 were aligned and oriented along the c axis (Figure 6a) and covered with a solution containing NiL_2 and 1^{2+} cation and the welding process was monitored using a microscope (see experimental section, ESI). The growth process led to the formation of the welded entity as a single crystal displaying the **Ni-Fe-Ni-Co-Ni** sequence (Figure 6b). The single crystal nature of the latter was established by X-ray diffraction on the welded crystal. Furthermore, cell parameters of different crystalline zones were determined by focussing the X-ray beam on desired domains (see experimental characterisation section, ESI). The same procedure was applied to weld 1_2-FeL_2 and 1_2-MnL_2 crystals (Figure 6c) by 1_2-NiL_2 . The process afforded the unsymmetrical **Ni-Fe-Ni-Mn-Ni** sequence composed of 5 crystalline interconnected zones (Figure 6d). The generality of the strategy was further demonstrated by welding 1_2-ZnL_2 and 1_2-CoL_2 crystals (Figure 6e) by 1_2-NiL_2 (Figure 6f) displaying the **Ni-Zn-Ni-Co-Ni** sequence.

Figure 6: Photographs of two aligned crystals along the c axis containing Fe and Co (a) and their welding by a crystalline phase containing Ni leading to the **Ni-Fe-Ni-Co-Ni** sequence (b) and two crystals containing Fe and Mn (c) and their welding by a crystalline phase based on Ni leading to the **Ni-Fe-Ni-Mn-Ni** sequence (d) and two aligned crystals contained Zn and Co (e) and their welding by a crystalline phase based on Ni leading to the **Ni-Zn-Ni-Co-Ni** sequence (f).

The stepwise strategy for the preparation of sequenced crystals by 3D epitaxial growth presented here is rather versatile and offers many design possibilities for the formation of crystalline mosaics composed of several zones. In particular, starting with a welded crystal of the **A-B-A** (Figure 7a), a core-shell crystal may be formed by epitaxial growth using a crystalline shell **C** (Figure 7b). Again, by neglecting the growth along the a and b axes, the single crystal thus obtained may be described as **C-B-A-B-A-B-C** sequence along the c axis composed of seven crystalline domains (Figure 7c).

Figure 7: Schematic representations of the welded crystal **A-B-A** (a) and the core-shell crystals **C@A-B-A** (b) leading to the **C-B-A-B-A-B-C** sequence (c) along the c axis.

Starting with the **Fe-Zn-Fe** welded crystal displaying the **Zn-Fe-Zn-Fe-Zn** sequence (Figure 8a), the formation of the core-shell

crystal **Ni@Fe-Zn-Fe** was achieved using a solution containing NiL_2 and 1^{2+} (Figure 8b). The latter is composed of **Ni-Zn-Fe-Zn-Fe-Ni** sequence displaying seven crystalline zones. Starting with the **Co-Cu-Co** welded crystal displaying the **Cu-Co-Cu-Co-Cu** sequence (Figure 8c), the same procedure using a solution containing MnL_2 and 1^{2+} afforded the core-shell crystal **Mn@Co-Cu-Co** displaying the **Mn-Cu-Co-Cu-Co-Cu-Mn** sequence (Figure 8d). Finally, starting with the **Ni-Co-Ni** welded crystal displaying the **Co-Ni-Co-Ni-Co** sequence (Figure 8e), the same procedure using a solution containing ZnL_2 and 1^{2+} produced the core-shell crystal **Zn@Ni-Co-Ni** composed of seven crystalline zones with the **Zn-Co-Ni-Co-Ni-Co-Zn** sequence (Figure 8f).

Figure 8: Photographs of two Fe based crystals welded by a Zn containing crystalline phase (a) and the core-shell crystal **Ni@Zn-Fe-Zn-Fe-Zn** with the **Ni-Zn-Fe-Zn-Fe-Zn-Ni** sequence and of two Co based crystals welded by a Cu containing phase (c) and the core-shell crystal **Mn@Cu-Co-Cu-Cu-Cu** with the **Mn-Cu-Co-Cu-Co-Cu-Mn** sequence (d) and of two Ni based crystals welded by a Co containing crystalline phase (e) and the core-shell crystal **Ni@Zn-Fe-Zn-Fe-Zn** with the **Ni-Zn-Fe-Zn-Fe-Zn-Ni** sequence and of two Co based crystals welded by a Cu containing phase (c) and the core-shell crystal **Zn@Ni-Co-Ni-Co** with the **Zn-Co-Ni-Co-Ni-Co-Zn** sequence (f).

In order to further extend the construction process, the formation of crystals composed of 9 zones was investigated. The strategy adopted may be based on the welding of two aligned and oriented core-shell crystals **B@A** (Figure 9a) by a crystalline phase **C** leading to **(B@A)-C-(B@A)** welded crystals (Figure 9b). Again, by neglecting the growth process along the a and b axes, the welded crystal displays the **C-B-A-B-C-B-A-B-C** sequence along the c axis (Figure 9c).

Figure 9: Schematic representations of two aligned core-shell crystals **B@A** (a) and the welded crystal **(B@A)-C-(B@A)** by **C** (b) leading to the **C-B-A-B-C-B-A-B-C** sequence (c) along the c axis.

Experimentally, the above mentioned strategy was demonstrated by welding two aligned and oriented core-shell crystals (**Cu@Co**) (Figure 10a) by a solution containing NiL_2 and

1^{2+} cation leading to **(Cu@Co)-Ni-(Cu@Co)** single crystal (Figure 10b). The latter displays along the *c* axis the symmetric **Ni-Cu-Co-Cu-Ni-Cu-Co-Cu-Ni** sequence. Starting with two aligned and oriented core-shell crystals **(Zn@Fe)** (Figure 10c), the same procedure produced the welded crystal **(Zn@Fe)-Ni-(Zn@Fe)** displaying the **Ni-Zn-Fe-Zn-Ni-Zn-Fe-Zn-Ni** symmetric sequence composed of nine different crystalline zones (Figure 10d). Finally, in order to verify the generality of the approach, two aligned and oriented core-shell crystals **(Mn@Fe)** (Figure 10e) were welded using a solution containing ZnL_2 and 1^{2+} cation leading to **(Mn@Fe)-Zn-(Mn@Fe)** single crystal (Figure 10b) displaying the **Zn-Mn-Fe-Mn-Zn-Mn-Fe-Mn-Zn** palindromic sequence along the *c* axis.

Figure 10: Photographs of two core-shell crystals **(Cu@Co)** (a) welded by 1^{2+}NiL_2 (b), two core-shell crystals **(Zn@Fe)** (c) welded by 1^{2+}NiL_2 (d) and two core-shell crystals **(Mn@Fe)** (e) welded by 1^{2+}ZnL_2 (f) leading to crystals displaying palindromic sequences composed of nine crystalline zones.

In conclusion, we have shown that, using a series of *isostructural* and almost *isometric* crystals differing by their colour, crystals with controlled sequence along the fastest growth axis can be designed and generated using a welding strategy in solution under mild conditions. The crystalline entity obtained displaying 5, 7 or 9 crystalline zones may be of interest for their optical properties owing to the differences in their refractive indices. The strategy presented here, although restricted to *isostructural* and almost *isometric* crystals, is rather versatile and may be applied to the design and preparation of a wide variety of crystalline materials. Research along these lines is currently under investigation using other series of crystals.

Conflicts of interest

There are no conflicts to declare.

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Graphical abstract

*Iso*structural and almost *isometric* crystals differing by their colour may be welded in solution and under mild conditions into crystalline materials with imposed sequences.

Ni Cu Co Cu Ni Co Cu Ni