Welding Molecular Crystals

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Both for fundamental and applied sciences, the design of complex molecular systems in the crystalline phase with strict control of order and periodicity at both microscopic and macroscopic levels is of prime importance for the development of new solid-state materials and devices. This may be achieved by the molecular tectonics approach.^[1] The design and fabrication of complex crystalline systems such as networks of crystals displaying task-specific properties is a step toward smart molecular materials.^[2] Here we report on welding, by 3D epitaxial growth, of isostructural and almost isometric crystals into networks of crystals.^[3]



Figure 1. a) H-bond donor tecton 1, b) H-bond acceptor metallatecton $[M^{II}L_2]^{4-}$ and c) isostructural crystals formed upon their combinations.

Upon combining the dicationic H-bond donor tecton **1** (Fig. 1a), with H-bond acceptor anionic metallatectons $[M^{II}L_2]^{4-}$ (M = Mn, Fe, Co, Ni, Cu or Zn) (Fig. 1b), a series of isostructural robust coloured molecular crystals has been obtained (Fig. 1c). These species, characterized by XRD methods, are described as H-bonded 3D networks **1**₂-ML₂. Taking advantage of their isostructurality, different crystals have been welded in solution by epitaxial growth of a crystalline region between two crystals (Fig. 2).



Figure 2. a) Schematic representation of crystal welding, b) seed and welded crystal pictures and c) welding prepared from core-shell crystals.

Welding of crystals by self-assembly processes into macroscopic networks of crystals is a powerful strategy for the design of new hierarchically organized periodic complex architectures composed of different subdomains displaying targeted characteristics. Furthermore, the crystal welding method can be combined with the preparation of core-shell type crystals by using the latter as seed crystals

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(Fig. 2c).^[4]

Crystal welding may be regarded as a first step toward the design of new hierarchically organized complex crystalline systems.

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