Supporting Information

The method used to build a crystal growth model.

When an epitaxy occurs between two crystals (A,B) having different structures, a common interface is generated where two faces $(hkl)_A$ and $(h'k'l')_B$ physically enter in contact.

A 2D lattice is associated to each of the two $(hkl)_A$ and $(h'k'l')_B$ faces, according to Royer's theory (1928, 1954). In order to obtain an epitaxial relation between the two crystals, a ***common 2D super-lattice*** must be generated from the super-position of the lattice planes: $hkl_{(A)}$ and $h'k'l'_{(B)}$. From the points making this 2D super-lattice, a ***2D- coincidence lattice cell is obtained.***

In the following, we will draw with a practical example (see Table 1, in the text) the way for obtaining a 2D- coincidence lattice cell**.**

We put forward the hypothesis that the face (001) of the Calcium citrate tetrahydrate (Ca-Cit-TH) can make epitaxy with the face (001) of the monoclinic Hydroxyapatite (HAp).

i) The vectors defining the (001) cell of HAp and (001) cell of Ca-Cit-TH are (in Å):

$[100]_{HAp} = 9.3253$; $[010]_{HAp} = 6.9503$

$[100]_{Ca\text{-}Cit\text{-}TH} = 5.9466$; $[010]_{Ca\text{-}Cit\text{-}TH} = 10.2247$

as separately represented in **Figure SI1**.

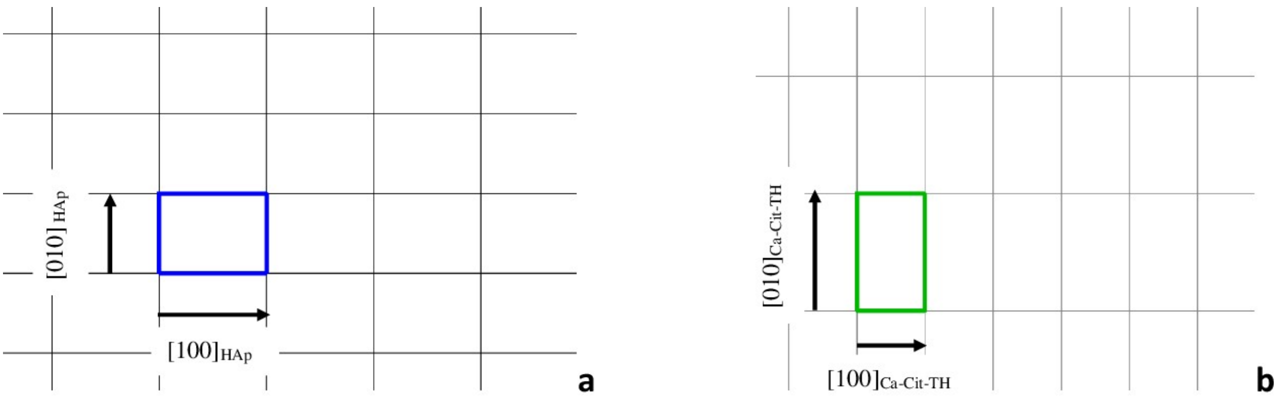

Figure SI1: a) the (001) cell of HAp and b) the (001) cell of Ca-Cit-TH

ii) Let's superpose the two cells: the origin is common and the rotation angle between their [100] vectors is null. As a result of the superposition, a 2D coincidence cell is found: the maximum linear misfits (Δ%) following from **Figure SI2** are, respectively:

$\{2\times[100]_{HAp} - 3\times[100]_{Ca\text{-}Cit\text{-}TH}\} / 3\times[100]_{Ca\text{-}Cit\text{-}TH} = -4.54\%$

$\{3\times[010]_{HAp} - 2\times[010]_{Ca\text{-}Cit\text{-}TH}\} 2\times[100]_{Ca\text{-}Cit\text{-}TH} = -1.74\%$

The multiplicity of the coincidence cell is the same (6×) for the two lattices, but the maximum percent area misfit (Δ%) is:

(388.882 - 364.813) Å^2 / 364.813 Å^2 = - 6.6%. The area misfit is higher than both the linear misfits, but this is not surprising, since the linear misfits cooperate, owing to their common sign (-).

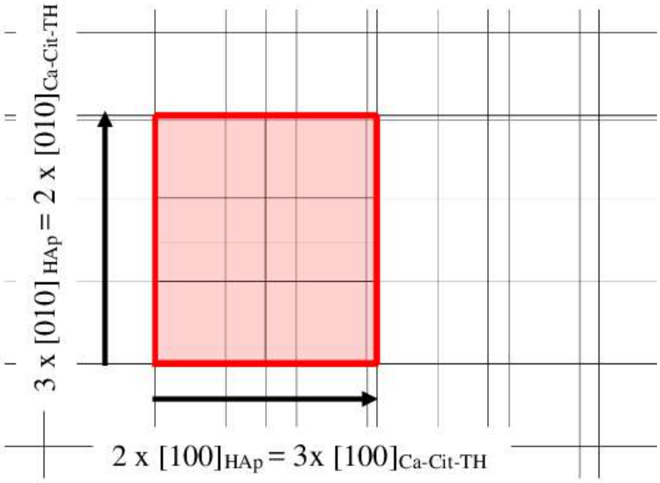

Figure SI2: 2D coincidence cell between the (001) cell of HAp and the (001) cell of Ca-Cit-TH as reported in Figure SI1.

iii) From i) and ii) one can deduce that the obtained 2D-coincidence lattice can correspond to a good epitaxy between HAp and Ca-Cit-TH, because the linear misfits are largely lower than 10%, which is the limiting constraint for epitaxy to occur.

Let's continue searching for another 2D- coincidence lattice, if any. The [100]$_{Ca-Cit-TH}$ vector is rotated clockwise by 25° with respect to the [100]$_{HAp}$ vector, while the common origin is maintained. A new 2D- coincidence lattice is found, as drawn in **Figure SI3.**

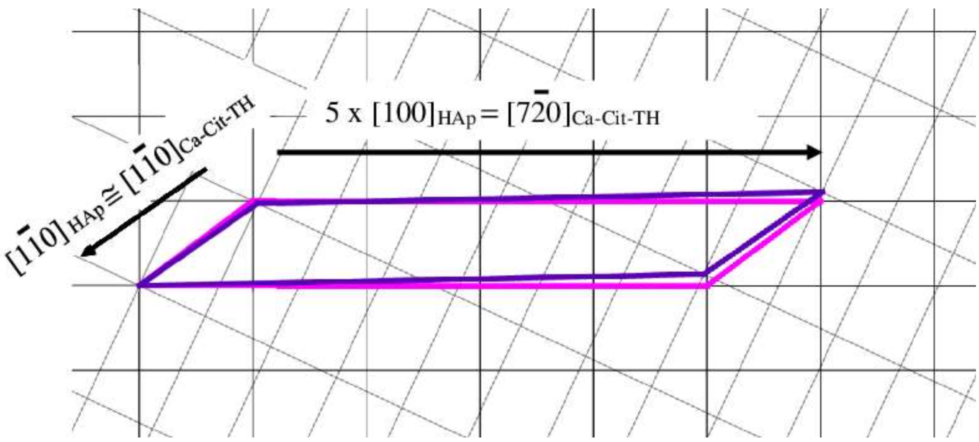

Figure SI3: A new 2D-coincidence cell obtained by rotating the [100]$_{Ca-Cit-TH}$ vector clockwise by 25° with respect to the [100]$_{HAp}$ vector, while the common origin is maintained.

The new misfits are:

{ $[1\bar{1}0]$ HAp - $[1\bar{1}0]$ Ca-Cit-TH } / $[1\bar{1}0]$ HAp = +1.86%

{ 5×$[100]$ HAp - $[7\bar{2}0]$ Ca-Cit-TH }$[7\bar{2}0]$ Ca-Cit-TH = - 0.49%

The multiplicity of the coincidence cell is the same (5×) for the two lattices, but is lower than that found in the preceding case. The maximum percent area misfit (Δ%) is the same we found when the mutual rotation angle was 0°, because the multiplicity is the same for the two lattices.

Four other 2D-coincidence lattices can be found when the mutual rotation angle varies in between 0 and 90°, as illustrated in Table 1a. Their multiplicities are higher (8×) and (13×). For rotation angles higher than 90°, coincidence lattices repeat, owing to the mirror 2D-symmetry of the HAp lattice.

When summarizing, from Table 1 (in the text) it follows that 6 coincidence lattices have been found between the Ca-Cit-TH- (001) and the face (001) of the monoclinic HAp. It is well-known that lower the multiplicity (area) of the 2D-coincidence cell, higher the probability of epitaxy to occur; in other words, smaller the 2D-coincidence cell area, higher the density of the potential well where the adsorbed guest lattice adapts its structure to that of the host crystal phase. For that reason, we indicated in the Tables 1-4, the ranking of the 2D-coincidence cell areas.

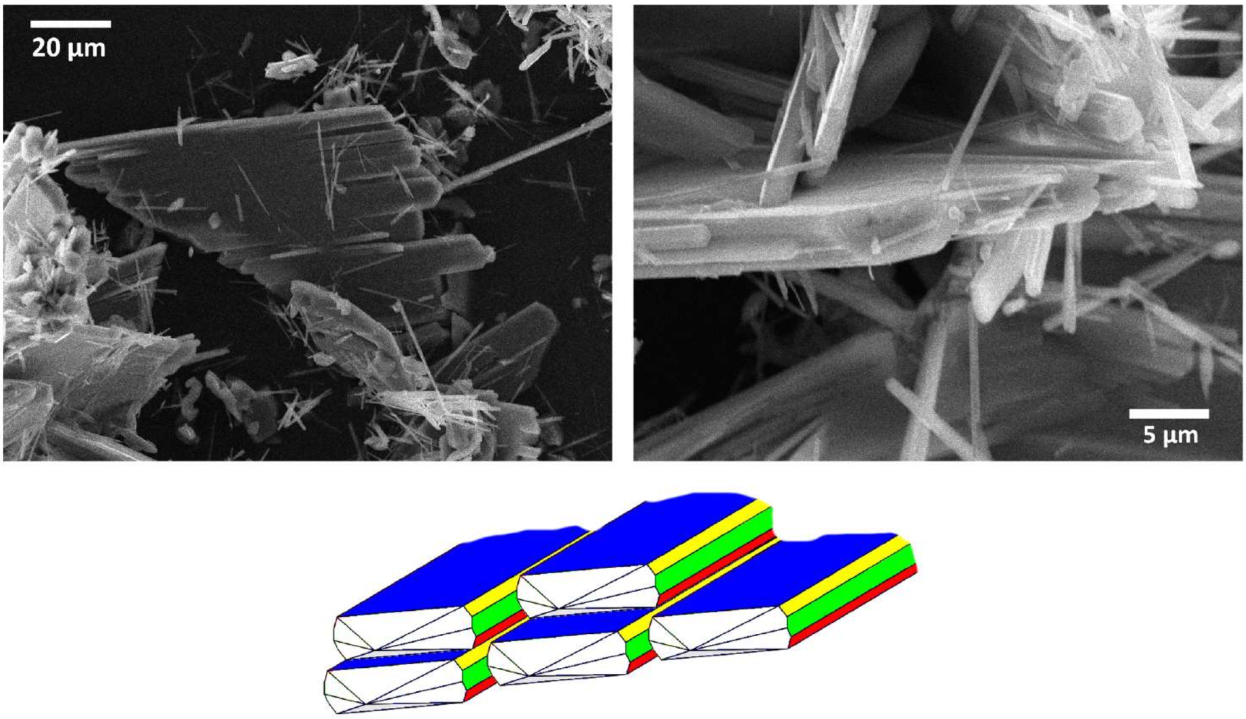

Figure SI4: Double fence-like aggregate of Hap crystals welded on both the $\{10\bar{1}\}$ (better visible on the left) and the $\{001\}$ faces (better visible on the right) and their reciprocal arrangement sketched in the scheme below.