Supplementary Information
for
Crystal form selectivity by humidity control: the case of the ionic co-crystals of nicotinamide and CaCl₂

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TGA measurements.
Despite all attempts to obtain pure compounds, the TGA curves suggests the presences of a small amount of CaCl₂ XH₂O. It is known that the dehydration process of CaCl₂ XH₂O strongly depends on the heating rate and a recent study shows that at ~142°C there is a complete conversion of CaCl₂ 6H₂O to the anhydrous form.¹
In figure S.I.1 the small step between 90-130°C could be ascribed to the release of water due to the presence of small percentage of CaCl₂ XH₂O not detectable by X-ray diffraction, while step between 130°C to 200°C the release of the crystallization water molecule of Nic·CaCl₂·H₂O (calc 7.16% obs. 6.59%) and the formation of the anhydrous form. At 250°C the decomposition occurred.
The variable temperature XRD shows no changes in the pattern between 90°C-130°C also after the sample was kept at 100°C for 1 hour (see figure S.I. 2)

Figure S1 1. TGA curves of Nic·CaCl₂·H₂O. Sample obtained by kneading CaCl₂ anhydrous and Nicotinamide with 1 drop of ethanol. The sample was kept at 75°C for at least 1 hour to remove adsorbed water. The first step between 90°C-140°C is ascribable to the release of water due to the presence of CaCl₂·xH₂O.
Nic·CaCl₂·H₂O loses three water molecules before 90°C. After this temperature the thermogram is comparable to that one observed for Nic·CaCl₂·H₂O; also in this case there is a step between 90°-130°C due to the presence of a small percentage of CaCl₂·XH₂O (Figure S.I. 3).

Rietveld refinements of patterns collected on powders exposed to different RH

Rietveld refinement of the diffractogram collected on the sample of Nic·CaCl₂ after been exposed to HR 12% for two weeks (θ range 5-40°, step size 0.02°, time/step 20 s, 0.04 rad soller, kVxmA 40x40). The pattern has been described by two crystalline phases: Nic·CaCl₂ and Nic·CaCl₂·H₂O. The refinement converged to $R_{wp} = 8.635\%$ and $\chi^2 = 1.734$ values.
Figure S.I. 4  Experimental (black dots), calculated (red line) and difference (grey line) patterns for Nic·CaCl$_2$·H$_2$O (black line) after two weeks at 12% RH. Peak positions are marked in red and green for Nic·CaCl$_2$ and Nic·CaCl$_2$·H$_2$O respectively.

Rietveld refinement of the diffractogram collected on the sample of Nic·CaCl$_2$ after been exposed to HR 53% for two weeks (20 range 5-40°, step size 0.02°, time/step 20 s, 0.04 rad soller, kVxmA 40x40). The pattern has been modelled using three phases: Nic·CaCl$_2$·H$_2$O, triclinic CaCl$_2$·4H$_2$O and trigonal CaCl$_2$·2H$_2$O. The refinement converged to $R_{wp} = 8.777\%$ and $\chi^2 = 1.426$ values.

Figure S.I. 5  Experimental (black dots), calculated (red line) and difference (grey line) patterns for Nic·CaCl$_2$·H$_2$O (black line) after two weeks at 54% RH. Peak positions are marked in red, green and blue for Nic$_2$·CaCl$_2$·2H$_2$O, CaCl$_2$·4H$_2$O and CaCl$_2$·2H$_2$O respectively.