**<u>Supporting material</u>**

Raman spectroscopy

The Raman spectra of the pink β-Co(OH)$_2$ and the sulfate-intercalated α-Co(OH)$_2$ are also measured to shed more light on the structure of the LDH. Fig. 5 displays the Raman active modes in the 100-1200 cm^{-1} range, which covers the metal-oxygen restricted symmetry inside the lattice. The two modes at 250 and 437 cm^{-1} are attributed respectively to E$_g$(T) and A$_{1g}$(T)[1], whereas it remains difficult to assign the modes at 504 and 601 cm^{-1}. Although E$_g$(R) mode appears at 700 cm^{-1} in layered hydroxide systems, it may come out as a weak and broad peak at lower frequencies such as 601 cm^{-1} due to structural defects[2,3]. More interestingly, Mockenhaupt *et al.*[4] suggested that the vibration at 504 cm^{-1} corresponds to the Raman inactive mode A$_{2u}$(T) that lies near 510 cm^{-1} in infrared measurements. Shieh *et al.*[3] propose that a Fermi resonance may take place between two close degenerate modes of identical character such as A$_{1g}$(T) and A$_{2u}$(T) as a result of an anharmonic coupling if the A$_{2u}$(T) assignment is correct. The weakening of the band at 250 cm^{-1} compared to the growing one at 504 cm^{-1} supports such hypothesis, but cannot absolutely confirm it.

On the other hand, α-Co(OH)$_2$ samples display further active Raman modes (E and A$_1$) due to the existence of tetrahedral Co(II) exhibiting a C$_{3v}$ symmetry. Unfortunately, it was tough to assign the corresponding peaks of these two modes as no Co(OH)$_2$ crystals holding exclusively Co(II) in tetrahedral coordination geometry exist for assessment[5]. Yet, we can still distinguish between the two polymorphs by detecting the divergence from the original spectrum of β-Co(OH)$_2$. For instance, the spectrum of α-Co(OH)$_2$ does not show peaks at 601 cm^{-1} and the peak at 502 cm^{-1} in the pink polymorph is shifted to 518 cm^{-1} in the blue one. Moreover, the Raman spectrum of the blue solid reveals definitely the low crystallinity of such polymorph in which the lattice structure is more distorted. Indeed, as the distortion of the crystal increases, the

lifetime of the phonons in their vibrational excited states decreases (due to the interaction of the phonons with these defects) which is according to the uncertainty principle inversely proportional to the energy released during the transition. As a result, the corresponding peaks of the α-Co(OH)$_2$ sample are broader than the analogous peaks of β-Co(OH)$_2$. Note that the appearance of the overtone peaks at 860, 920, 1036, 1104, and 1164 cm^{-1} may reflect as well the poor crystallinity of the blue solid if they are not attributed to any impurities.
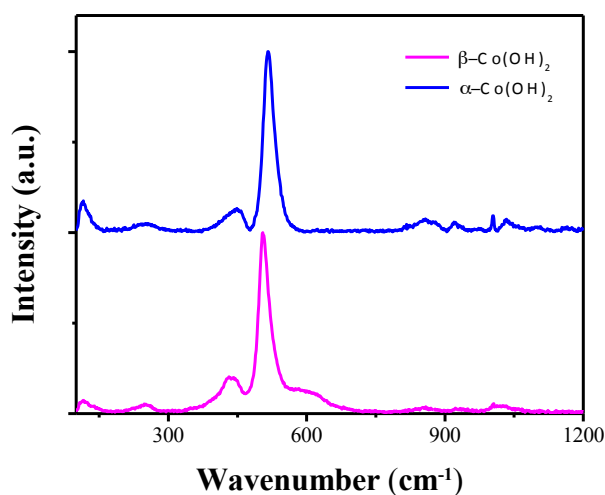

Raman spectra of α-Co(OH)$_2$ intercalated with sulfate crystals and β-Co(OH)$_2$ crystals.

UV-Vis spectroscopy

UV-Vis diffuse reflectance experiments are carried out on all powdered solids as shown in Fig. 6 to inspect the origin of their colors and to confirm the existence of tetrahedral Co(II) in α-Co(OH)$_2$ samples. Co(II) (d^7) in an octahedral environment possesses a center of symmetry wherein d-d transitions (knowing that d orbitals are symmetric to inversion) are forbidden according to Laporte selection rule. Therefore, the weak bands appearing in the visible region at $\sim$530 nm (or $\sim$19050 cm^{-1}) are comparable to the weak $^4T_{1g}(p) \leftarrow {}^4T_{1g}(F)$ absorption transition

($v_3(O_h) = 20200$ cm^{-1}) and the bands at 650 nm (or ~15300 cm^{-1}) are similar to the weak $^4A_{2g} \leftarrow$ $^4T_{1g}$ absorption transition ($v_2(O_h) = 16000$ cm^{-1}) encountered in octahedral Co(II) complexes[6,7].

In addition to the octahedral spectroscopic feature that is exhibited by all α-Co(OH)$_2$ samples around 500 nm, two supplementary strong peaks are observed at 590 and 640 nm (or ~15600 and 16950 cm^{-1}) as shown in Fig. 6(A,B,C). These peaks which appear at lower energies (15596 and 16883 cm^{-1})[6,8] are accredited to the presence of Co(II) in tetrahedral coordination geometry[9]. Indeed, such intense peaks are due to the tetrahedral arrangement of Co(II) which lacks a center of symmetry and allows transitions between states of different parity. As a result, α-Co(OH)$_2$ crystals display a green/blue color in which tetrahedral Co(II) have replaced some of the octahedral Co(II) in the basic brucite layer. Nevertheless, the appearance of pale pink β-Co(OH)$_2$ crystals reflect the sole presence of Co(II) in octahedral coordination symmetry.
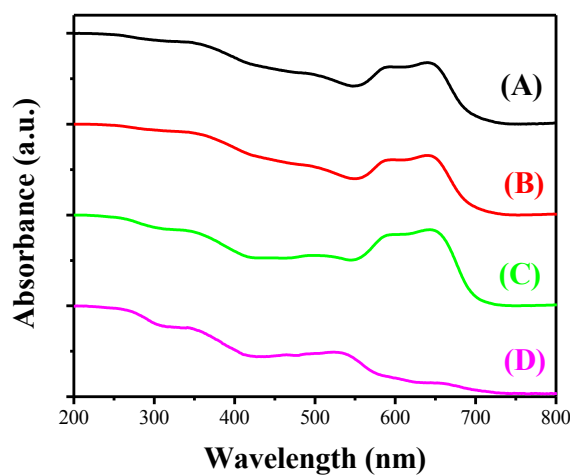
UV−vis diffuse reflectance spectra of α-Co(OH)$_2$ crystals intercalated with bromide (A), chloride (B), sulfate (C) anions, and β-Co(OH)$_2$ crystals (D).

Rhodamine intercalation in α-Co(OH)₂ crystals
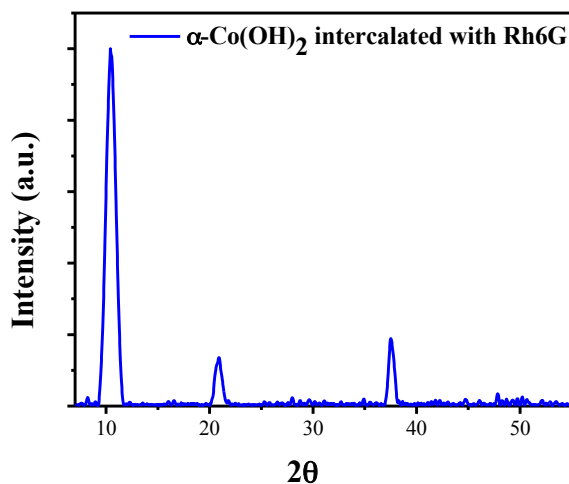
XRD pattern of α-Co(OH)₂ crystals intercalated with chloride anions and rhodamine molecules.

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