

# Supporting Information

## Computational and experimental Methods

### *Computational details*

All geometry (atom positions + unit cell parameters) optimizations are performed using ab initio plane-wave pseudopotential approach as implemented in the Vienna Ab initio Simulation Package (VASP 5.4)<sup>[1]</sup>. The Perdew-Burke-Ernzerhof (PBE) functional<sup>[2]</sup> has been chosen to perform the periodic DFT calculations with an accuracy on the overall convergence tested elsewhere<sup>[3]</sup>. The valence electrons are treated explicitly and their interactions with the ionic cores are described by the Projector Augmented-Wave method (PAW)<sup>[4]</sup>, which allows to use a low energy cut off equal to 500 eV for the plane-wave basis. A  $2 \times 2 \times 4$ ,  $4 \times 2 \times 4$  and  $4 \times 4 \times 4$  Monkhorst-Pack mesh of k-Points is used in the Brillouin-zone integration for COM, COD and COT, respectively. The partial occupancies of the wave functions are determined using the tetrahedron method with Blöchl corrections.<sup>[4a]</sup>

In order to account for the dispersion interaction in the systems, DFT-D2 (here PBE-D2) approach of Grimme<sup>[5]</sup> and DFT-D3 (here PBE-D2)<sup>[6]</sup> were used, as implemented in VASP, which consists in adding a semi-empirical dispersion potential to the conventional Kohn-Sham DFT energy. vdW-DF<sup>[7]</sup> was used by means of the optPBE functional<sup>[8]</sup>.

vdW-DFT IR vibrational intensities were calculated using DFPT (Density-Functional Perturbation Theory), also known as LRT (Linear Response Theory), following the method of Giannozzi and Baroni<sup>24</sup>. In this case, the linear response calculation was carried out and the calculated Born effective charges were determined for all atoms.

The Raman intensities were estimated by the derivative of the macroscopic dielectric tensor (polarizability) with respect to the normal mode, following the method of Fonari and Stauffer<sup>[9]</sup>.

### *Experimental Details*

Calcium chloride ( $\text{CaCl}_2$ ) and sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) were purchased from Sigma-Aldrich and used without further purification. All synthesis were carried out using ultrapure water.

## COM, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

At ambient temperature, equimolar aqueous solutions of  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{CaCl}_2$  ( $0.1 \text{ mol.L}^{-1}$ ) were added simultaneously dropwise in few mL of water under magnetic stirring. The obtained

mixture was then filtered and washed 3 times with cold water before drying under air.

### **COD, CaC<sub>2</sub>O<sub>4</sub>.xH<sub>2</sub>O**

A Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> aqueous solution (0.1 mol.L<sup>-1</sup>) and a CaCl<sub>2</sub> one (1.0 mol.L<sup>-1</sup>, Ca/Ox = 10) were prepared the day prior to the reaction and store between 2-6°C overnight. The solution of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added dropwise to the CaCl<sub>2</sub> one in an ice bath (T < 4°C) under magnetic stirring. The obtained mixture was then filtered and washed 3 times with cold water before drying under air.

### **COT, CaC<sub>2</sub>O<sub>4</sub>.3H<sub>2</sub>O**

In an ice bath, two equimolar dilute (0.001 mol.L<sup>-1</sup>) aqueous solutions of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and CaCl<sub>2</sub> were slowly added simultaneously dropwise in few mL of water under vigorous magnetic stirring. The obtained mixture was then filtered and washed 3 times with cold water before drying under air.

All three components are obtained as white fine powders. COD and COT are rapidly stored between 2-6°C while COM can be stored at ambient temperature.

The synthetic calcium oxalate samples vibrational structures were probed using infrared transmission measurements at the infrared beamline AILES (Advanced Infrared Line Exploited for Spectroscopy), at SOLEIL Synchrotron.<sup>[10]</sup> The IR spectra in the 600 cm<sup>-1</sup> - 4000 cm<sup>-1</sup> range (4 cm<sup>-1</sup> resolution) were measured using a Bruker IFS125HR Fourier transform spectrometer equipped with a KBr beamsplitter and combined with a MCT detector. The interferometer was maintained under/at low pressure of 10<sup>-6</sup> mbar to avoid absorption by water and residual gas. The spectra of the synthetic calcium oxalate polyhydrates were obtained by measuring the signal transmitted in the far infrared (MIR) and by dividing by a reference provided by the signal measured through an opening of the same size as the sample. An average of 50 scans for both the sample and the reference were used to calculate the transmission (T). The absorbance (A) was then evaluated using the relation usual relation  $A = -\log T$ . All measurements were performed for samples cooled down between 8 and 5 K by use of a pulse tube cryostat, in order to obtain the very narrow vibrational bands comparable with those in the theoretically calculated spectra.

Raman spectra of synthetic calcium oxalate samples<sup>[11]</sup> were collected with a 0.5 cm<sup>-1</sup> spectral resolution on a “LabRam Evolution” microRaman spectrometer (Horiba, Japan) equipped with an Newton 971 EM-CCD detector (Andor, UK) using a 633 nm laser source (1.6 mW) and a 80 X objective (N.A. 0.75).

## References

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