

**Matrix-free synthesis of spin crossover micro-rods showing large hysteresis loop  
centered at room temperature**

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## I- Experimental section

### Materials:

All solvents and reagents were purchased from Sigma Aldrich and used without further purification.

**Synthetic procedure:** Samples **1** was prepared by rapidly mixing in a small glass tube (5 mL) two acidic aqueous solutions (3 wt%  $\text{CF}_3\text{SO}_3\text{H}$ ) containing  $\text{Fe}(\text{CF}_3\text{SO}_3)_2$  (236 mg; 0.33 mol/l) and the 1,2,4-triazole ligand (130 mg; 0.94 mol/l), respectively. The resulting 2 ml limpid solution was let for very slow evaporation at room temperature; the flask being half covered. Following *ca.* 2 months, the precipitate were centrifuged, and washed by 10 ml of distilled water and 30 ml of absolute ethanol and finally dried under vacuum. Yield: 300 mg (*ca.* 80%). Sample **2** was prepared as sample **1** but in absence of  $\text{CF}_3\text{SO}_3\text{H}$ . Yield: 54 mg (*ca.* 20%). Elemental analysis: calculated for sample **1**  $[\text{Fe}(\text{Htrz})_3](\text{CF}_3\text{SO}_3)_2 \cdot 1.2\text{H}_2\text{O}$ : C 16.47 %, H 1.95 %, N 21.61 %; measured: C 16.41 %, H 1.60 %, N 22.30 %. Elemental analysis: calculated for sample **2**  $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{CF}_3\text{SO}_3)$ : C 20.43 %, H 1.95 %, N 30.65 %; measured: C 19.03 %, H 1.41 %, N 28.07 %.

### Size and physical measurements

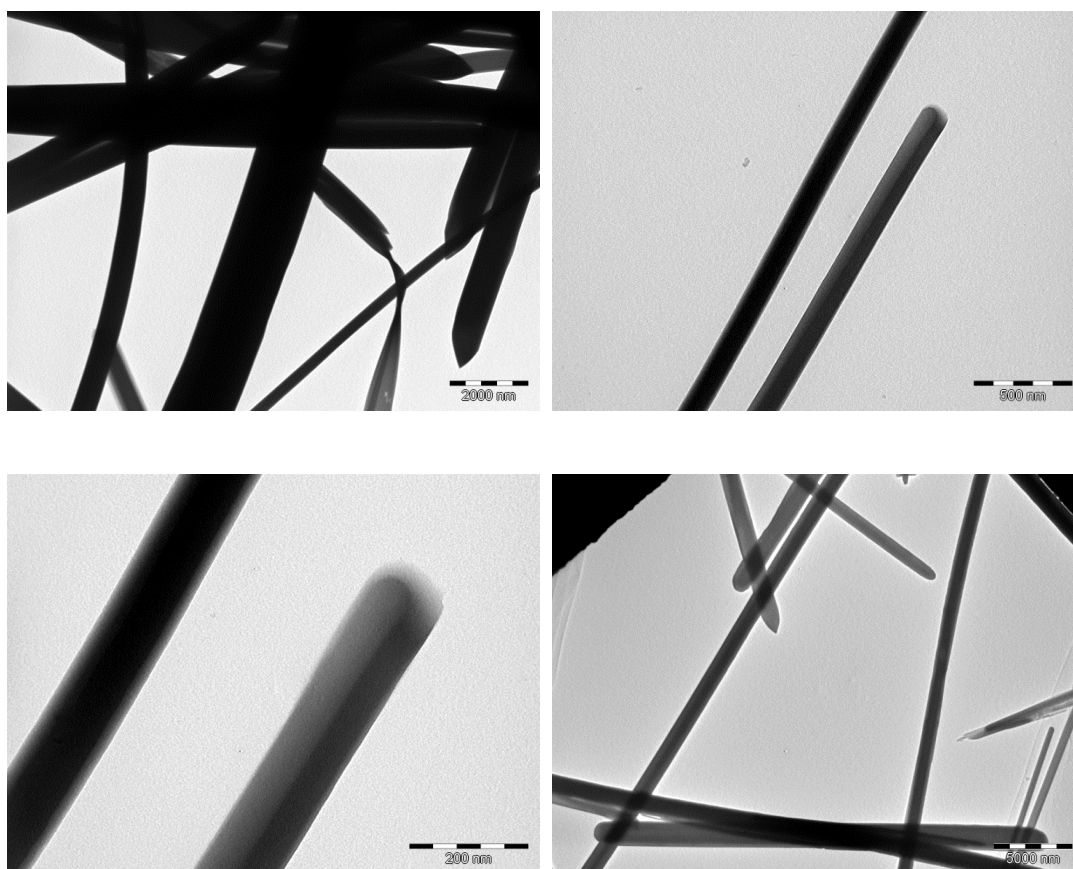
Particle sizes were determined by transmission electron microscopy (TEM) using a JEOL JEM-1011 (100 kV) and by scanning electron microscopy using a JEOL FEG JSM 6700F. High-resolution imaging was performed on a JEOL JSM 2100F (200 kV) equipped also with a SDD Bruker EDX detector (resolution: 127 eV) for elemental analysis. TEM samples were prepared by placing on a carbon coated copper grid a drop (10  $\mu\text{l}$ ) of the particles suspended in ethanol.

FTIR spectra were recorded at room temperature with a Perkin Elmer Spectrum 100 spectrometer in ATR mode (resolution *ca.* 1 cm<sup>-1</sup>) between 650 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>. Variable temperature Raman spectra were acquired using a LabramHR (Horiba) Raman microspectrometer (resolution *ca.* 3 cm<sup>-1</sup>) in conjunction with a Linkam THMS600 cryostage. The 632.8 nm line of a HeNe laser (0.1 mW) was focused on the sample by a  $\times 50$  objective (numerical aperture = 0.5), which was also used to collect the scattered photons. Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer at heating and cooling rates of 2 K·min<sup>-1</sup> at a magnetic field of 1 kOe. Optical reflectivity ( $\lambda=550$  nm) measurements were performed at 4 K·min<sup>-1</sup>. Zero-field <sup>57</sup>Fe Mössbauer spectra were recorded using a flow-type liquid nitrogen cryostat and a conventional constant acceleration type Mössbauer spectrometer.  $\gamma$ -rays were provided by a <sup>57</sup>Co(Rh) source (*ca.* 20 mCi). The samples (~30 mg) were enclosed in a plexiglass sample holder with an optimized diameter. The spectrum evaluations were done with the assumption of Lorentzian line shapes using the Recoil software. The PXRD patterns of the samples have been recorded at room temperature using a Panalytical MPD XPertPro powder diffractometer [CuK $\alpha$ 1, Ge (111) monochromator, X'Celerator detector] within the range 5 - 80° (2 $\theta$ ) by using a scan speed of 30° per hour. UV spectroscopy was recorded using UV/Vis spectrophotometer equipped with a Labsphere RSA-PE-20 integrating sphere.

## II- Electron Microscopy

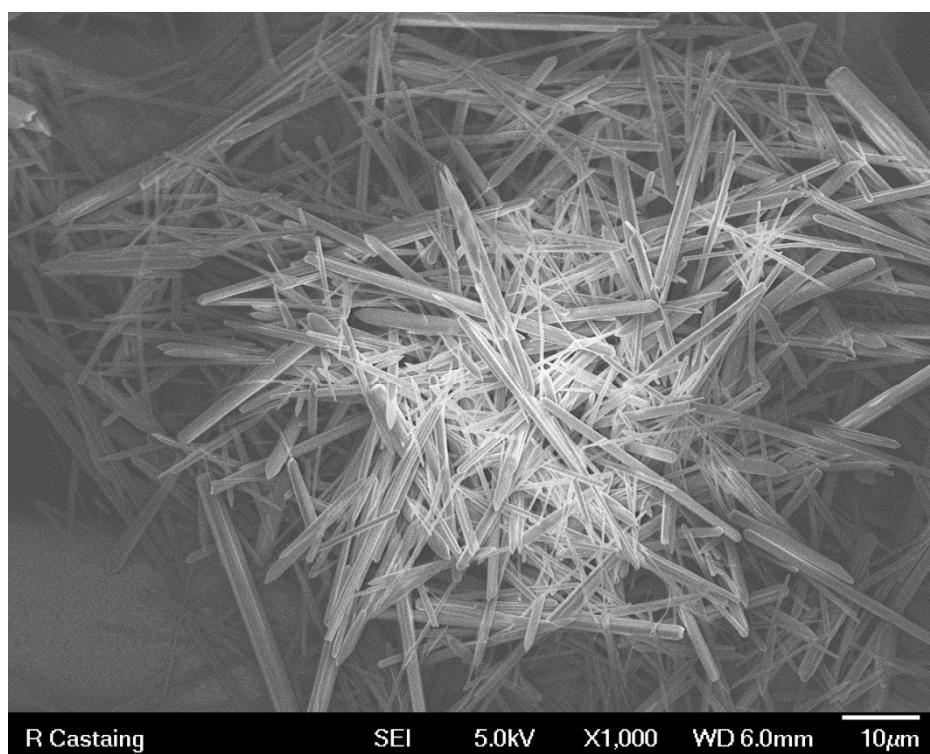
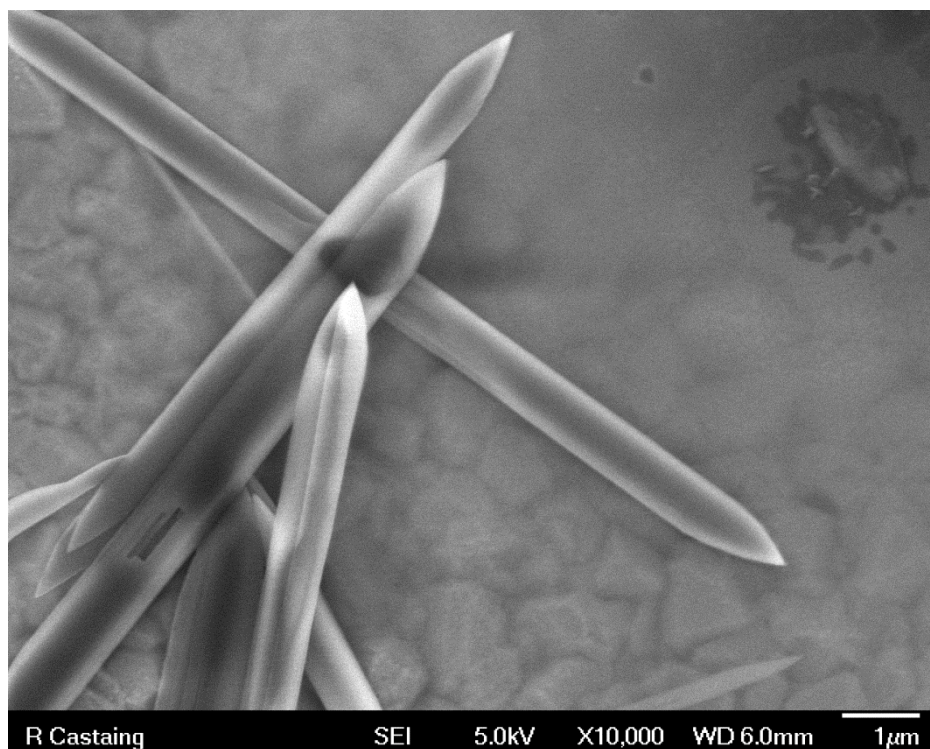
Transmission Electronic Microscopy (TEM), Scanning Electronic Microscopy (SEM), High Resolution Transmission Electronic Microscopy (HRTEM), High Resolution Scanning Transmission Electronic Microscopy (HRSTEM) and Energy Dispersive X-ray spectroscopy (EDX) analyses of micro-rods

**Figure S1:** TEM images for sample 1

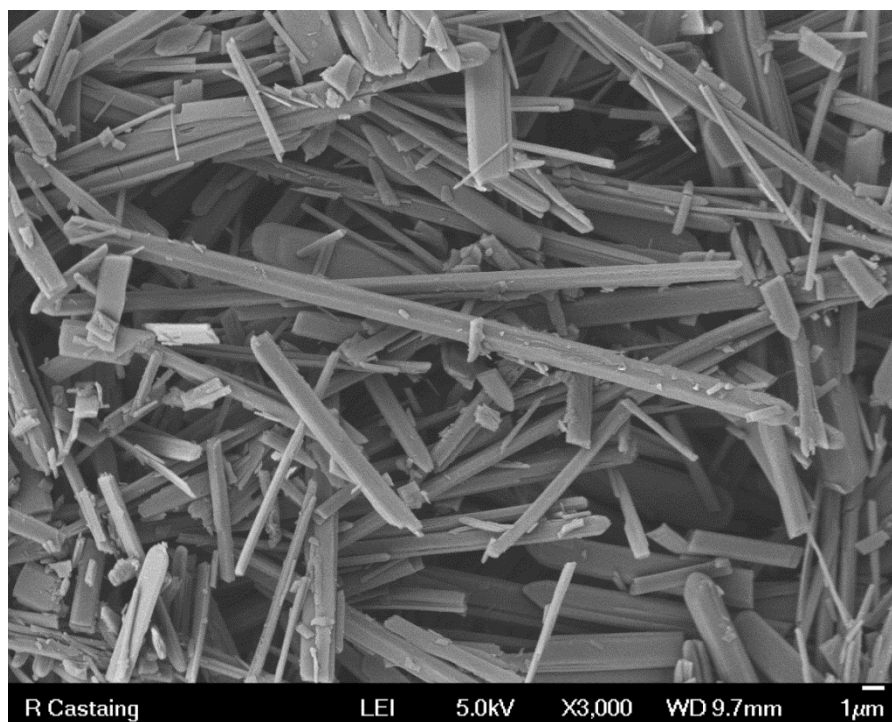
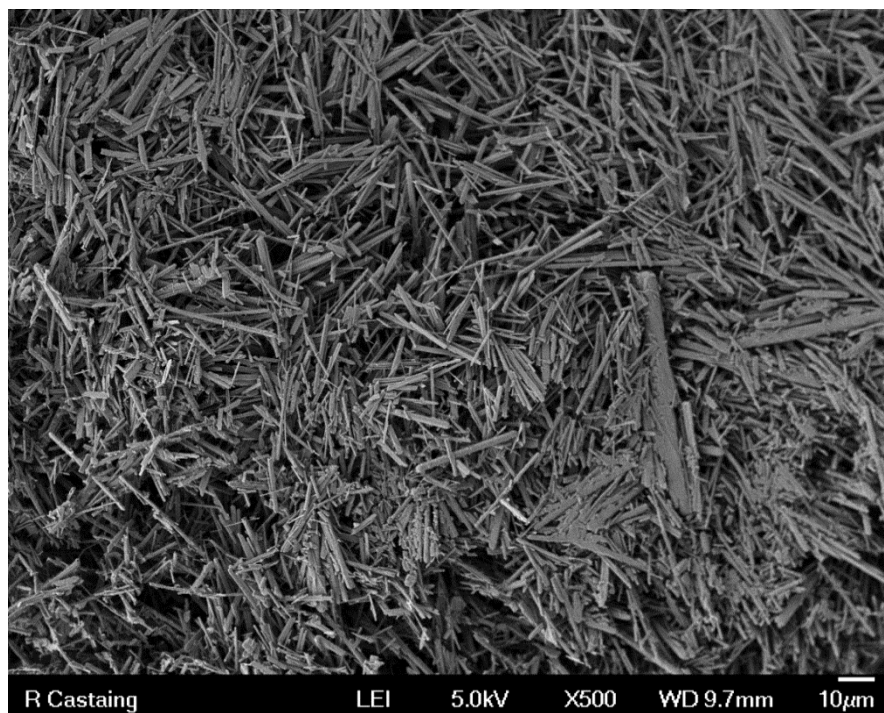


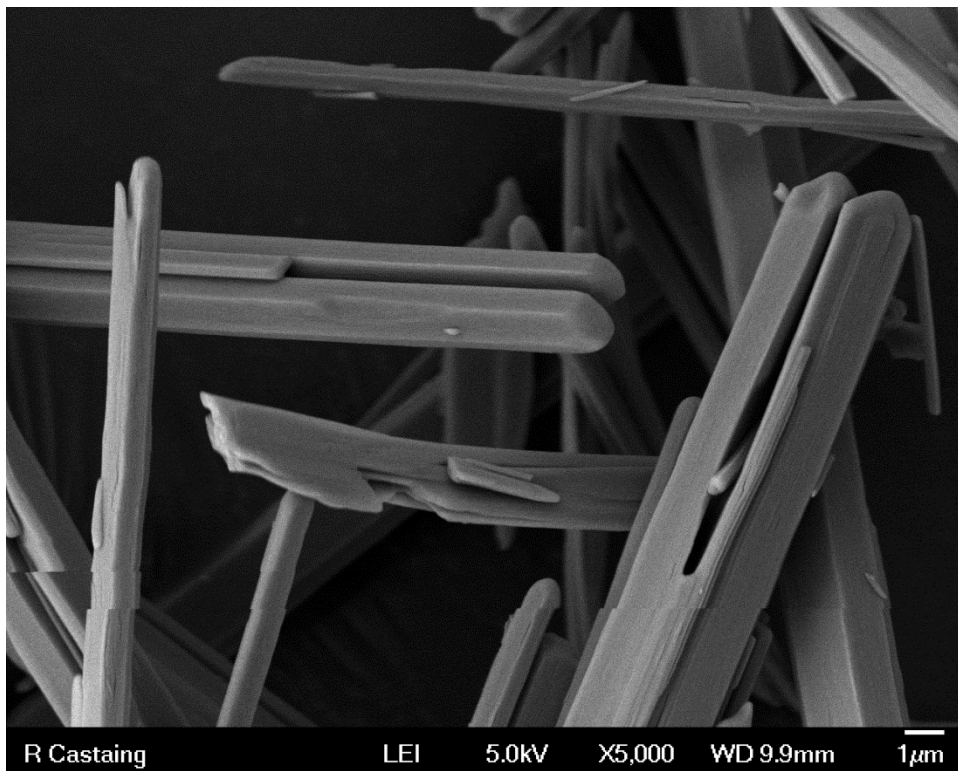
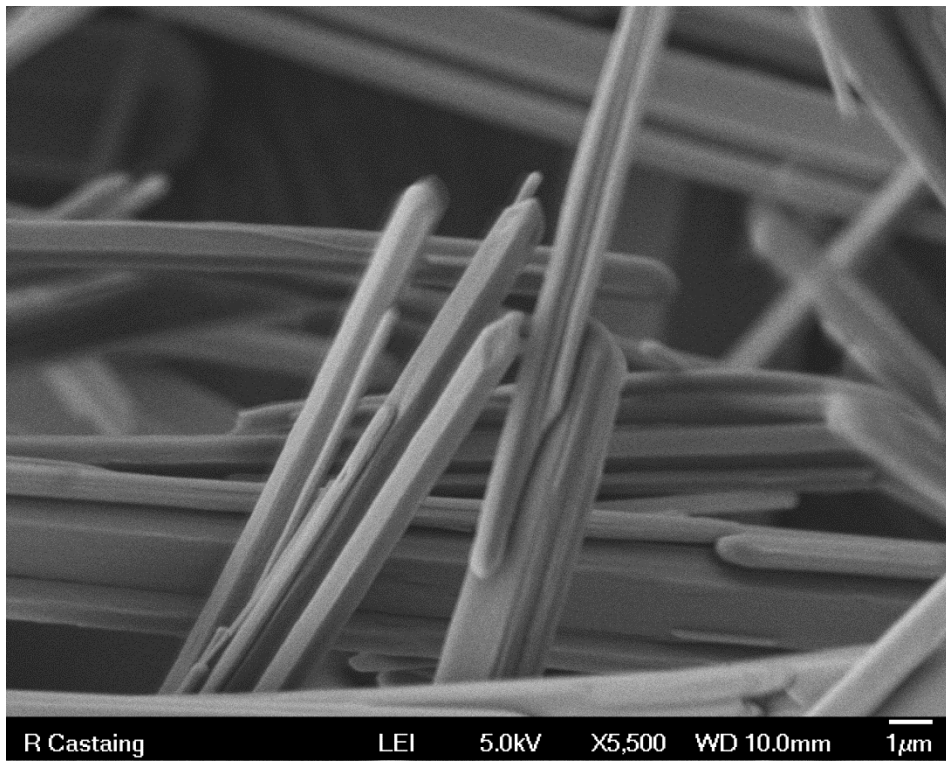
**Figure S2:** SEM images of sample 1

The following two SEM pictures were realized without any additional conductive film



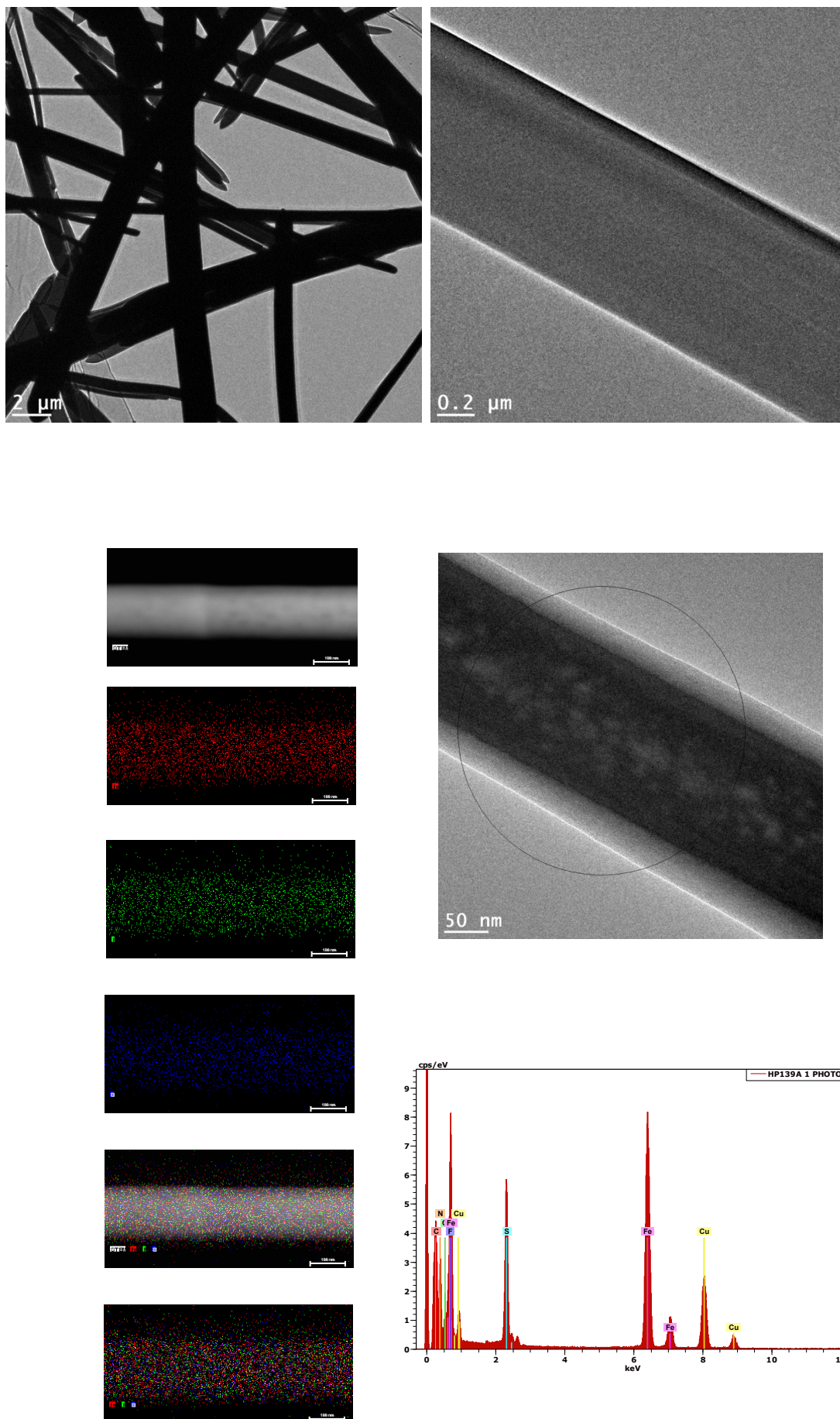
The following four SEM pictures were realized with an additional conductive Platinum film







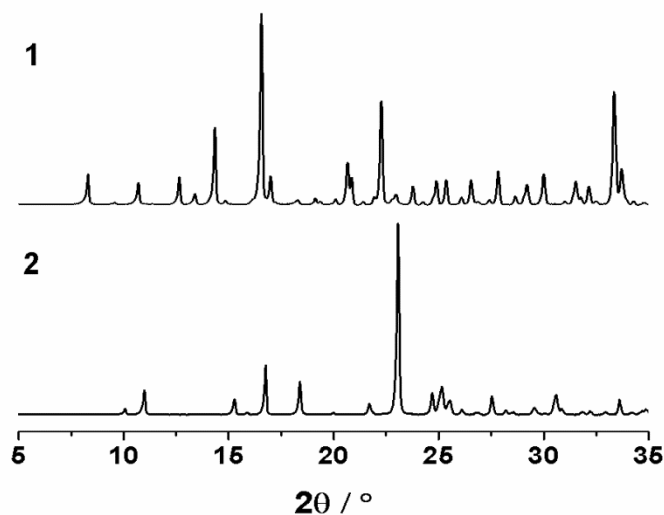
**Figure S3:** HRTEM and EDX analyses of sample 1





### III- Powder X-ray diffraction

**Figure S4:** X-ray powder diffraction patterns of sample **1** and **2** at room temperature (HS state)

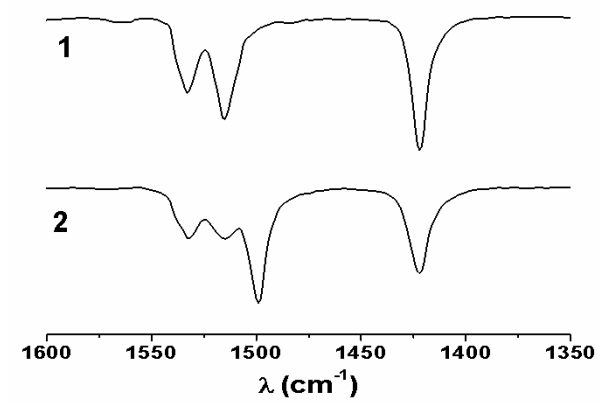


X-ray diffraction allows also for the estimation of the crystallite size using the Scherrer equation. The crystallite size ( $D$ ) can be calculated using the equation  $D = k\lambda/\beta \cos\theta$ , where  $k$  is the shape factor,  $\lambda$  the wavelength of the incident irradiation,  $\beta$  is the full-width at half maximum (FWHM) of the peak and  $\theta$  is the Bragg angle. In the Scherrer equation, the  $\beta$  parameter needs to be corrected to eliminate the instrumental effects; in our case this correction was achieved measuring a  $\text{LaB}_6$  reference sample. The average crystallite size for both samples was measured at about 80 nm

**Reference:** Scherrer, P. *Göttinger Nachrichten Math. Phys.* **2**, 98–100 (1918).

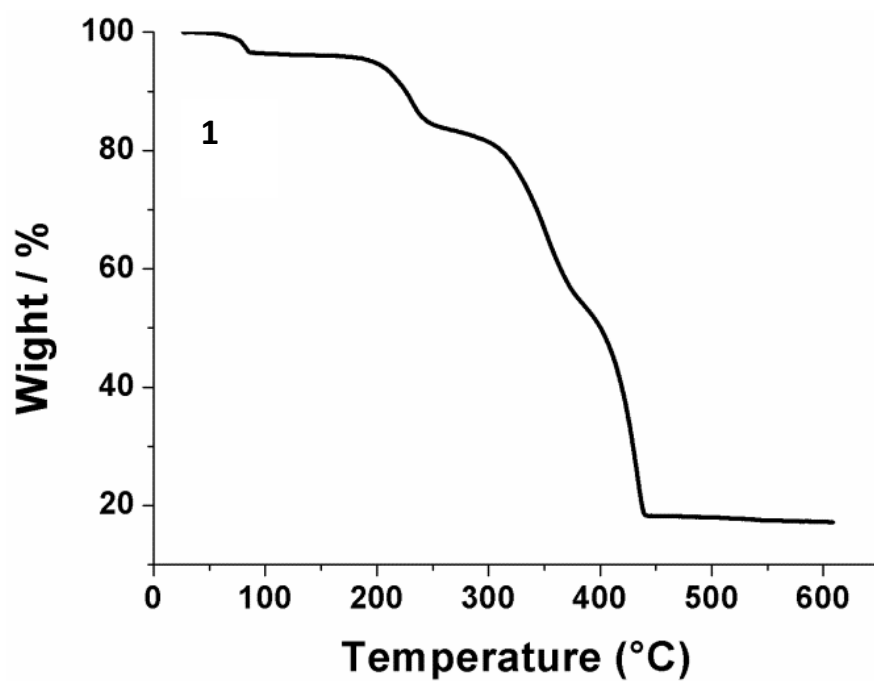
#### IV- Infrared Spectroscopy

**Figure S5:** Selected infrared absorption spectra of samples **1** and **2** recorded at room temperature.

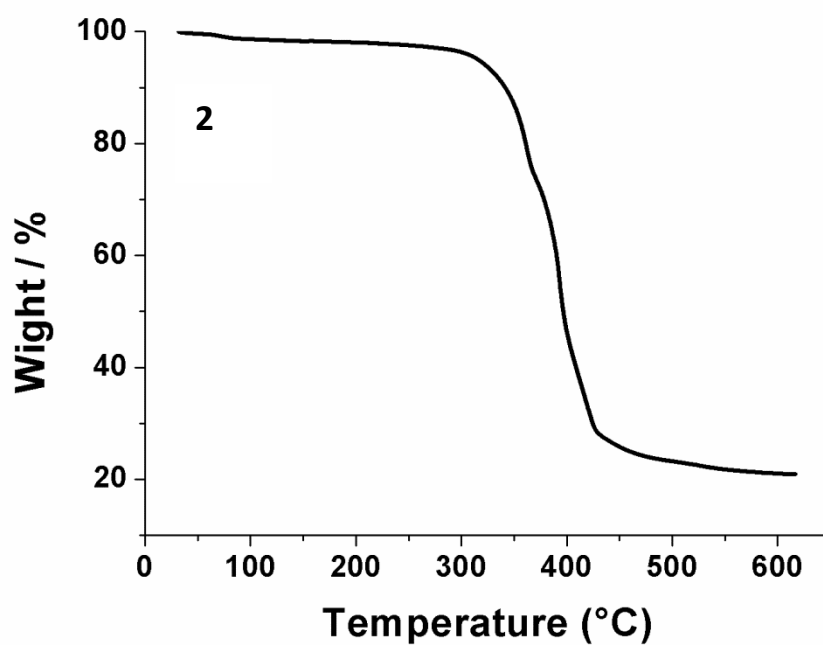


## V- TGA analyses

Figure S6: TGA analysis of sample 1 and 2

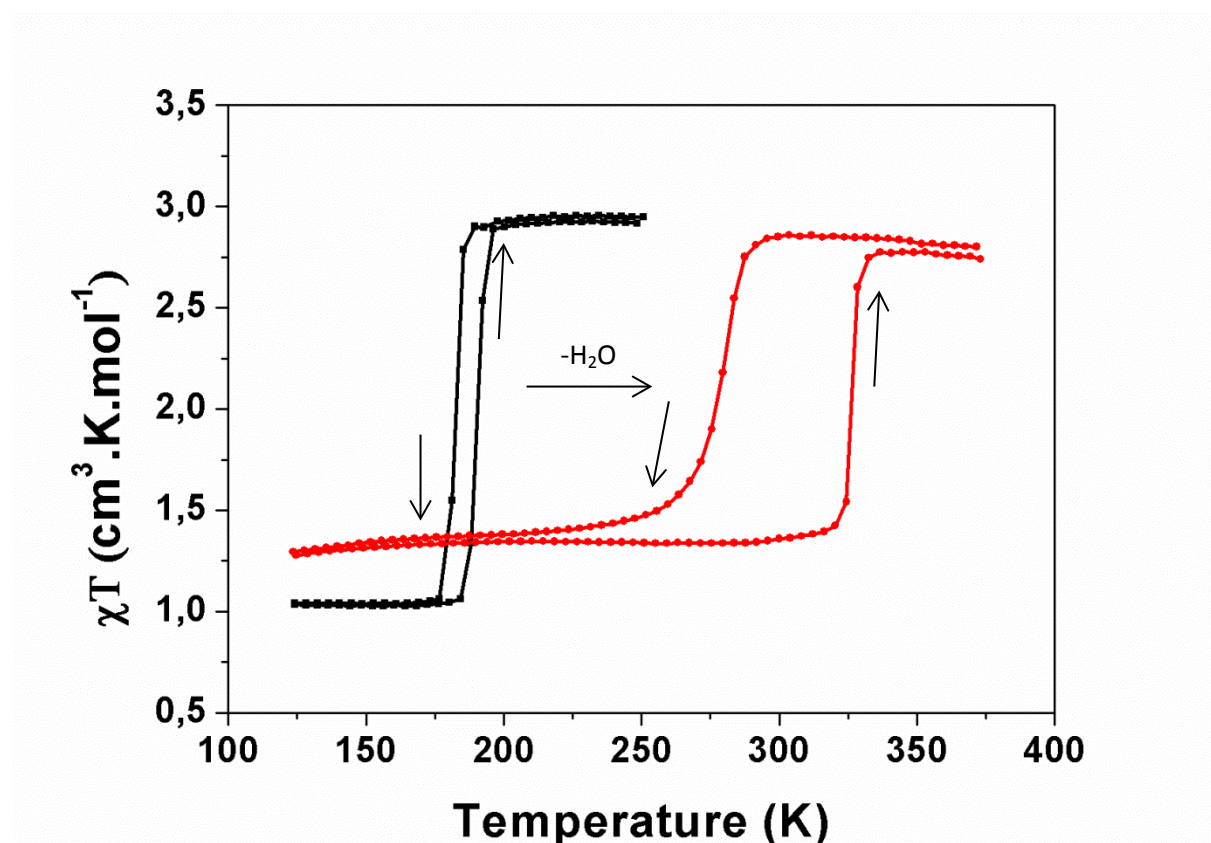


The weight loss is 4.1% ( $1.2.H_2O$ ) for the first step and 13, 28 and 37% for the following steps (decomposition of the compound).

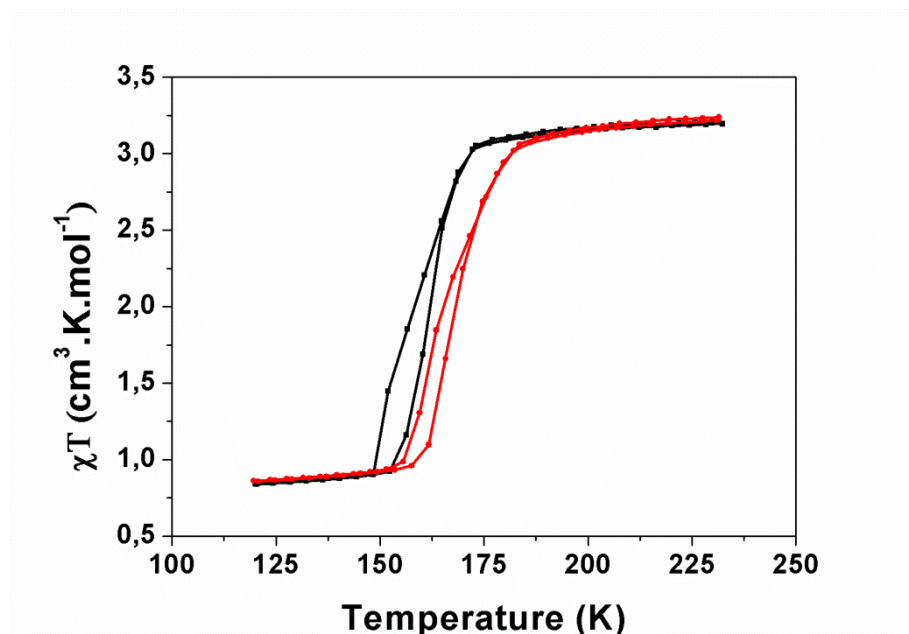


## VI- Magnetic measurements

**Figure S7:** Magnetic measurements for sample **1** (hydrated sample in black and dehydrated sample in red).

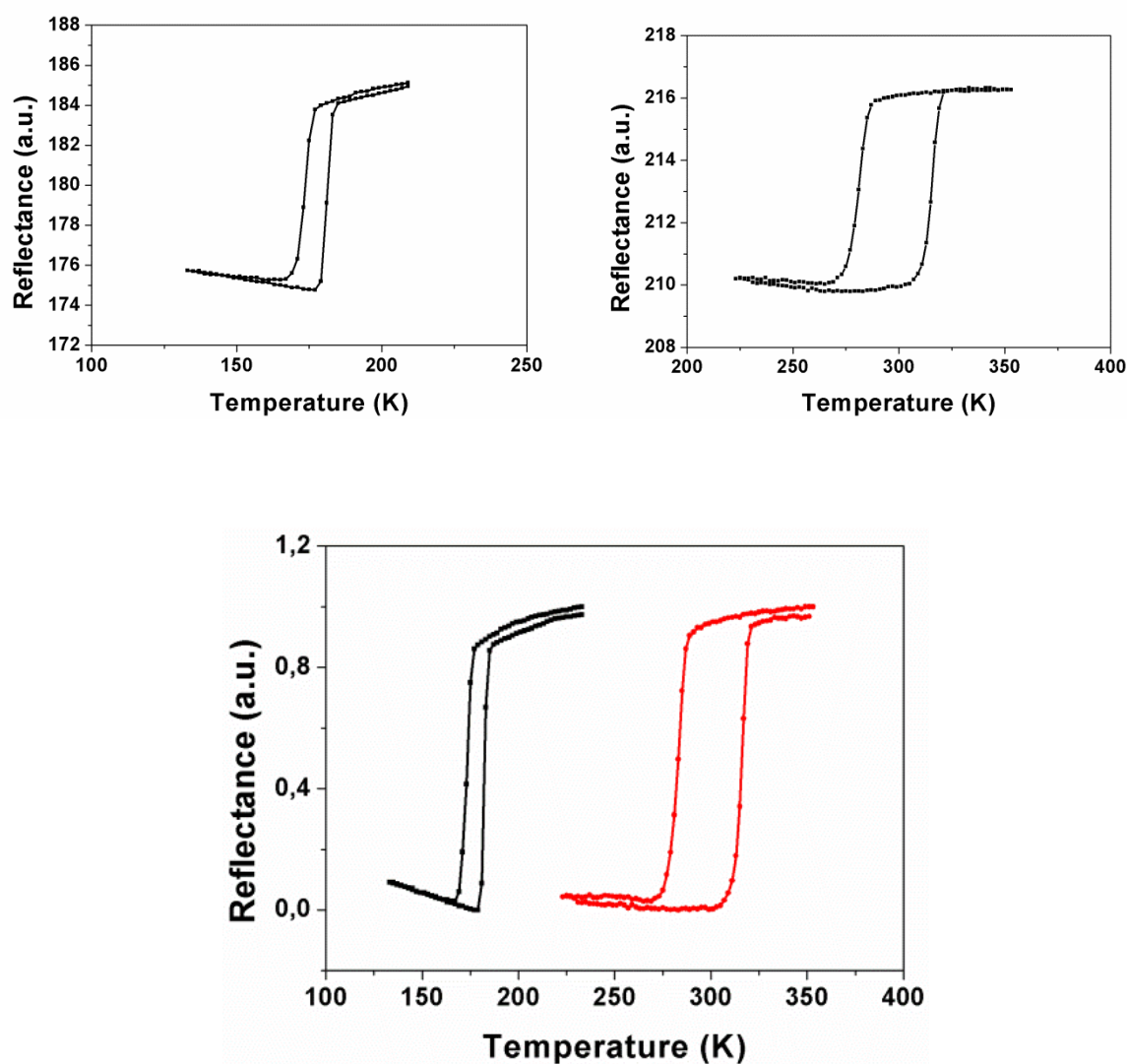


**Figure S8:** Magnetic measurements for sample **2** ( $\lambda=550$  nm, two consecutive thermal cycles).



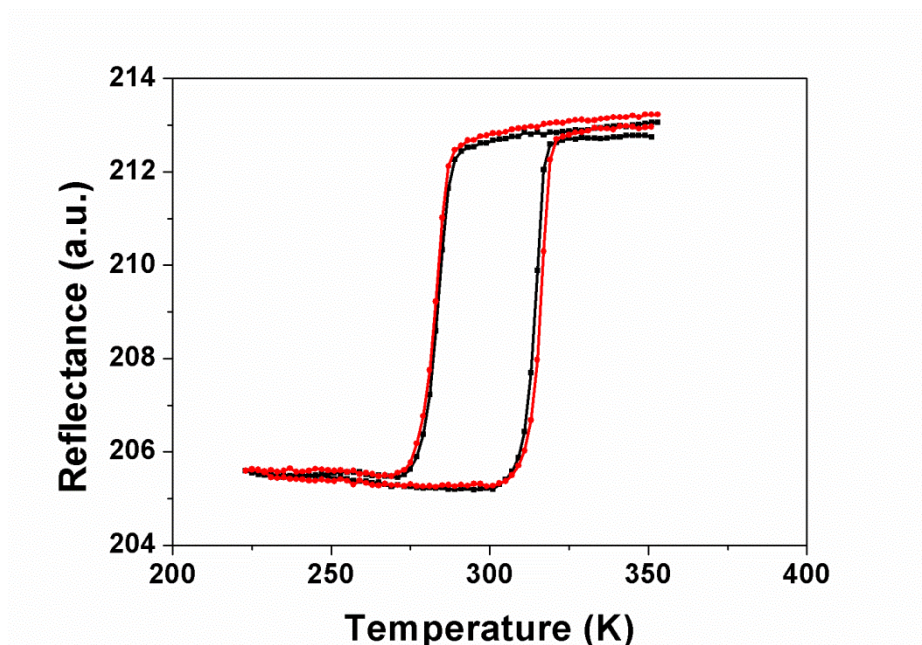
## VII- Reflectivity measurements

**Figure S9:** Optical reflectivity measurements of sample **1** ( $\lambda=550$  nm). Hydrated sample (left), dehydrated sample (right) and the corresponding normalized measurements (the two consecutive cycles were not measured at the same position).

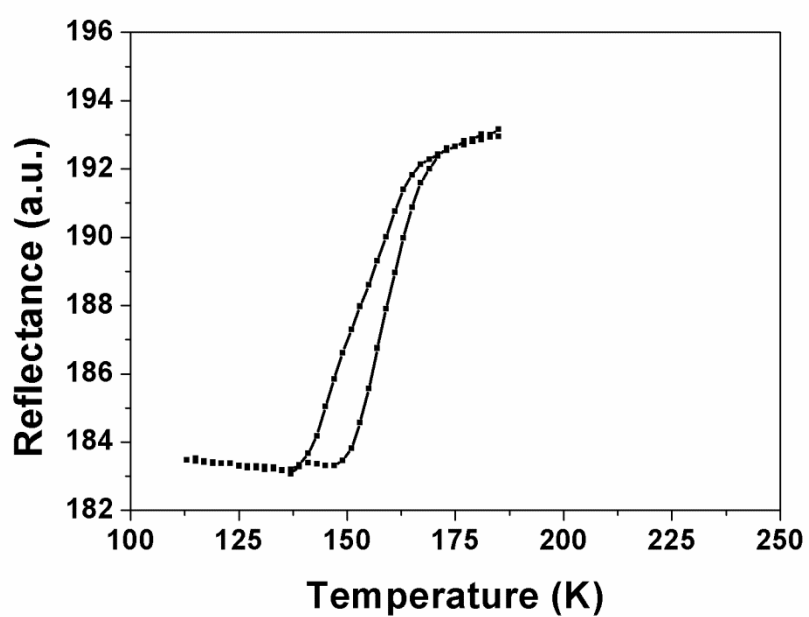




**Figure S10:** Optical reflectivity measurements for testing the hysteresis reproducibility of sample 1 ( $\lambda=550$  nm, in black cycle 1 and in red cycle 10).

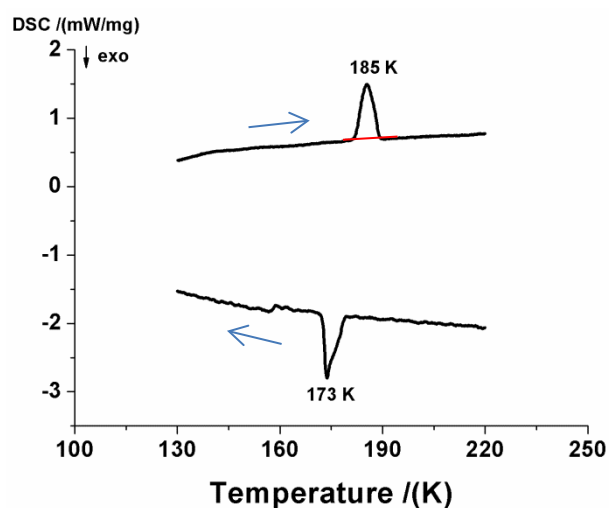


**Figure S11:** Optical reflectivity measurements of sample 2 ( $\lambda=550$  nm).

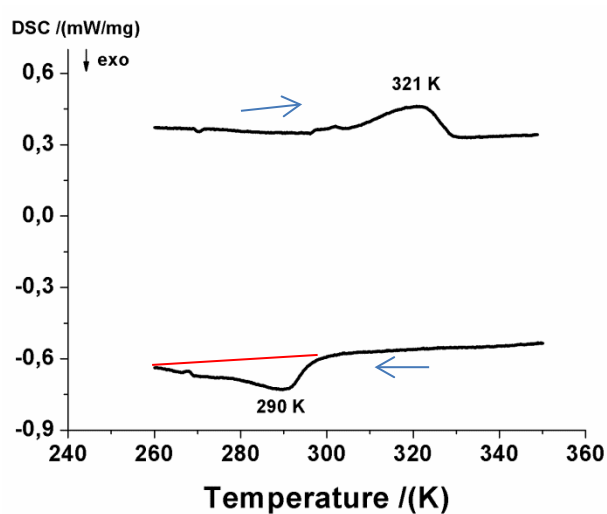


## VIII- DSC measurements

**Figure S12:** DSC measurements of the hydrated sample **1** on heating/cooling modes



**Figure S13:** DSC measurements of the dehydrated sample **1** on the heating/cooling modes



Calculation for the dehydrated sample

$$\text{Area} = 17.05 \text{ J/g}$$

$$\Delta H = 9.5 \text{ KJ/mol (with } M = 563 \text{ g/mol)}$$

$$\Delta S = \Delta H/T_{1/2} = 32 \text{ J/mol}\cdot\text{K (with } T_{1/2} = 290 \text{ K)}$$

The residual HS fraction at low temperature is ca. 30%, so the estimated  $\Delta H$  and  $\Delta S$  associated with the complete SCO are 12 KJ/mol and 43 J/mol·K, respectively.

## IX- $^{57}\text{Fe}$ Mössbauer measurements

**Figure S14:** Variable temperature Mössbauer measurements of the dehydrated sample **1**

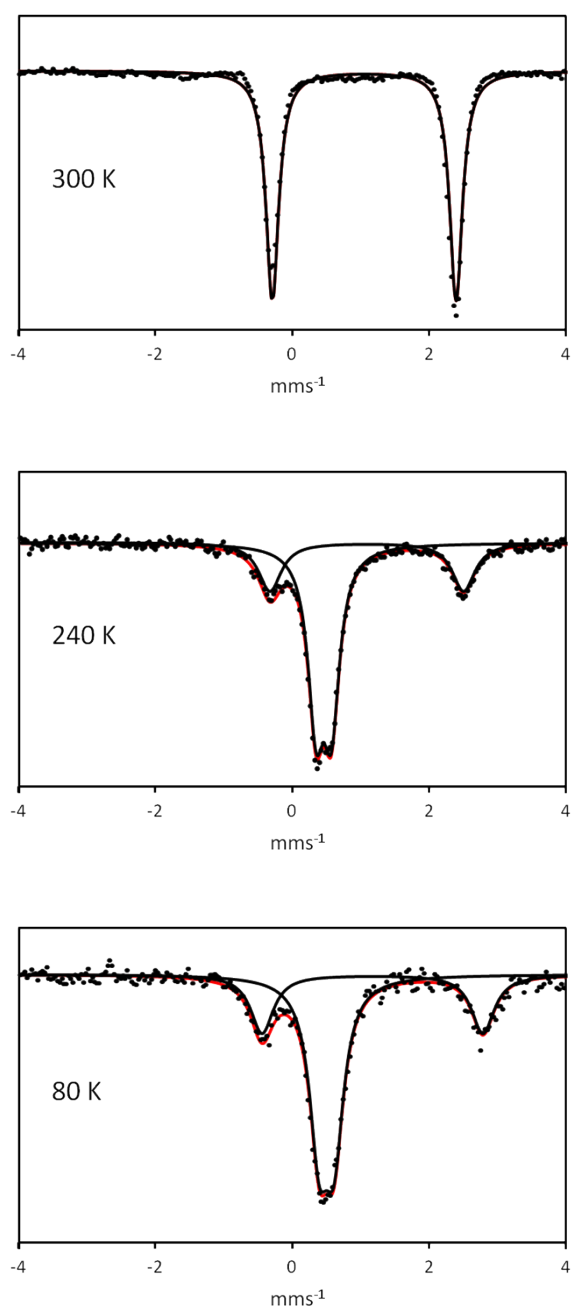
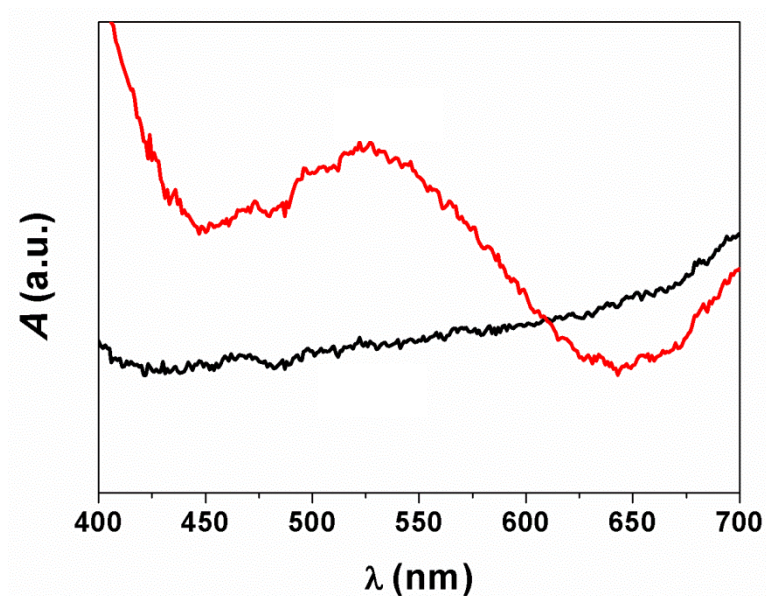


Table of the Mössbauer hyperfine parameters ( $\delta$  = isomeric shift,  $\Delta E_Q$  = quadrupole splitting,  $\Gamma/2$  = half width at half maximum)

| Sample 1 | HS state |              |            | LS state |              |            | HS fraction |
|----------|----------|--------------|------------|----------|--------------|------------|-------------|
|          | $\delta$ | $\Delta E_Q$ | $\Gamma/2$ | $\delta$ | $\Delta E_Q$ | $\Gamma/2$ |             |
| 300 K    | 1.05(80) | 2.68(16)     | 0.11(12)   |          |              |            | 100%        |
| 240 K    | 1.09(13) | 2.83(25)     | 0.20(21)   | 0.46(35) | 0.23(63)     | 0.14(58)   | 29%         |
| 80 K     | 1.17(16) | 3.23(32)     | 0.20(27)   | 0.50(59) | 0.22(13)     | 0.17(11)   | 30%         |

## X- UV Spectroscopy

**Figure S15:** Reflectance UV spectroscopy of the dehydrated sample **1** at 300 K following cooling (red curve) and heating (black curve) process.



Both measurements in the LS and HS states were performed at room temperature (within the hysteresis loop). The sample was heated or cooled out of the UV-Visible setup using an oven or liquid nitrogen.