

## **Spin-Crossover Coordination Nanoparticles**

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**Spin crossover coordination nanoparticles of the cyanide bridged three dimensional network Fe(pyrazine){Pt(CN)<sub>4</sub>} were prepared at three different sizes using microemulsion. The 14 nm particles present a transition centered around 265 K with a hysteresis of 6 K.**

*Synthetic procedure* : Two reverse microemulsions of  $w = [\text{H}_2\text{O}]/[\text{AOT}] = 10$  (NaAOT is sodium bis(2-ethylexyl sulfosuccinate)) were prepared separately, one containing  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  and pyrazine and the other containing  $\text{K}_2\text{Pt}(\text{CN})_4$ . To 3 mL of  $\text{K}_2\text{Pt}(\text{CN})_4$  aqueous solution (0.08 M), 33 mL of 0.5 M NaAOT in heptane was added, and the biphasic system was stirred until a clear microemulsion was obtained. The same procedure was applied to 3 mL of a 0.08 M aqueous solution of  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  with 10 equivalent of pyrazine. The two microemulsions were then cooled in an ice bath and mixed. The mixture's color changes from yellow to orange. After 10 minutes of stirring, 9 equivalents relative to the iron of *p*-nitrobenzylpyridine in 9 mL of EtOH were added to the reaction mixture. The resulting flocculate was centrifuged, washed with 50 mL of acetone and then dried under vacuum. This led to sample **2**.

*Elemental analysis* combined with *thermogravimetric studies* (Figure S4) leads to the following percentages: Exp Fe 10.59 Pt 35.34 C 26.27 H 2.26 N 15.87, Calc for  $\text{Fe}\{\text{Pt}(\text{CN})_4\}(\text{C}_4\text{N}_2\text{H}_4)_{0.55}(\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2)_{0.45} \cdot 2.7\text{H}_2\text{O}$  Fe 10.29 Pt 35.96 C 25.48 H 2.22 N 15.48. Sample **1** was obtained by the same procedure but with a concentration in metal ions of 0.14 M : Exp Fe 9.76 Pt 32.77 C 29.78 H 2.57 N 14.90, Calc for  $\text{Fe}\{\text{Pt}(\text{CN})_4\}(\text{C}_4\text{N}_2\text{H}_4)_{0.28}(\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2)_{0.77} \cdot 3.1\text{H}_2\text{O}$  Fe 9.32 Pt 32.56 C 28.84 H 2.52 N 14.25.

*Analysis of the magnetic data with relation to the particles' size*: The bulk compound undergoes almost complete HS towards LS transition upon cooling down since the  $\chi_{\text{MT}}$  value is equal to  $0.16 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at low temperature. This is not the case for the nanoparticle' samples. The  $\chi_{\text{MT}}$  values for samples **1** and **2** are equal to 1.6 and  $1.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  respectively ; which correspond to a low temperature remaining HS fraction of 34 and 45 % for **1** and **2** respectively. The smallest particles possess the largest residual HS sites which correspond to what is expected from surface effect assuming that part or all of the peripheral complexes remain in the HS state. It is possible to estimate the percentage of peripheral Fe(II) ions within a particle providing the size of the particles is known. In the present case, the study of largest particles (Fig. S1c) indicate platelet like particles with a thickness much

smaller than the two other directions. Thus, only when the thickness is known, a quantitative analysis is possible. It is however possible to calculate the thickness assuming that all the peripheral Fe(II) ions remain in the HS state. Considering the cubic structure of the compound and knowing that the Fe–Fe distances within the PtFe plane is 1 nm and between the planes is equal to 0.7 nm, one can easily compute the fraction of surface metal ions and extract the thickness using the magnetic data. We find the following dimension for the particles : 14.7x14.7x5 nm and 7.7x7.7x3 nm. This of course has to be confirmed by three dimensional imaging of the nanoparticles.

At any rate, Mossbauer studies are underway to quantify the HS and LS fractions at different temperatures.

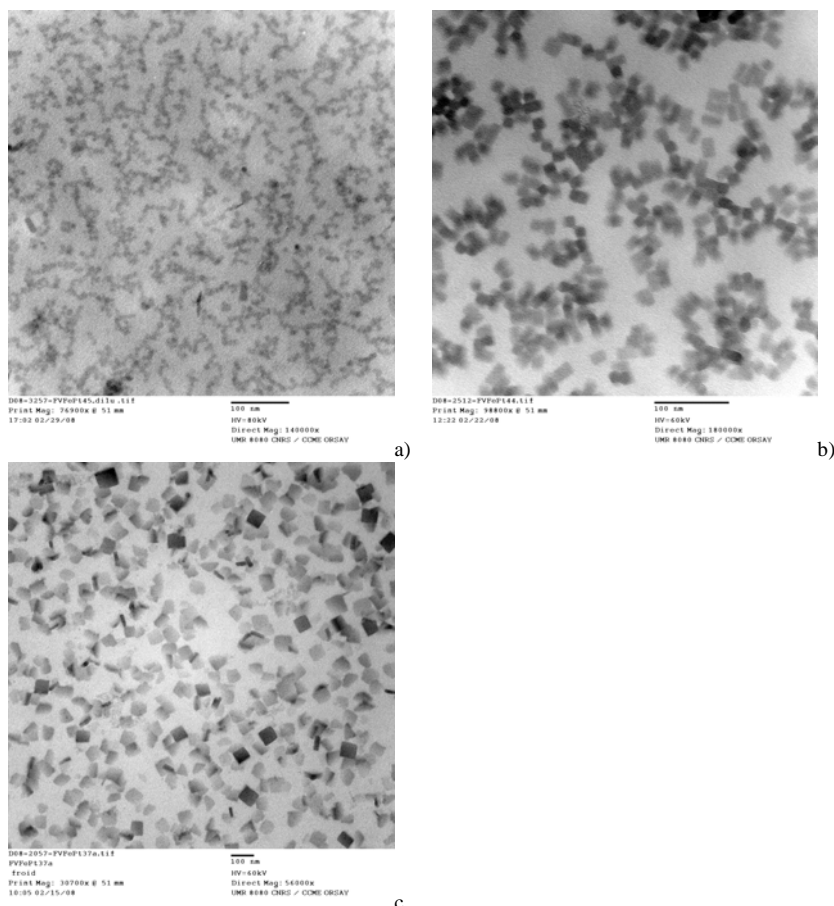


Figure S1. TEM images of nanoparticles obtained from three different concentration of the metallic salt precursors : 0.14(a), 0.08 (b) and 0.02 M (c).

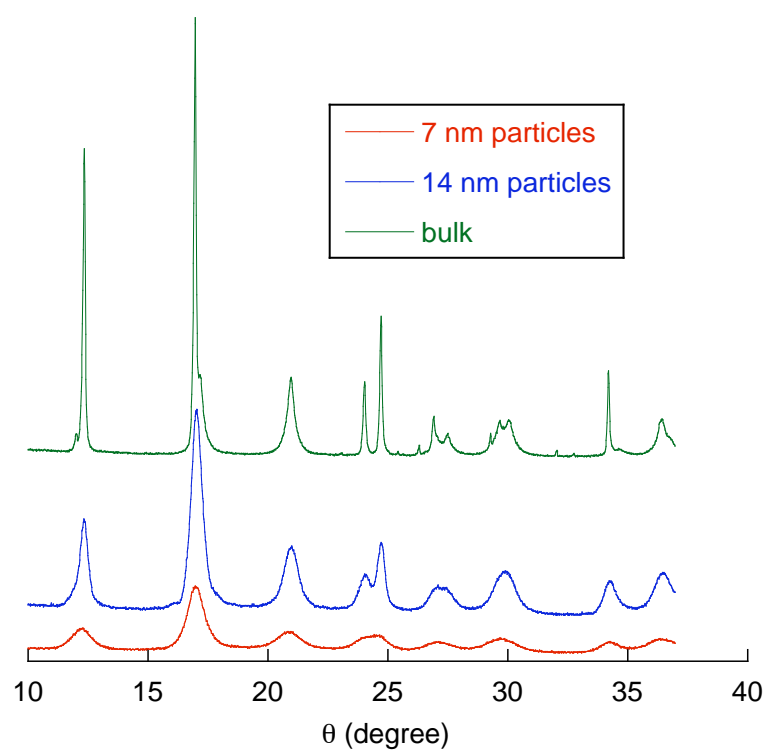


Figure S2. X-ray powder diffraction diagrams for the nanoparticles compared to the bulk sample.

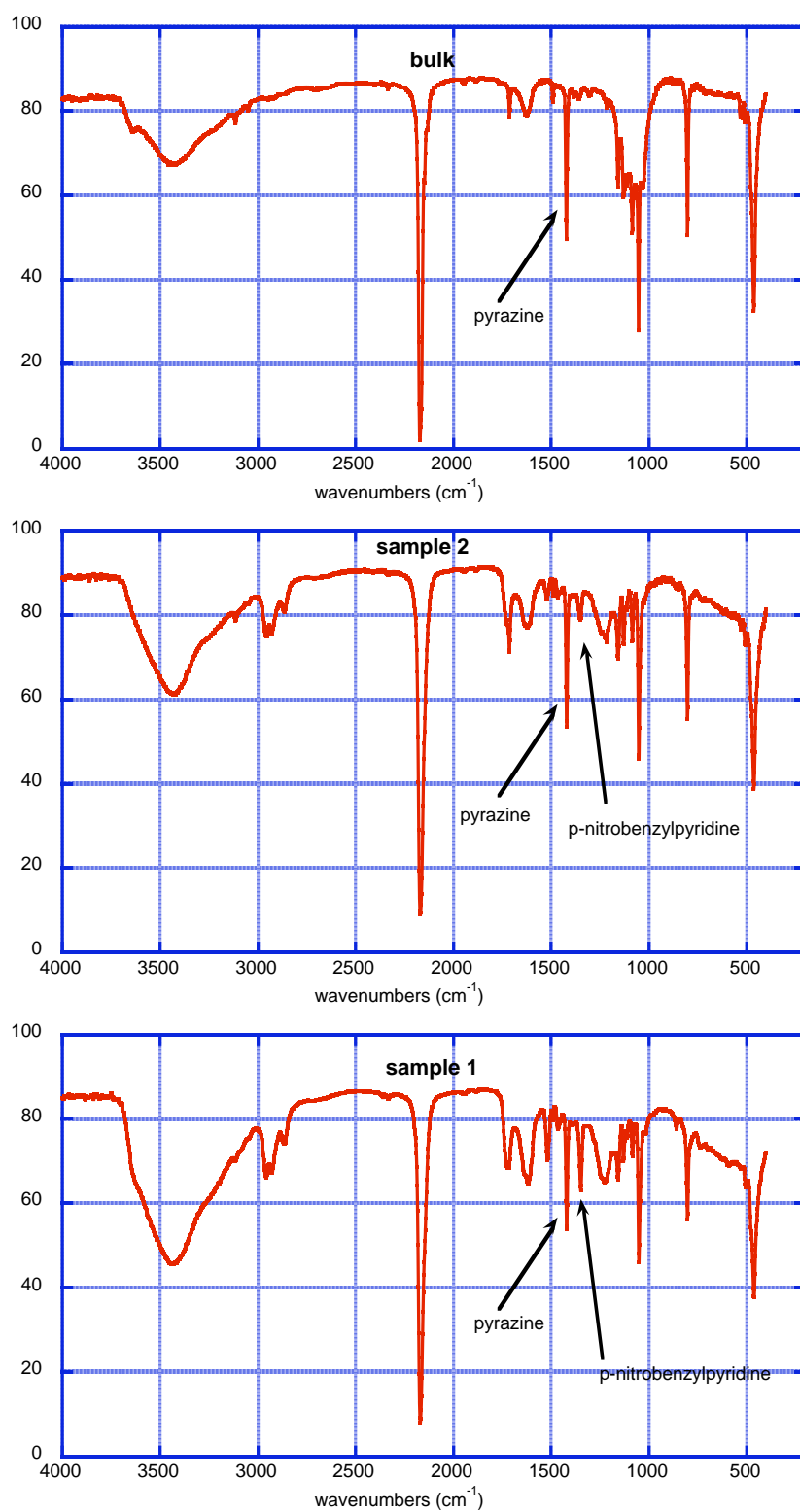


Figure S3. Infra-red spectra of the bulk compound (top), the 14 nm particles (middle) and the 7 nm particles (bottom).

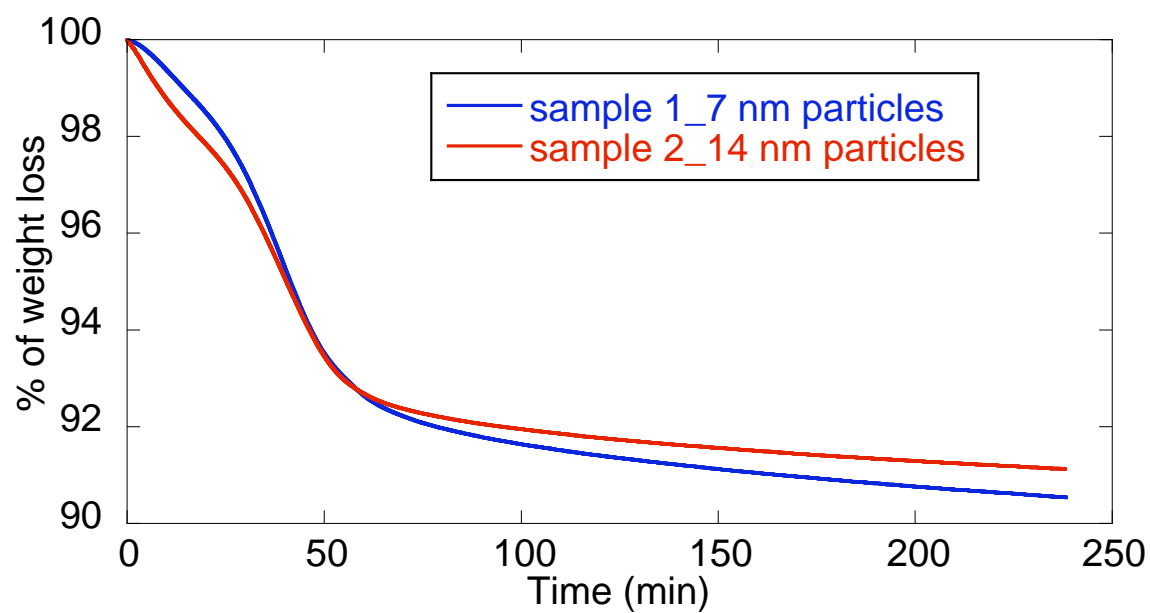
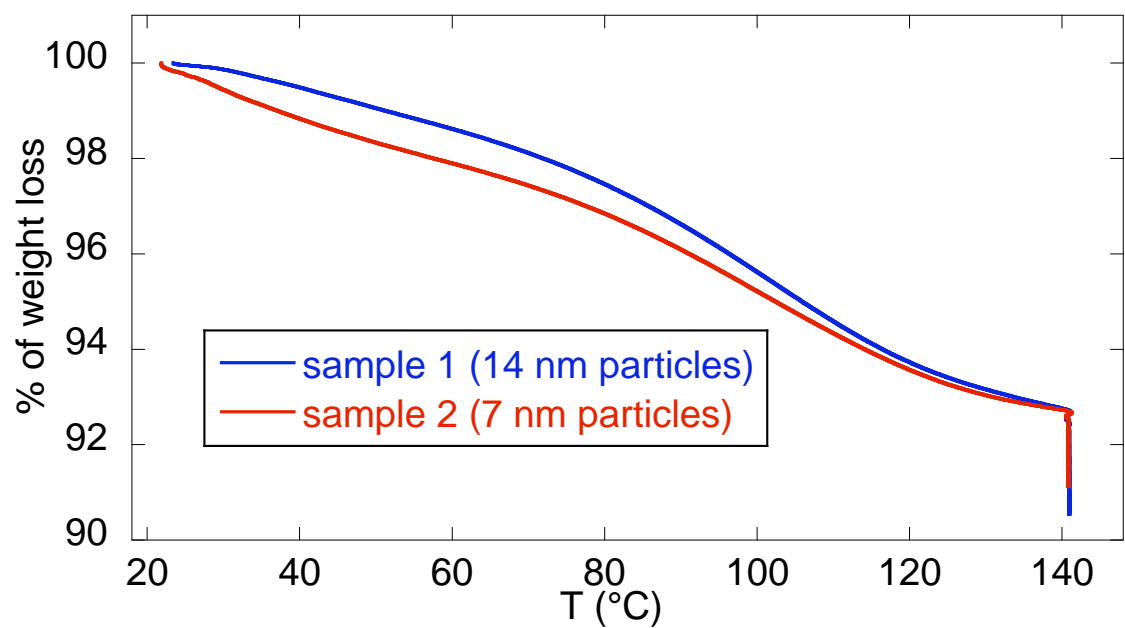


Figure S4. Variation of the percentage of weight loss versus temperature (top) and time (bottom) for **1** and **2**.

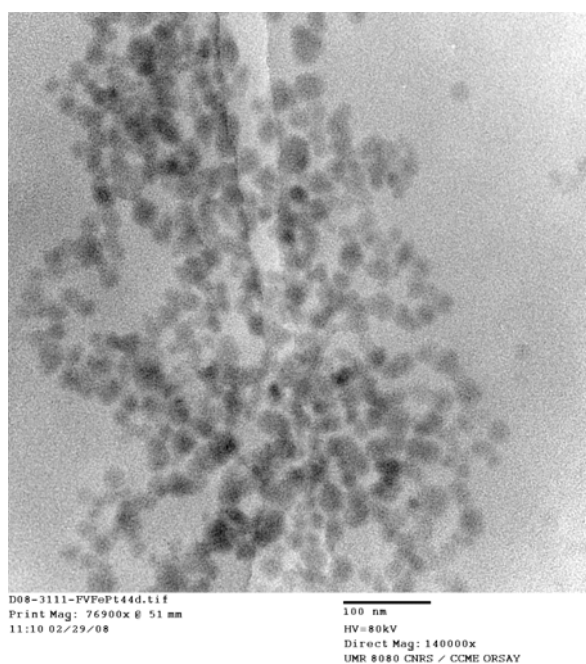


Figure S5. TEM image of the 14 nm particles dispersed in DMF

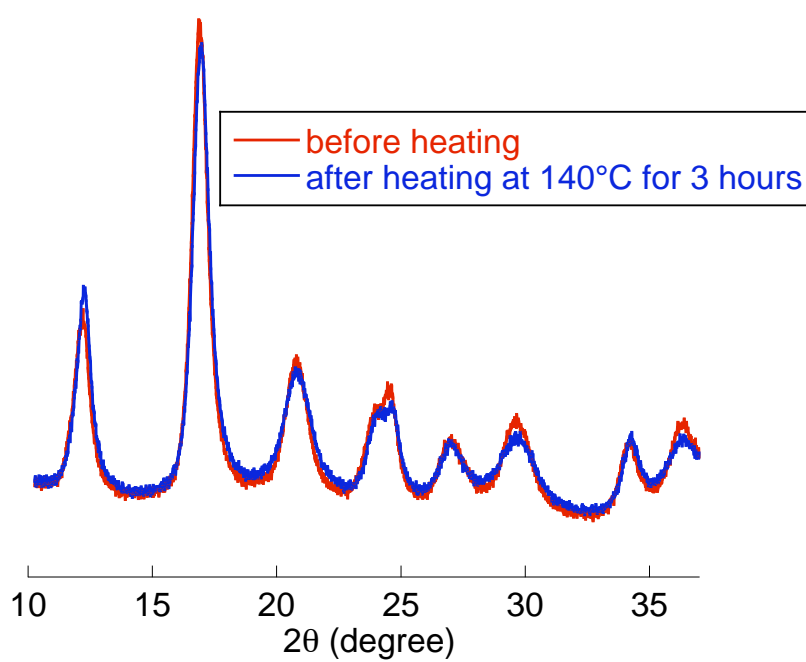


Figure S6. XRPD diagrams of the sample **1** before and after the heating process