

## Downsizing the switchable Prussian blue analog $\text{Rb}^I_x\text{Mn}^{II}[\text{Fe}^{III}(\text{CN})_6]_{(2+x)/3}\cdot z\text{H}_2\text{O}$ (RbMnFe) for magnetic properties and optical nonlinearities at the nanoscale

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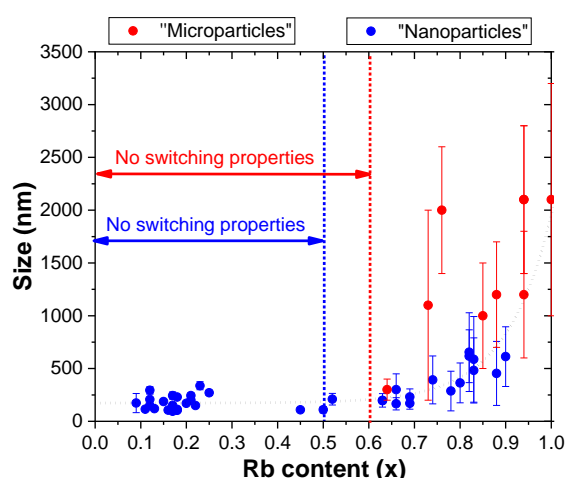
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Rubidium Manganese hexacyanoferrate,  $\text{Rb}^I_x\text{Mn}^{II}[\text{Fe}^{III}(\text{CN})_6]_{(2+x)/3}\cdot z\text{H}_2\text{O}$  (RbMnFe), one of the Prussian blue analogues, is an interesting material with multifunctional properties arising from the electron transfer between the  $\text{Mn}^{II}$  and the  $\text{Fe}^{III}$ . This electron transfer can be triggered by external stimuli such as temperature, light, pressure, and electrical field and is associated to a change in the properties with memory effect around room temperature over 100 K range. At low temperature, the  $\text{Mn}^{III}$  ion exhibits a Jahn-Teller distortion giving rise to the change in the symmetry from cubic high temperature phase (F-43m) to tetragonal low temperature phase (I-4m2). Both phases are non-centrosymmetric leading to second harmonic generation. Therefore, we can follow the electronic transition by probing the change in the magnetic susceptibility, in the second order non-linear susceptibility, in the structure and in the vibrations of the compound. These changes of properties depend on the amount of  $\text{Rb}^+$  inserted in the 3D structure. The RbMnFe properties have been studied extensively in the micro-scale, however there is a huge lack of investigation of this compound at the nanoscale of importance for further integration in multifunctional devices.

In this study, we report the rational design of switchable RbMnFe nanoparticles. This required to combine both the size reduction of the compound to the nanoscale and to preserve high Rb content to observe the switching properties. We also shed the light on how to have access to the composition of the compound with high accuracy using two different reliable techniques (inductively coupled plasma and X-ray diffraction refinement). Furthermore, we illustrate not only the size reduction effect on the magnetic and non-linear optical properties, but also the composition impact on these properties.

[1] S. Ohkoshi, T. Matsuda, H. Tokoro, K. Hashimoto, Chem. Matter. 17, 81 (2005)

[2] S. Ohkoshi, S. Saito, T. Matsuda, T. Nuida, H. Tokoro, J. Phys. Chem. C 112, 13095 (2008)



**Figure 1** : The evolution of the size vs. Rb content (x) for “microparticles” (in red) and “nanoparticles” (in blue).

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