

Supporting Informations

Control of the thermal hysteresis of the prototypal spin-transition $\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2$ compound *via* the microcrystallites environment: experiments and mechanoelastic model.

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- 1- Characterizations of $[\text{Fe}(\text{phen})_3(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$ (1)**
- 2- Characterizations of microparticles (2-matrix)**
- 3- Magnetic properties of microparticles (2-matrix)**
- 4- Magnetic properties of polycrystalline samples (bulk and bulk-matrix) of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{3-MeO-SalEen})_2\text{PF}_6$**

1- Characterization of $[\text{Fe}(\text{phen})_3(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$ (**1**)

The X-ray diffraction pattern of the powder **1** was collected at room temperature. Figure S1 shows the diffraction pattern limited to the diffraction angles 2θ angles between 8 and 30 °. A number of sharp lines (for example at $2\theta \approx 8.61, 9.51, 9.86, 10.55, 22.71, 24.51$ and 25.62°) can be considered as specific markers of this material.

IR (KBr pellet, Fig. S2) ν/cm^{-1} : 3097, 3077, 3052 (ν_{stretch} of $\text{CH}_{\text{aromatic}}$), 2050 (ν_{stretch} of CN_{NCS^-}), 1629 1600, 1423 and 1409 (ν_{stretch} of CN and CC_{phen}), 844 and 722 (ν_{deform} of CH_{phen}).

2- Characterizations of the microparticles (2-matrix)

In Figure S1, the X-Ray diffraction patterns of microparticles (**2**, **2-PVP**, **2-PEG**, **2-PEG heated**) present new peaks whose positions and relative intensities compare to those calculated from the previously reported single-crystal structure of $\text{Fe}(\text{phen})_2(\text{NCS})_2$.¹ Moreover, no diffraction peaks of $[\text{Fe}(\text{phen})_3(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$ can be observed. These observations confirm the formation of crystalline particles of $\text{Fe}(\text{phen})_2(\text{NCS})_2$.

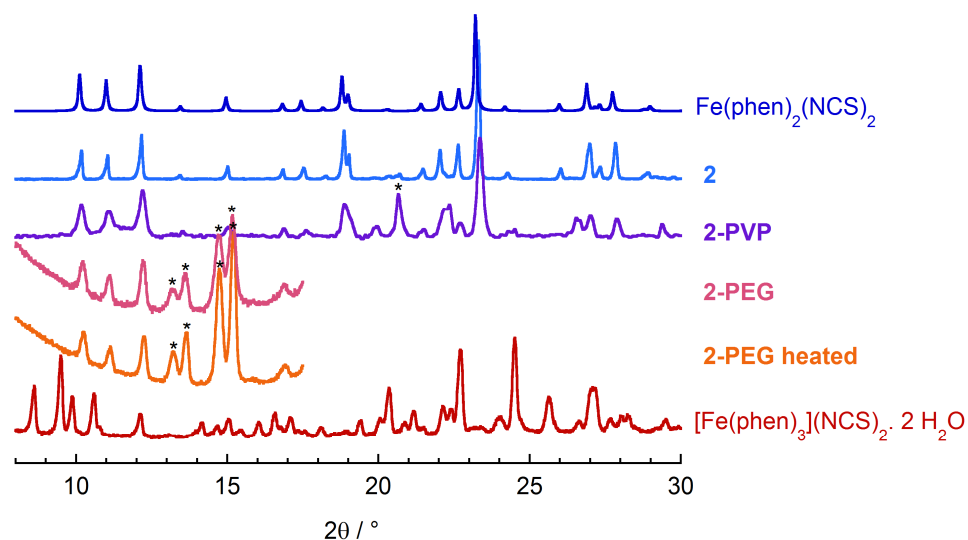


Figure S1: Powder X-ray diffraction patterns recorded for the bare (**2**) and embedded (**2-PEG**, **2-PEG heated** and **2-PVP**) microparticles. They are compared with those of $[\text{Fe}(\text{phen})_3(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (calculated from [2]). Patterns of samples **2-PEG** and **2-PEG heated** are limited to the 8-18° interval, as diffraction peaks of crystalline polymers (noted with *) prevent the observation of any particles peak at higher angles.

The 293 K FT-IR spectrum (Figure S2) of **2** (KBr pellet) is consistent with the data previously reported for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (ν/cm^{-1} : 2074, 2062 (ν_{stretch} of CN_{NCS^-}), 1624, 1591, 1573,

1513, 1492, 1449, 1424 and 1413 (ν_{stretch} of CN and CC_{phen}), 847 and 723 (ν_{deform} of CH_{phen}).² At 100 K, the frequencies at 2106 and 2115 cm^{-1} (ν_{stretch} of CN_{NCSe} , LS form) appear whereas the corresponding HS frequencies disappear.²

The IR spectrum of **2-PVP** (KBr pellet) shows the coexistence of vibrational peaks corresponding to the complex and PVP. A number of peaks can only be observed in the spectra of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ (2074 and 2061, 1440, 1102, 864, 638, 471, 418, and 280 cm^{-1}).

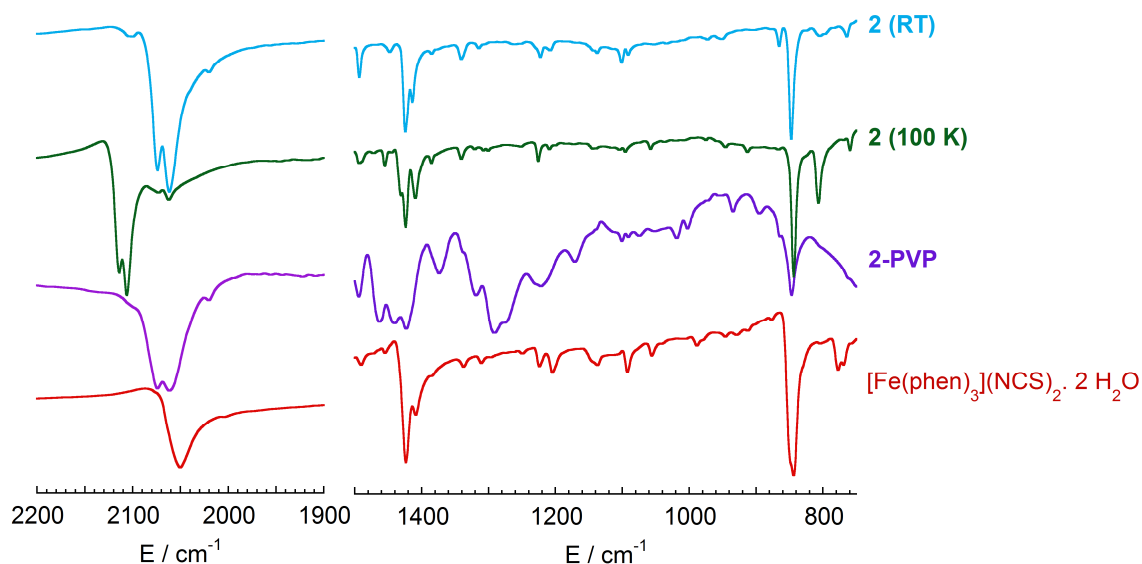


Figure S2: Infra-Red spectra of **2** (at 293 and 100 K) and **2-PVP** in KBr pellets compared with the spectrum of $[\text{Fe}(\text{phen})_3(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$, the starting compound.

3- Magnetic properties of the microparticles

The magnetic properties of microparticles embedded in different matrices (**2-PEG**, **2-PEG heated**, **2-PEG dispersed**, **2-PVP** and **2-glycerol**) were recorded with a SQUID magnetometer at a $1\text{K} \cdot \text{min}^{-1}$ sweeping rate. Due to the presence of an important amount of diamagnetic species (polymer or glycerol) around the particles, some approximations have to be made to extract the $\chi_M T$ vs. T curves:³

- consistently with the FT-IR and X-ray diffraction data, all the composites are considered as HS species at 293 K.
- at low temperature (between 10 and 80 K), it is assumed that the composites follow a Curie Law (*i.e.* the samples do not contain magnetic impurities, as it has been checked with field dependent measurements).

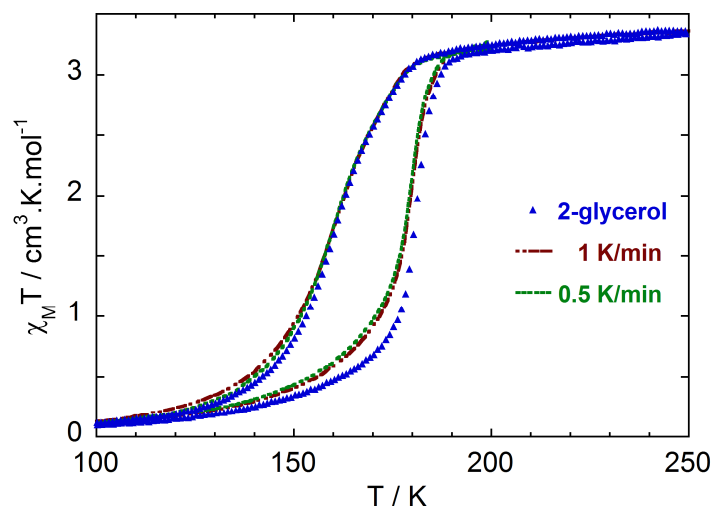


Figure S3: Magnetization measurements performed on particles embedded in glycerol with different experimental conditions: at 1 K/min after quenching at 10 K (**2-glycerol**), at 1 K/min starting from 250 K (**1 K/min**) and at 0.5 K/min starting from 250 K (**0.5 K/min**).

For the **2-glycerol** sample, very small changes (figure S3) are observed when the sweeping rate is decreased from 1 to 0.5 K/min, indicating that the observed hysteresis is not related to thermalization issues. More interestingly, measurements at the same sweeping rate but with different cooling procedures (slow cooling at 1 K/min and fast quenching at 10 K) present sizeable differences, especially in the heating regime.

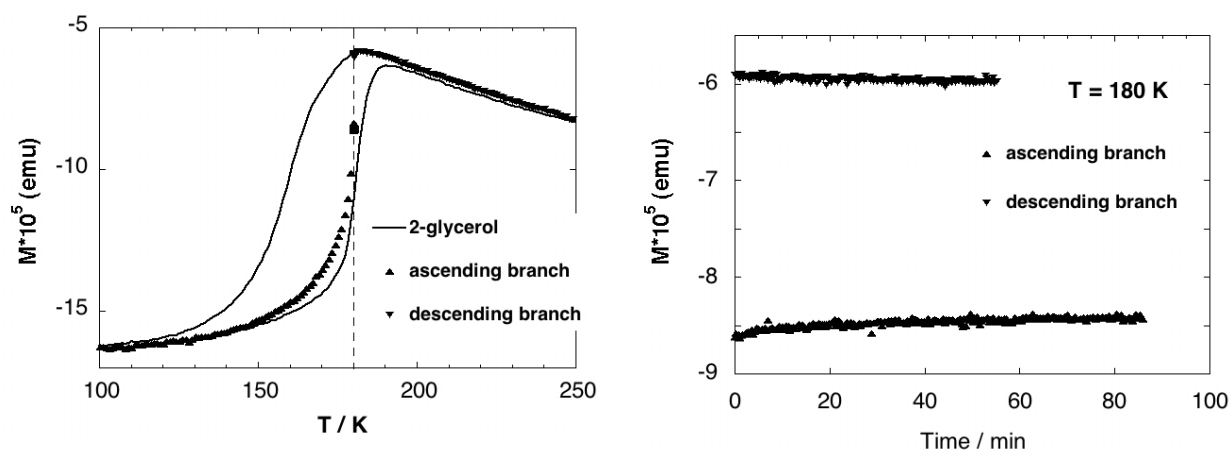


Figure S4: Evolution of the magnetization of **2-glycerol** (dispersion of **2** in glycerol, 1.65% wt). (left) temperature dependance of M observed after the sample supercooling at 10 K, the first thermal cycle between 70 and 250 K (sweeping rate at 1 Kmin⁻¹) was followed by a cooling down to 10 K, the measurement of the ascending branch between 100 and 180 K (left side, sweeping rate at 1 Kmin⁻¹), then the kinetic of magnetization at 180 K (right side). Finally the

sample was warmed to 250 K, then the measurement of the descending branch was carried out between 250 and 180 K (left side, sweeping rate at 1 Kmin⁻¹), temperature at which the kinetic of magnetization was also recorded (right side).

4- Magnetic properties of microcrystalline samples (bulk and bulk-matrix) of Fe(phen)₂(NCS)₂ and Fe(3-MeO-SalEen)₂PF₆

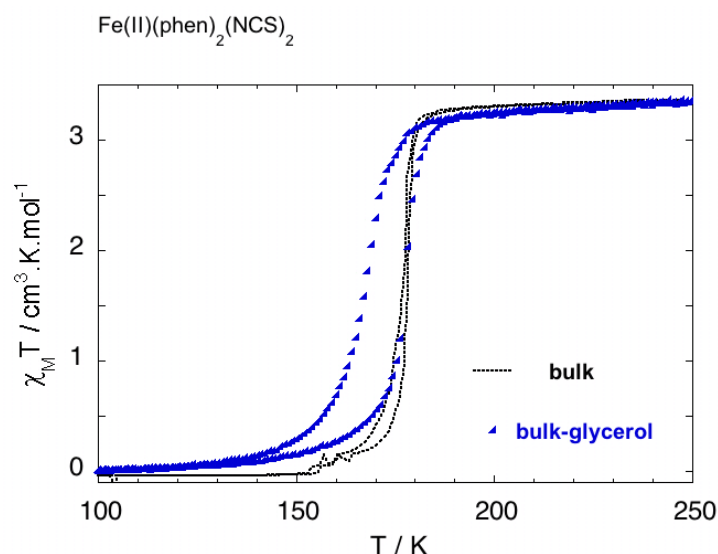


Figure S5: Magnetic behaviors of the polycrystalline sample (bulk, polymorph I, reference 4,) of Fe(phen)₂(NCS)₂, before and after the crystallites dispersion in glycerol (1.3 % wt). The magnetic measurements were performed at a sweeping rate of 1 Kmin⁻¹, after an initial freezing at 10 K (**bulk-glycerol**).

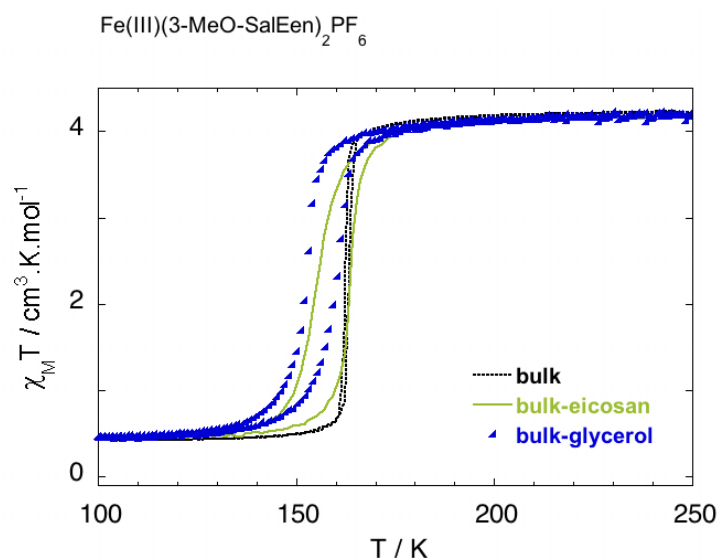


Figure S6: Magnetic behaviors of the polycrystalline sample of $\text{Fe}^{\text{III}}(3\text{-MeO-SalEen})_2\text{PF}_6$ before (bulk, starting material in reference 3) and after the crystallites dispersion in eicosan (1.28% wt) or glycerol (1.45% wt). The measurements were performed at a sweeping rate of 1 Kmin^{-1} ; the samples dispersed in glycerol or eicosan were first freezed at 10 K, then thermally cycled.

References

- ¹ B. Gallois, J.-A. Real, C. Hauw and J. Zarembowitch, *Inorg. Chem.* 1990, **29**, 1152.
- ² G. Brehm, M. Reiher, S. Schneider and *J. Phys. Chem. A*, 2002, **106**, 12024.
- ³ A. Tissot, L. Rechignat, A. Bousseksou and M.-L. Boillot, *J. Mater. Chem.*, 2012, **22**, 3411.
- ⁴ A. Bousseksou, N. Negree, M. Goiran, L. Salmon, J.-P. Tuchagues, M.-L. Boillot, K. Boukheddaden and F. Varret, *Eur. Phys. J.*, 2000, **13**, 451-456 ; A. Bousseksou, J. J. McGarvey, F. Varret, J.-A. Real, J.-P. Tuchagues, A. C. Dennis and M.-L. Boillot, *Chem. Phys. Lett.*, 2000, **318**, 409-416.