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Supplementary Information:
Non-Extensivity of Thermodynamics at the Nanoscale in Molecular Spin Crossover Materials: A Balance between Surface and Volume

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1 Evaluation of the entropy by Monte Carlo simulations

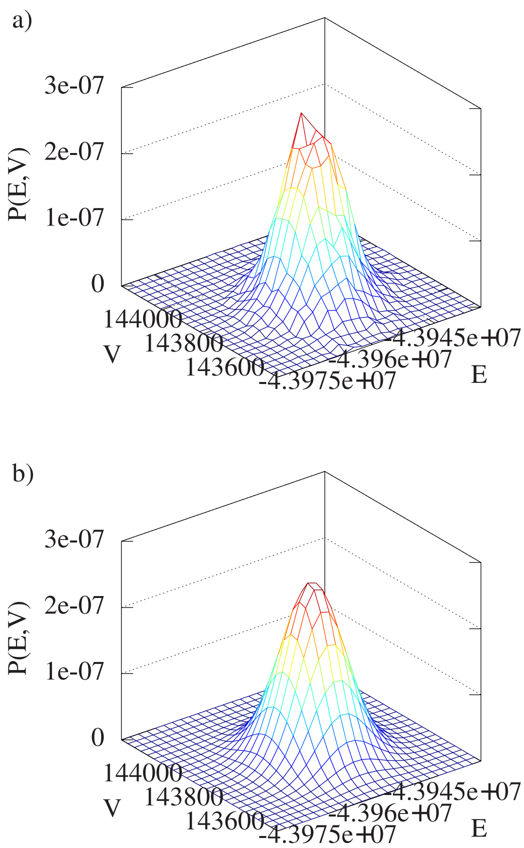

Fig. S1 (a) 2D Histogram of probability density as a function of the volume and the energy for a 60x60 2D square system. (b) Fit by a 2D gaussian curve of the Histogram of probability density for a 60x60 2D square system.

To asses the entropy, the probability density of the system has to be estimated.

$$\langle S \rangle = -k_B \sum_i p(H_i, V_i) \log(p(H_i, V_i)) \quad \text{(S1)}$$

We used the MC Histogram reweighting technique to extract the probability density (Figure S1). This technique was introduced by Ferrenberg and Swendsen[S1] for the canonical ensemble and extended to the

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isothermal-isobaric ensemble by Conrad and Pablo.[S2] The histogram $h_{T,P}(H,V)$ for energies and volumes, which are associated with the successive visits from the simulation, is proportional to the density of states $g(H,V)$:

$$h_{T,P}(H,V) \propto g(H,V)\ \mathrm{e}^{-(H+PV)/(k_B T)} \tag{S2}$$

The density of probability of the system is given by:

$$p(H,V) = \frac{h_{T,P}(H,V)}{\int_{-\infty}^{+\infty}\int_{0}^{+\infty} \mathrm{d}H\mathrm{d}V\ h_{T,P}(H,V)} \tag{S3}$$

Finally, the entropy is given by this following relation:

$$\langle S \rangle = \int_{-\infty}^{+\infty}\int_{0}^{+\infty} \mathrm{d}H\mathrm{d}V\ p(H,V)\log(p(H,V)) \tag{S4}$$

References

S1 A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.*, 1989, **63**, 1195–1198.

S2 P. Conrad and J. de Pablo, *Fluid Phase Equilibri.*, 1998, **150–151**, 51–61.