Electronic Supplementary Material (ESI) for Nanoscale.

Supplemental Material:

Effects of the surface energy and surface stress on the phase stability of spin crossover nano-objects: a thermodynamic approach

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I. The exact stationary solution of thin film model

$$\frac{B_{HS}V_{HS}}{2}(\gamma_o-1)\left[\left(\frac{V_{min}}{V_{HS}}-1\right)^2-\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)^2\right]+(\Delta H-T\Delta S)+kTln\left(\frac{x^b}{1-x^b}\right)=0 \quad , \tag{S1}$$

$$\frac{B_{HS}V_{HS}}{2}(\gamma_o-1)\left[\left(\frac{V_{min}}{V_{HS}}-1\right)^2-\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)^2\right]+(\Delta H-T\Delta S)+kTln\left(\frac{x^s}{1-x^s}\right)+\frac{B_{HS}V_{HS}R_\gamma}{2a_{HS}^0}\left(1-\frac{a_{HS}^0\Gamma_\gamma}{a_\downarrow^0 m}\right)+\frac{1}{2}B_{HS}$$
$$R_\sigma V_{min}^{2/3}[1-\alpha]-\frac{B_{HS}R_\sigma V_{HS}}{2a_{HS}^0}\left[1-\frac{a_{HS}^0\alpha}{a_{LS}^0 m}\right]=0 \quad , \tag{S2}$$

$$(L^{tot}-2L^s)B_{HS}(\gamma_o-1)\left[x^b\left(\frac{V_{min}}{V_{HS}}-1\right)+(1-x^b)\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)\right]+2L^sB_{HS}(\gamma_o-1)$$
$$\left[x^s\left(\frac{V_{min}}{V_{HS}}-1\right)+(1-x^s)\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)\right]+\frac{2}{3}L^sB_{HS}R_\sigma V_{min}^{-1/3}\left[x^s+(1-x^s)\alpha\right]=0 \quad , \tag{S3}$$

II. Spherical core-shell model

Assuming that the nanoparticle is in the HS state and that the shell is made up of a monolayer, the core volume is: $V_b=N_{HS}^bV_{HS}=\frac{4\pi R_1^3}{3}$, where R_1 is the core radius and V_{HS} the equilibrium volume of a molecule in the HS state. Then, the shell volume can be deduced: $V_s=N_{HS}^sV_{HS}=NV_{HS}-N_{HS}^bV_{HS}=\frac{4\pi R^3}{3}-\frac{4\pi R_1^3}{3}$, where R is the radius of the nanoparticle. Finally, the number of molecules in the core (N^b) and in the shell (N^s) can be expressed as:

$$N^b=N\left(\frac{R_1}{R}\right)^3 , \tag{S4}$$

$$N^s=N\left(1-\left(\frac{R_1}{R}\right)^3\right). \tag{S5}$$

Besides, considering that all the molecules at the surface are in the HS state, the relation between the area of a single molecule and the total surface area of the nanoparticle is:

$$N^a \frac{V_{HS}}{a_o^{HS}} = 4\pi R^2, \tag{S6}$$

where N^a stands for the total number of molecules at the surface and a_0^{HS} is HS lattice parameter. On the other hand, the relation between the volume of a single molecule and the total volume of the particle is:

$$NV_{HS} = \frac{4\pi R^3}{3}. \tag{S7}$$

From eqn (S6) and eqn (S7), the number of molecules at the surface N^a can be deduced:

$$N^a = N\frac{3a_o^{HS}}{R}. \tag{S8}$$

The N_{HS}^a and N_{LS}^a in eqn (18) of the main text can be calculated as follow:

$$N_{HS}^a = x^s N^a = x^s N\frac{3a_o^{HS}}{R}, \tag{S9}$$

$$N_{LS}^a = (1-x^s)N^a = (1-x^s)N\frac{3a_o^{HS}}{R}, \tag{S10}$$

Considering the shell is made up of a monolayer of molecules ($N^s = N^a$ in this case), the total energy of the spherical system is written as:

$$G_{total}(V_{min}, x^b, x^s) = N\left(\frac{R_1}{R}\right)^3 \frac{B_{HS}V_{HS}}{2}(\gamma_o - 1)\left[x^b\left(\frac{V_{min}}{V_{HS}} - 1\right)^2 + (1-x^b)\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}} - \frac{1}{m}\right)^2\right]_+$$

$$N\left(1 - \left(\frac{R_1}{R}\right)^3\right)\frac{B_{HS}V_{HS}}{2}(\gamma_o - 1)\left[x^s\left(\frac{V_{min}}{V_{HS}} - 1\right)^2 + (1-x^s)\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}} - \frac{1}{m}\right)^2\right]_+$$

$$N\left[x^s\left(1 - \left(\frac{R_1}{R}\right)^3\right) + x^b\left(\frac{R_1}{R}\right)^3\right](\Delta H - T\Delta S) + N(H_{LS} - TS_{LS})_+$$

$$NkT\left(\frac{R_1}{R}\right)^3\left[x^b\ln\left(x^b\right)+\left(1-x^b\right)\ln\left(1-x^b\right)\right]_+$$

$$NkT\left(1-\left(\frac{R_1}{R}\right)^3\right)\left[x^s\ln\left(x^s\right)+\left(1-x^s\right)\ln\left(1-x^s\right)\right]_+$$

$$N\frac{3B_{HS}V_{HS}R_\gamma}{2R}\left[x^s+\left(1-x^s\right)\frac{a_{HS}^0\Gamma_\gamma}{a_{LS}^0 m}\right]_+$$

$$N\frac{B_{HS}V_{HS}R_\sigma}{R}\left[x^s\left(\frac{V_{min}}{V_{HS}}-1\right)+\alpha\frac{a_{HS}^0}{a_{LS}^0}\left(1-x^s\right)\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)\right], \quad \text{(S11)}$$

The exact stationary solution of the spherical model is found using eqn (24) à the main text, which brings out the equation set:

$$\frac{B_{HS}V_{HS}}{2}(\gamma_o-1)\left[\left(\frac{V_{min}}{V_{HS}}-1\right)^2-\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)^2\right]+(\Delta H-T\Delta S)+kTln\left(\frac{x^b}{1-x^b}\right)=0, \quad \text{(S12)}$$

$$\left(1-\left(\frac{R_1}{R}\right)^3\right)\left[\frac{B_{HS}V_{HS}}{2}(\gamma_o-1)\left[\left(\frac{V_{min}}{V_{HS}}-1\right)^2-\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)^2\right]+(\Delta H-T\Delta S)+kTln\left(\frac{x^s}{1-x^s}\right)\right]+\frac{3B_{HS}V_{HS}R_\gamma}{2R}\left(1-\frac{a_{HS}^0\Gamma_\gamma}{a_{LS}^0 m}\right)+\frac{B_{HS}V_{HS}R_\sigma}{R}\left[\frac{V_{min}}{V_{HS}}-1-\alpha\frac{a_{HS}^0}{a_{LS}^0}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)\right]=0, \quad \text{(S13)}$$

$$B_{HS}\left(\frac{R_1}{R}\right)^3(\gamma_o-1)\left[x^b\left(\frac{V_{min}}{V_{HS}}-1\right)+\left(1-x^b\right)\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)\right]+B_{HS}(\gamma_o-1)\left(1-\left(\frac{R_1}{R}\right)^3\right)\left[x^s\left(\frac{V_{min}}{V_{HS}}-1\right)+\left(1-x^s\right)\frac{m}{\beta}\left(\frac{V_{min}}{V_{HS}}-\frac{1}{m}\right)\right]+\frac{B_{HS}R_\sigma}{R}\left[x^s+\alpha\frac{a_{HS}^0}{a_{LS}^0}\left(1-x^s\right)\right]=0, \quad \text{(S14)}$$

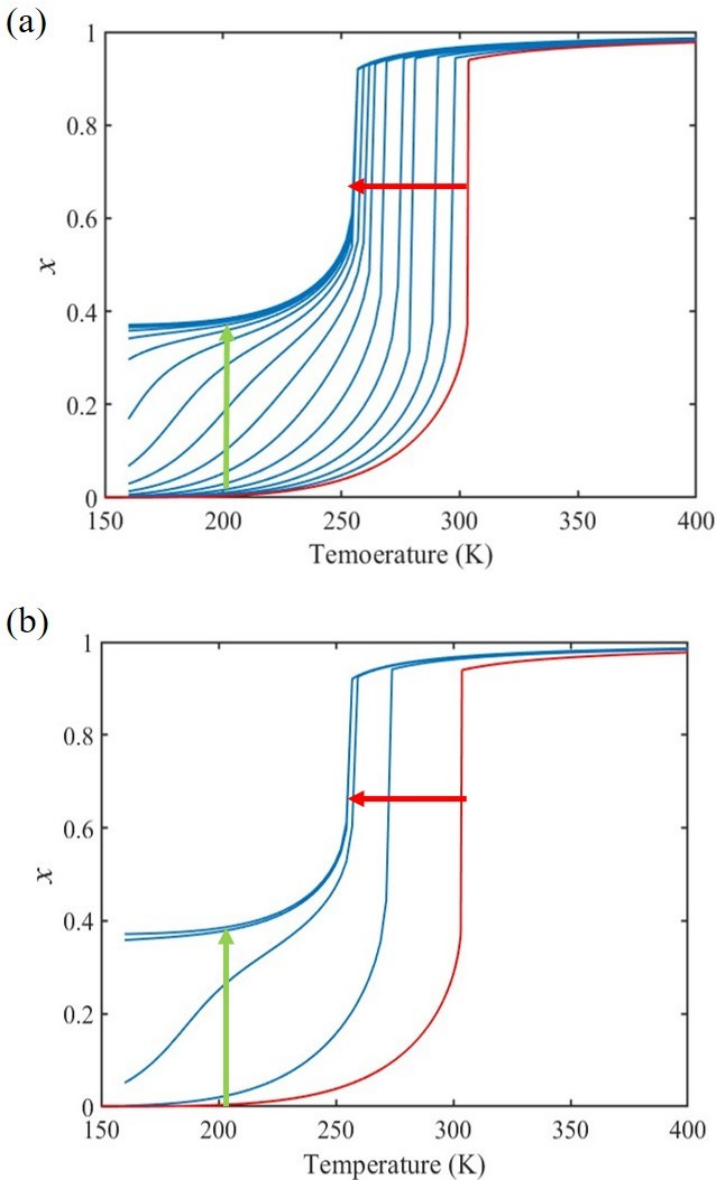

Fig. S1. Calculated temperature dependence of the HS fraction (heating mode) in a 5 nm spherical particle of [Fe(pyrazine)][Ni(CN)$_4$] in the case of (a) $\Gamma_\gamma = \frac{\gamma_{LS}}{\gamma_{HS}} = 1.4$ and (b) $\Gamma_\gamma = \frac{\gamma_{LS}}{\gamma_{HS}} = 2.4$ for different values of γ_{HS} varying from 10 to 190 mJ/m^2 with an increment of 10 mJ/m^2. The red curve represents the bulk material. Green and red arrows are guides for the eye to follow the evolution the residual HS fraction and the equilibrium temperature, respectively, with increasing of γ_{HS}.

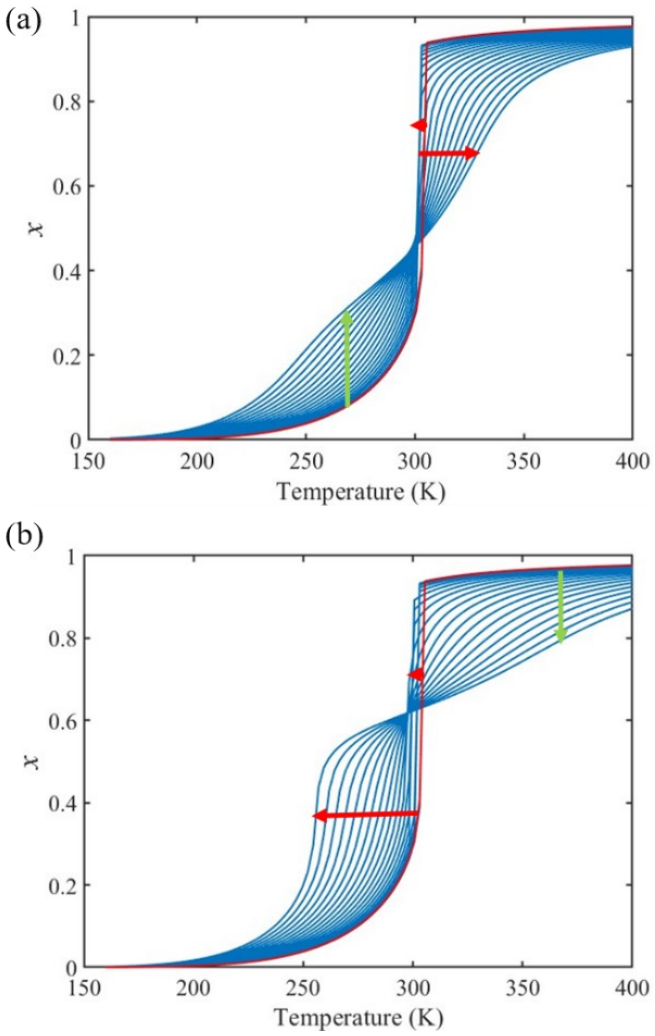

Fig. S2: Calculated temperature dependence of the HS fraction (heating mode) in a 5 nm spherical particle of [Fe(pyrazine)][Ni(CN)$_4$] in the case of $\alpha = \frac{\sigma_{LS}}{\sigma_{HS}} = 1.4$ for different values of σ_{HS} ranging from (a) +10 to +410 mJ/m^2 and (b) -410 to -10 mJ/m^2 with an increment of 20 mJ/m^2. The red curve represents the bulk material. Green and red arrows are guides for the eye to follow the evolution the residual LS fraction and the equilibrium temperature, respectively, with increasing of σ_{HS}.

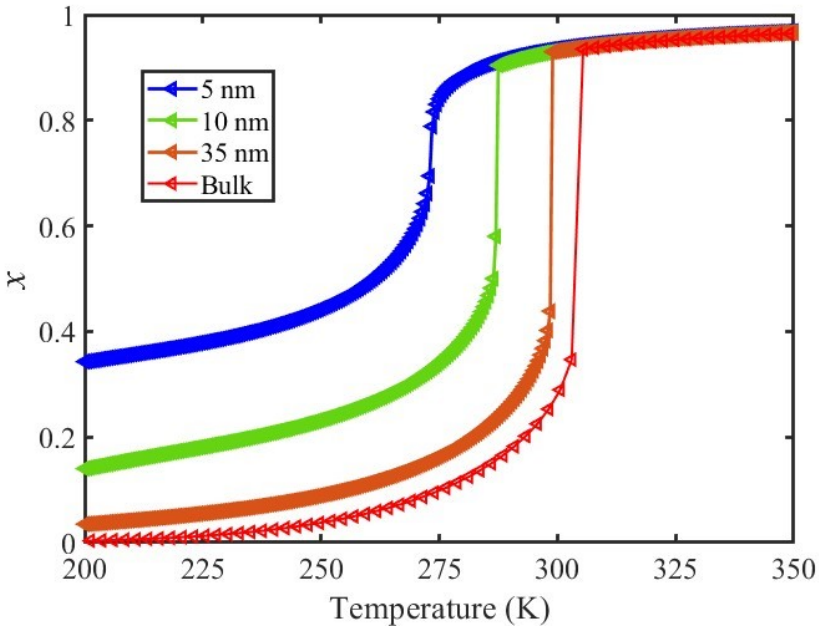

Fig. S3. Calculated temperature dependence of the total HS fraction (heating mode) for different particle radii of the compound [Fe(pyrazine)][Ni(CN)$_4$].

III. Molecular dynamics calculations

Since no surface energy data in the literature for SCO materials have been found, we employed molecular dynamics (MD) simulations to calculate the surface energy of [Fe(pyrazine)][Ni(CN)$_4$] in the HS and LS spin states. The surface energy is related to the excess of potential energy per unit area in a system having free surfaces in comparison with its bulk counterpart. Accordingly, the *slab method* is used in the present MD simulation,[1] where the potential energies of a bulk material, i.e. without surface and a finite-size system with free surfaces (or surface-vacuum interface) are needed to be calculated separately.

First, the [Fe(pyrazine)][Ni(CN)$_4$] structure with 20×20×20 unit-cells is built in the LS state and the HS state, which corresponds to simulation box sizes of 140.26 × 140.26 × 135.52 Å^3 and 145.15 × 145.15 × 145.15 Å^3, respectively, containing 128 000 atoms. Periodic boundary conditions are applied along the *x*, *y* and *z* directions to simulate the bulk material.

Then, a thin film having two solid-vacuum interfaces constituted with equivalent pyrazine-terminated surfaces at the top and at the bottom is created in the HS and LS states (see Fig. S4). The model system with free surfaces, containing 130 400 atoms, is composed with 20×20 unit-cells in the *x* and *y* directions and 21 layers in the *z* direction. Periodic boundary conditions are applied along the *x* and *y* directions, while open boundary conditions are applied along the *z* direction to avoid self-interactions between the two surfaces. The surface energy (E_{sur}) is simply estimated as follow:[1]

$$E_{sur} = \frac{E_{tot} - \sum_i n_i E_{bulk-i}}{2S}, \quad \text{(S15)}$$

where S is the surface area after mechanical relaxation, E_{tot} is the total energy of the model system with free surfaces. n_i corresponds to the total number of atoms i (i=Ni, Fe, C and N) at the surface and E_{bulk-i} stands for the energy of a single i atom in the bulk material.

The present calculations are performed through the large-scale atomic/molecular massively parallel simulator package (LAMMPS) [2] with a recently constructed [Fe(pyrazine)][Ni(CN)$_4$] force field.[3] The temperature and pressure are controlled by the Nosé-Hoover method [4, 5] and a timestep of 1 fs is selected. Each modeled system has been fully relaxed at 300 K for 100 000 MD steps to reach equilibrium state under the isothermal-isobaric (NPT) ensemble.

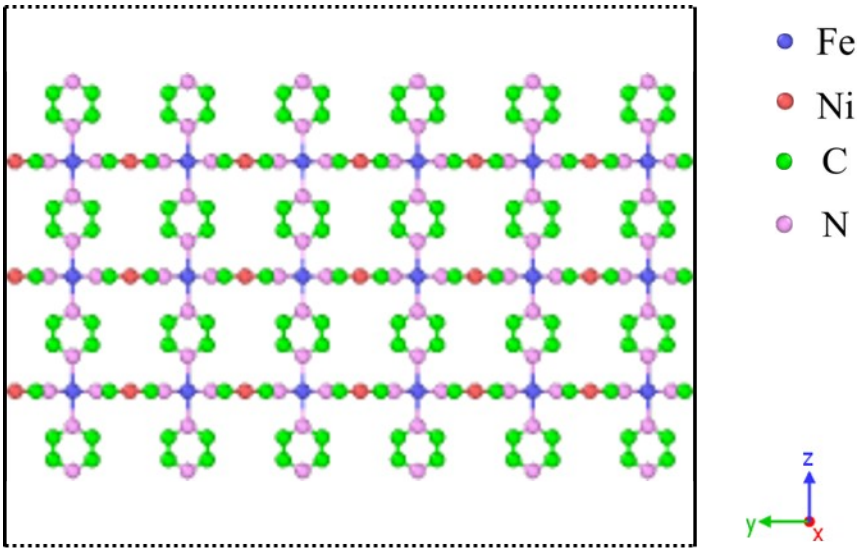

Fig. S4: Schematic representation of the [Fe(pyrazine)][Ni(CN)$_4$] film structure with periodic boundary condition along the *x* and *y*-directions.

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S2. S. Plimpton, *J. Comput. Phys.*, 1995, **117**, 1-19.
S3. S. Mi, A. Fahs, G. Molnár, W. Nicolazzi and A. Bousseksou, *Chem. Phys. Lett.*, 2023, **811**, 140232.
S4. S. Nosé, *J. Chem. Phys.*, 1984, **81**, 511-519.
S5. W. G. Hoover, *Phys. Rev. A*, 1985, **31**, 1695.