Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Evidencing size-dependent cooperative effects on spin crossover nanoparticles following their HS→LS relaxation.

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Supporting information

Table S1 Parameters used for the synthesis of [Fe(pz)Pt(CN)$_4$] nanoparticles, based on the reverse micelle technique.

Size (nm)	**$Fe(BF_4)_2 \cdot 6H_2O$ (mg)**	**Py (mg)**	**$H_2$0 (mL)**	**$K_2[Pt(CN)_4]$ (mg)**	**$H_2$0 (mL)**	**NaAOT (g)**	**Octane (mL)**
32	67.4	64.0	2	86.0	2	9.9	44
50	81.0	76.9	3	103.5	3	7.5	33
142	33.7	32.0	2	43.1	2	9.9	44
383	101.1	96.0	6	129.3	6	29.61	133
563	67.4	64.0	4	86.2	4	19.7	88

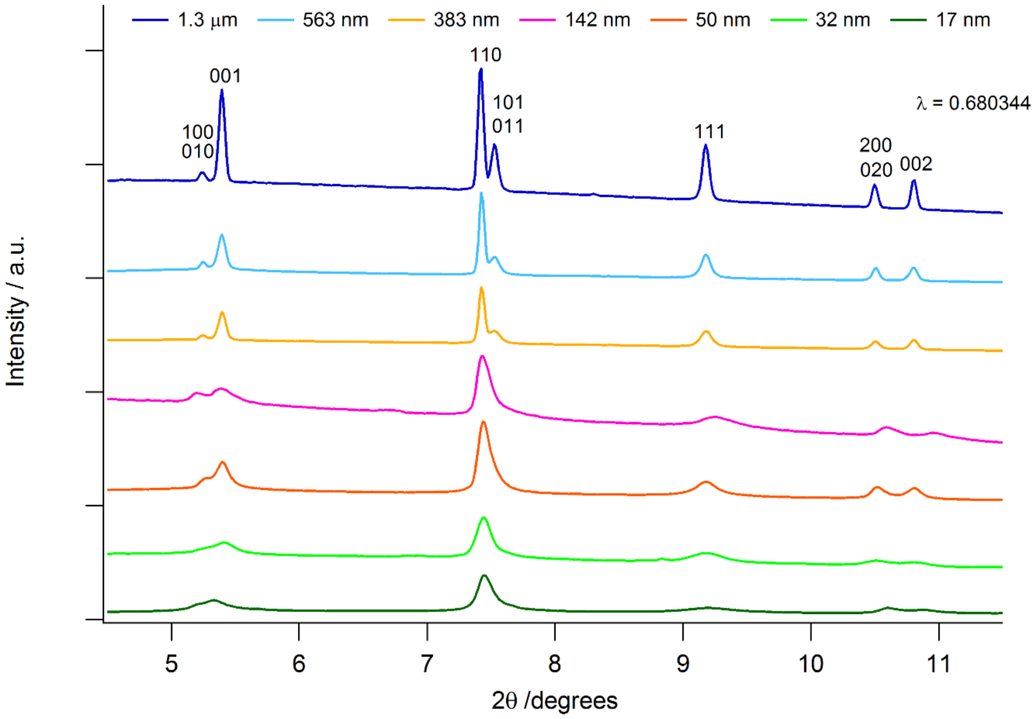

Fig. S1 Comparison of the diffraction patterns of the samples. All the samples are isostructural (space group *P*4/*mmm*).

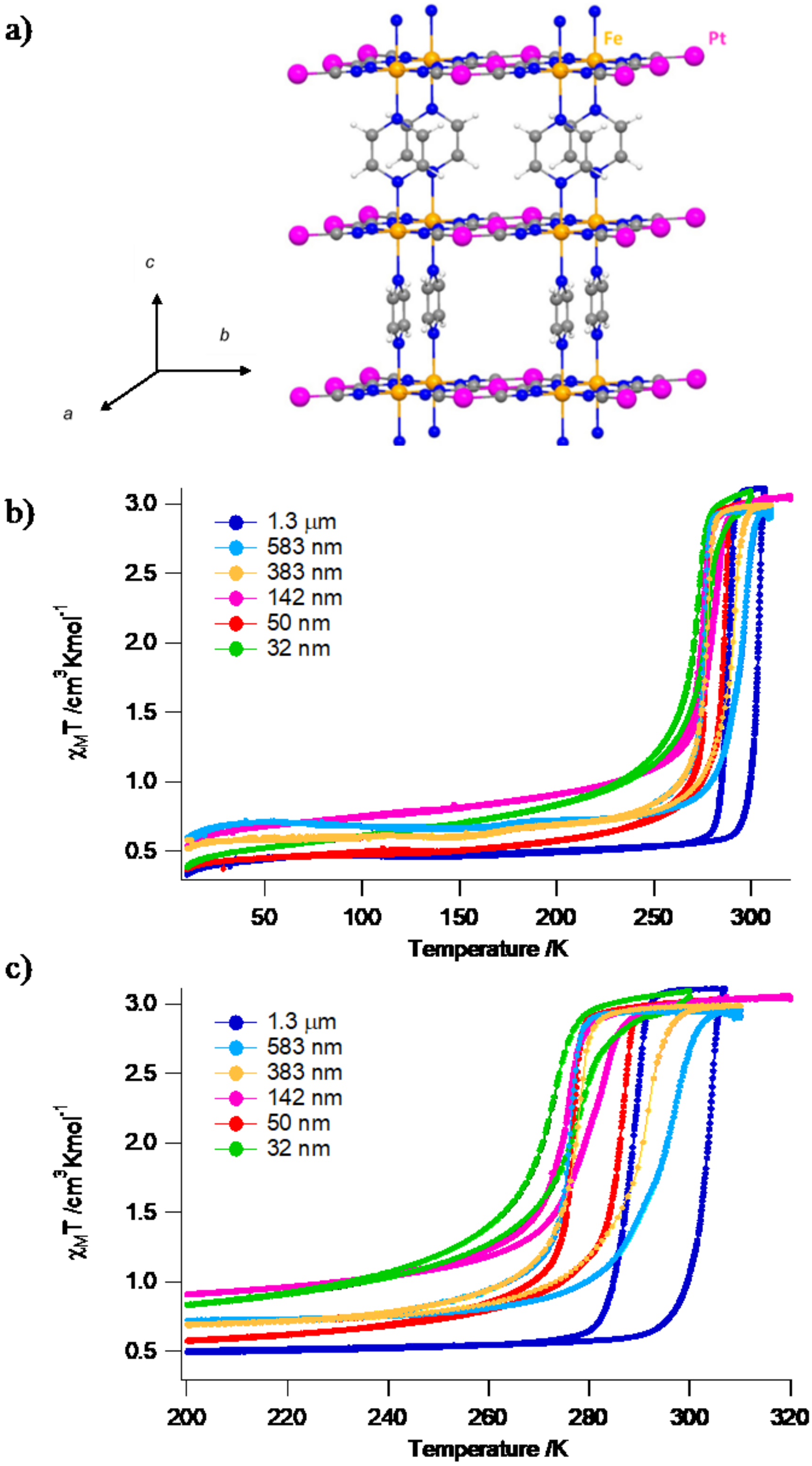

Fig. S*2* a) Schematic representation of the $[Fe(pz)Pt(CN)_4]$ structure b) Evolution of the magnetic properties of the samples recorded from 10 to 320 K during heating and cooling at 1 K/min and c) enlarged region between 180 and 320 K.

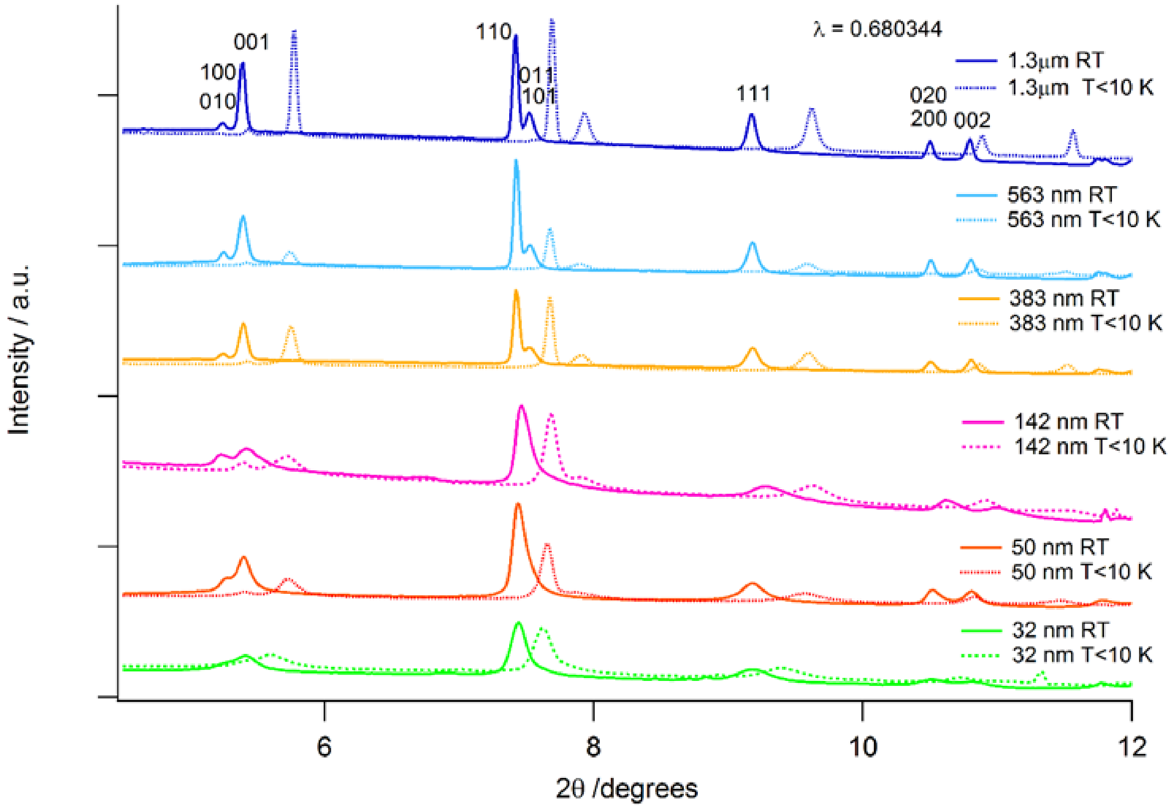

Fig. S3 XRD patterns of all samples used in the photoexcitation experiment at room temperature and 15 K.

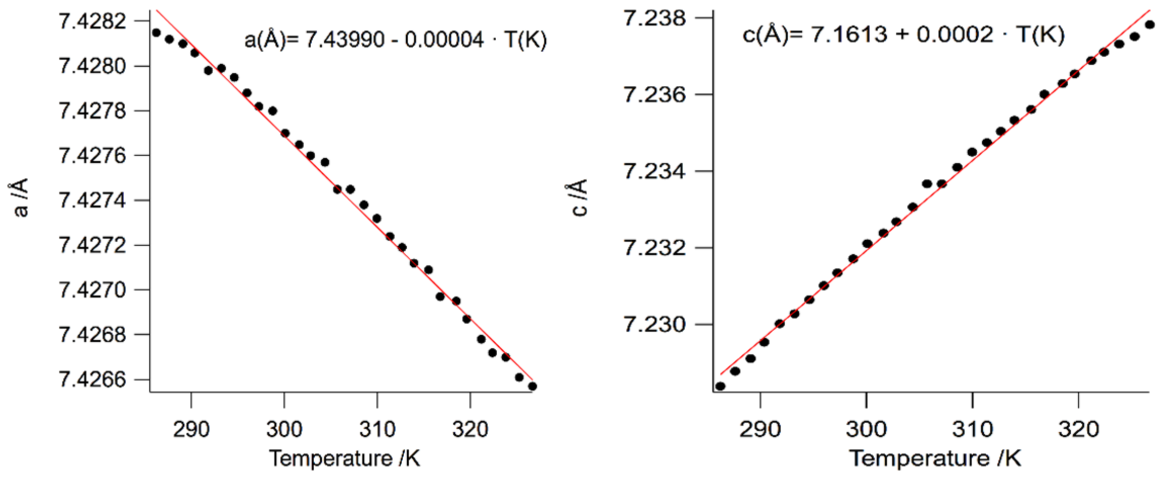

Fig. S4 Thermal expansion of the unit cell parameters between 326 K and 286 K for the bulk.

Photo-induced LS→HS spin conversion and the HS→LS relaxation followed by X-ray diffraction based on synchrotron radiation. Model used for the fit:

In the case of the 32 nm, 50 nm and 142 nm particles a total number of 13 parameters are refined:

-Two unit-cell parameters

-For each of the 5 peaks, one integrated intensity I_{hkl} and one FWHM.

-A global mixing parameter η of the pseudo-Voigt profile, the same for all the peaks.

In the case of the 383 nm and 583 nm particles the fit parameters of the mixed HS/LS are:

-One integrated intensity Ikhl and two FWHM for each of the 5 split pseudo-Voigt peak.

-Two global mixing parameter η of the split pseudo-Voigt profile, the same for all the peaks.

-Two unit-cell parameters.

whereas for the purely LS phase the parameters that are fitted are:

-One integrated intensity Ikhl and one FWHM for each peak.

-A global mixing parameter η of the pseudo-Voigt profile for all the peaks.

- two unit-cell parameters are added.

Thus, in the case of the 383 nm and 583 nm particles, a total number of 32 parameters are fitted during the refinement. Due to the high number of parameters, some limits to stabilize the refinements are used on the peak widths and on the relative intensities of the peaks.

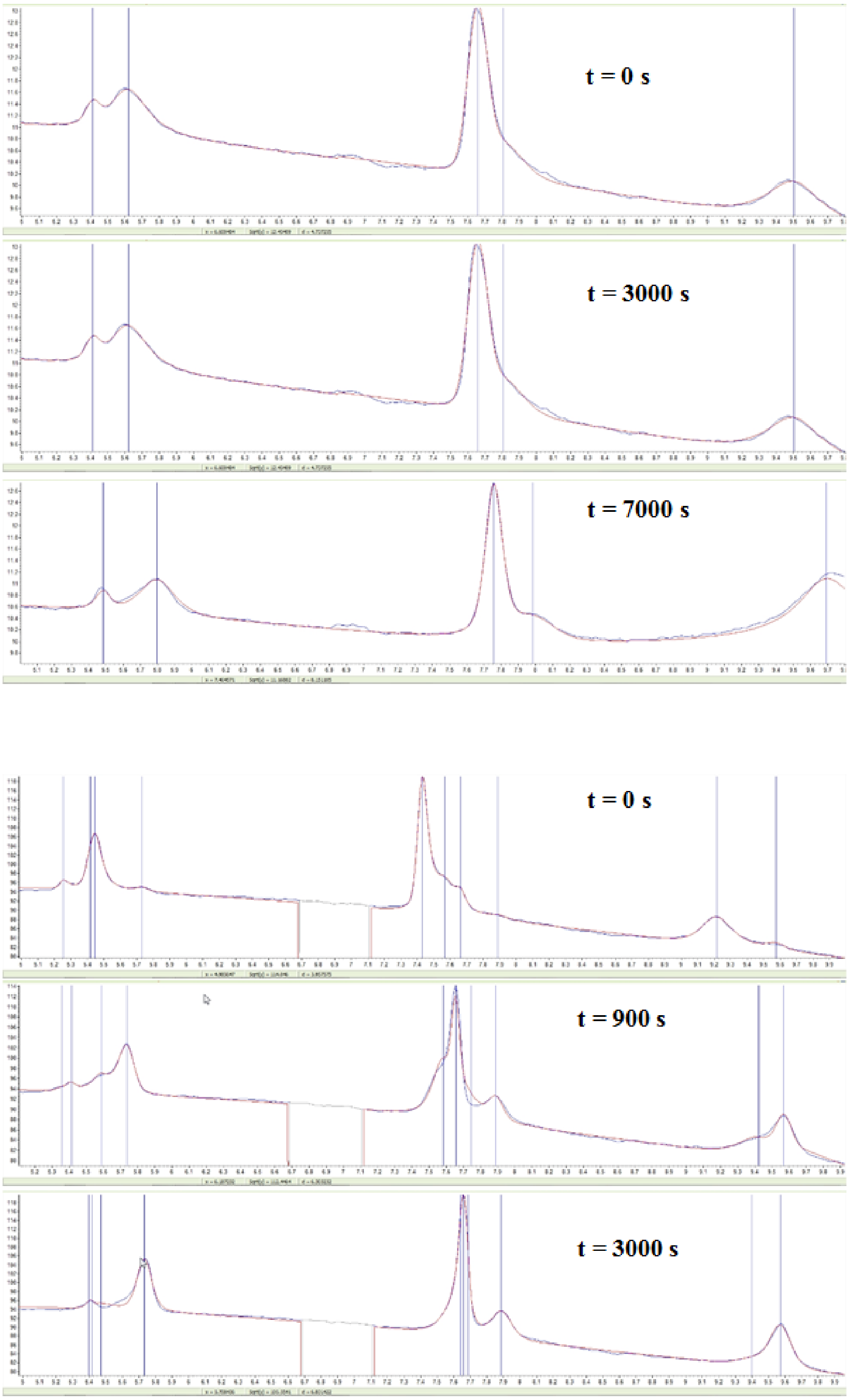

Fig. S5a Fit of the 142 nm sample at different times during the relaxation using a pseudo-Voigt model and one mixed phase (top) and fit of the 383 nm sample at different times during the relaxation using a split pseudo-Voigt model and two different phases (bottom).

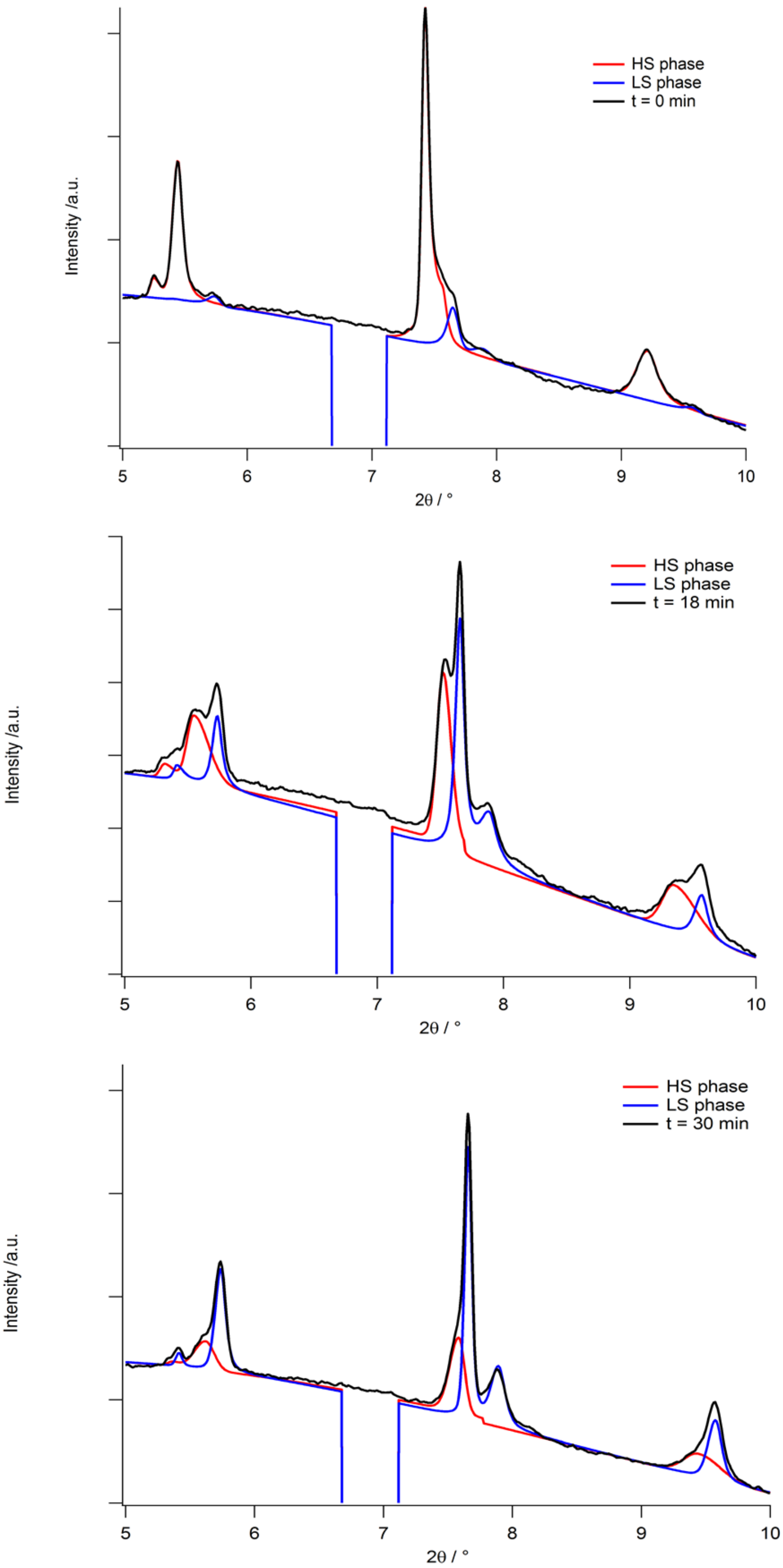

Fig. S5b Separated mixed HS/LS (red) and pure LS phase (blue) fitting during the relaxation of the 383 nm sample at *t* = 0, 18 and 30 min following irradiation at 10 K.

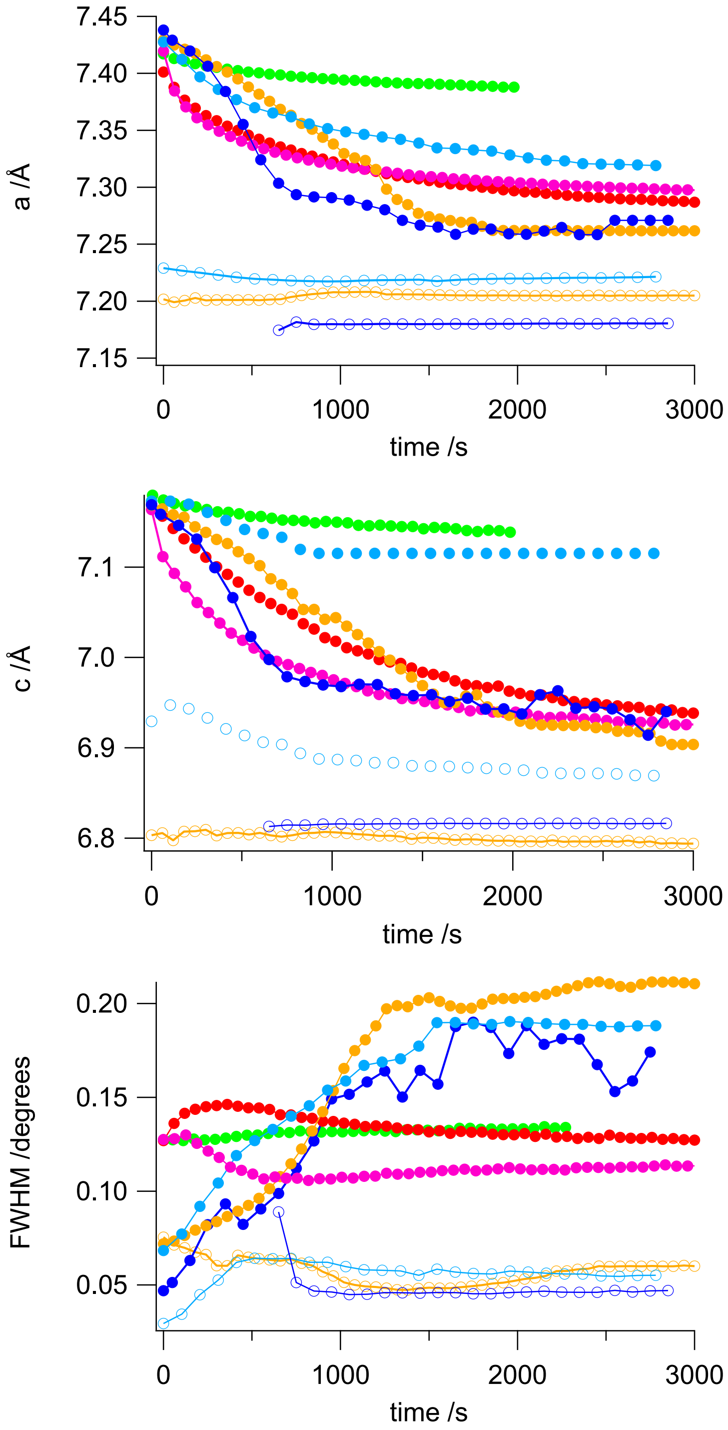

Fig. S6 Time evolution of the cell-parameter *a* and *c* and integrated full width at the half maximum during the HS→LS relaxation after photo excitation with 532 nm laser at 7mW during 20 minutes at 15 K of all the samples. Legend: 32 nm (green), 50 nm (red), 142 nm (pink), 383 nm (orange), 583 nm (clear blue) and bulk (dark blue); mixed phase (filled circles) and LS phase (empty circles).

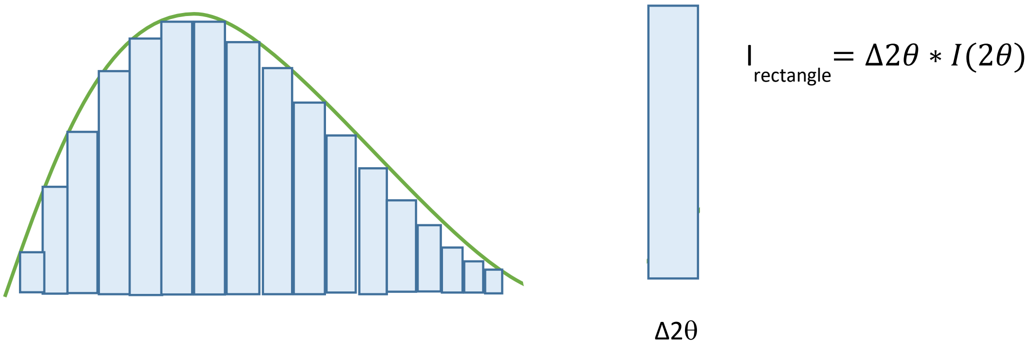

Fig. S7 Decomposition of the contribution of the asymmetric (110) peak. A rectangle integration is made. The area of a rectangle $I_i(t)$ centered at 2θ is calculated as $= \Delta 2\theta \cdot I(2\theta)$.

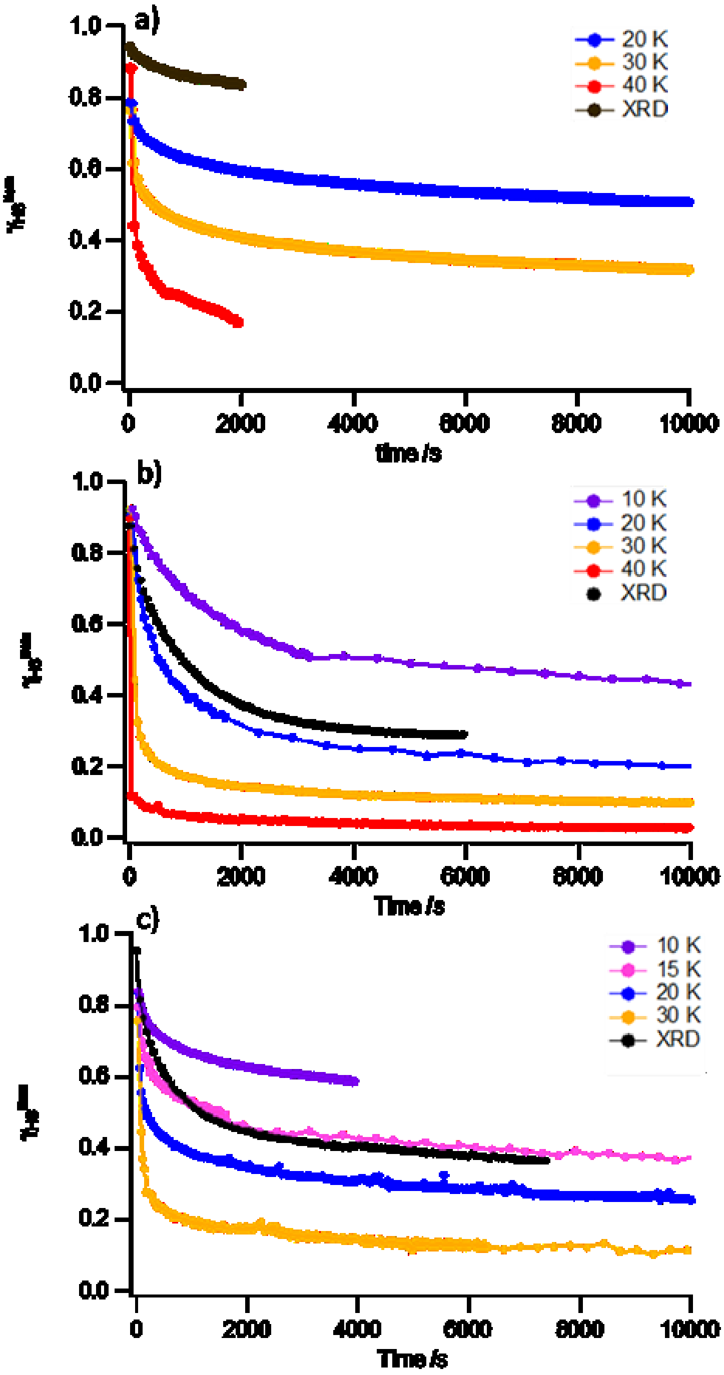

Fig. S8 Comparison of the HS fraction relaxation curves obtained by absorption spectroscopy of a) 32 nm, b) 50 nm and c) 142 nm samples after LS→HS photo excitation with 532 nm laser during LIESST experiment after irradiation at 10K and relaxation at different temperatures and comparison with the relaxation curve obtained by powder X-ray diffraction at synchrotron at 15 K.

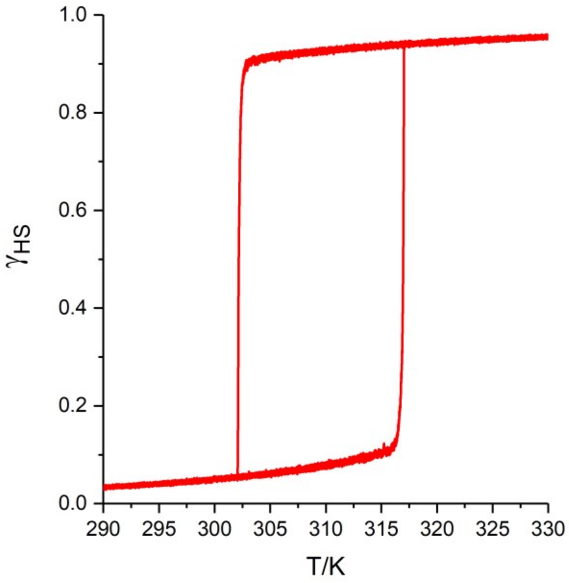

Fig. S9 Simulation of the thermal transition for k=6N/m.

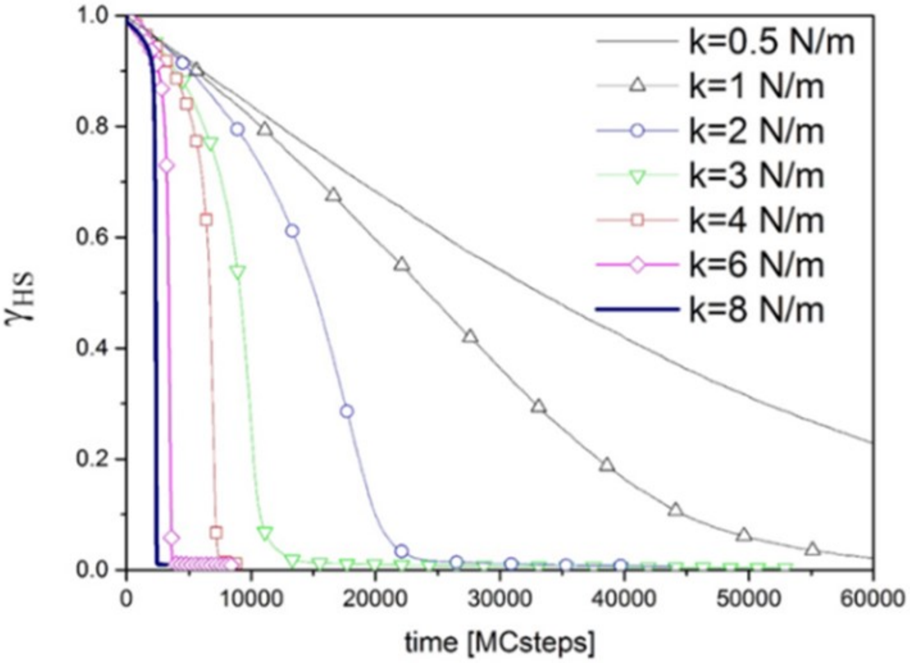

Fig. S10 Relaxation curves calculated in the framework of the mechanoelastic model for different values of the spring constant (T = 15 K).

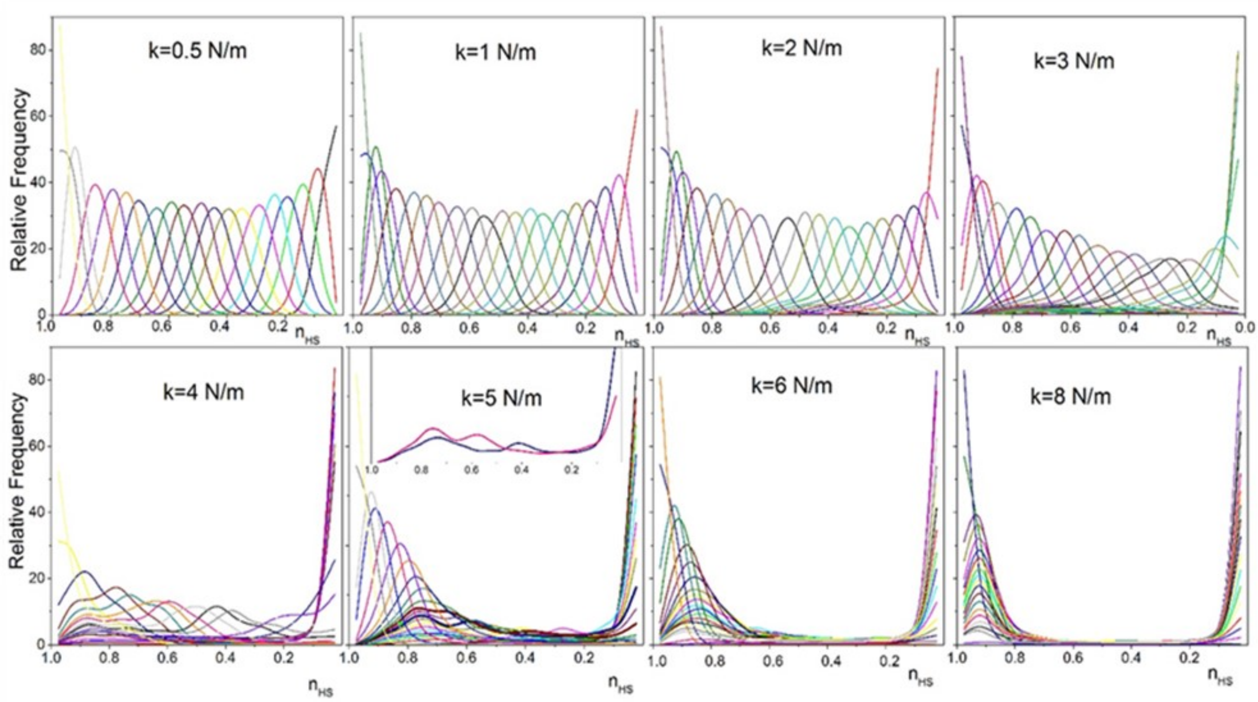

Fig. S11 Evolution of the corresponding X-ray powder diffraction peaks during the HS-LS relaxations with a large range of elastic constant. In the inset: two selected curves showing multi-peaks behaviour.

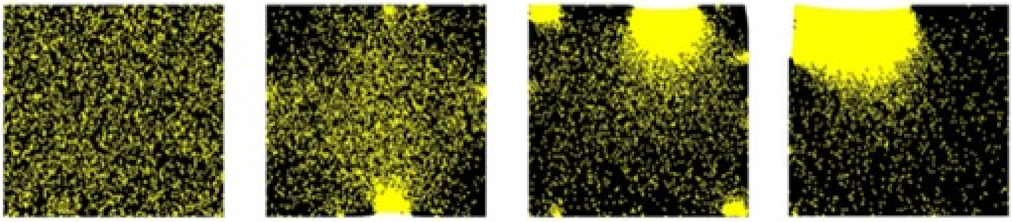

Fig. S12 Snapshots of the evolution of the system at $\gamma_{HS} = 0.7$ for different values of the spring constant *k* (from left: *k* = 0.5 N/m, *k* = 3N/m, *k* = 6 N/m, *k* = 8 N/m).

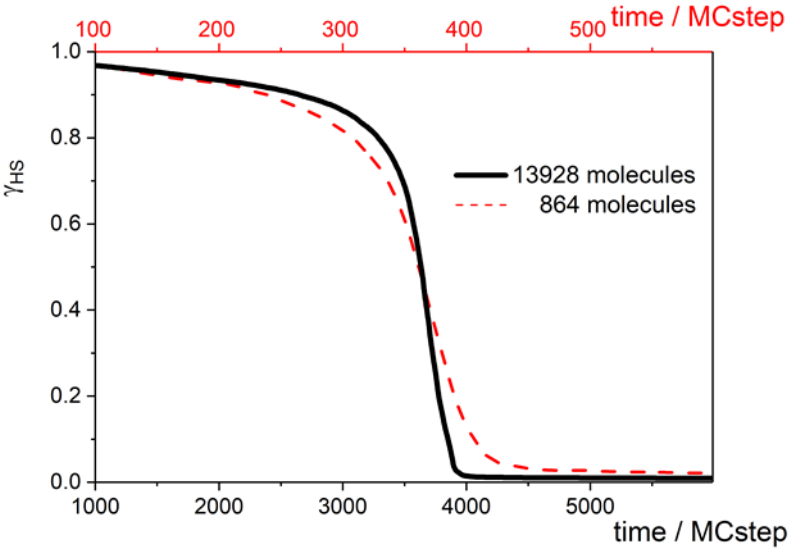

Fig. S13 Size dependence of the HS-LS relaxation curves has been calculated with $k = 6$ N/m.

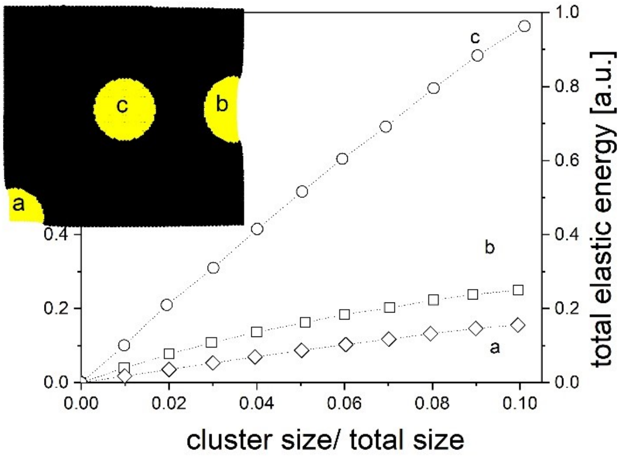

Fig. S14 Increase of the elastic energy of the system for clusters starting from either a corner (a), an edge (b), or the centre (c), characterized by a $\pi/2$ contact angle.

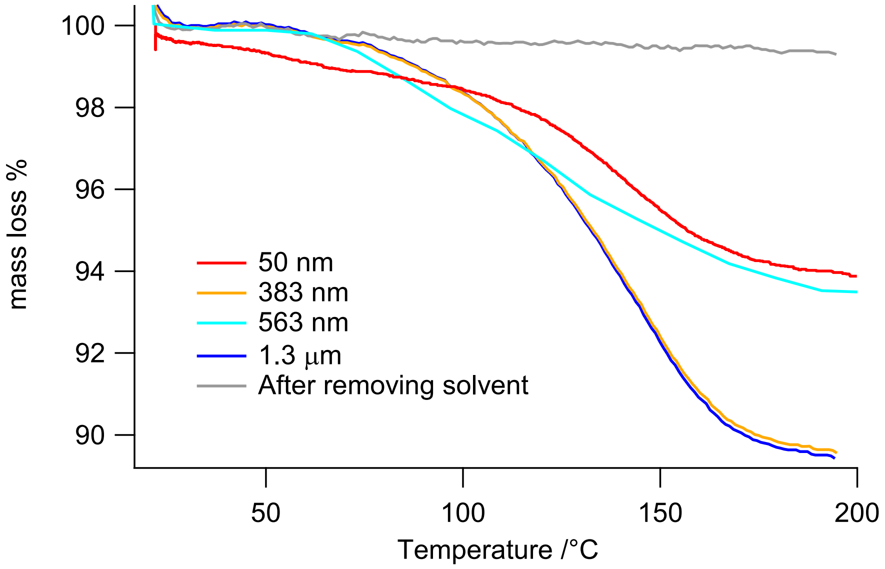

Fig. S15 Thermogravimetric analysis of the [Fe(pz)Pt(CN)$_4$] crystalline powder and [Fe(pz)Pt(CN)$_4$] nanoparticles.

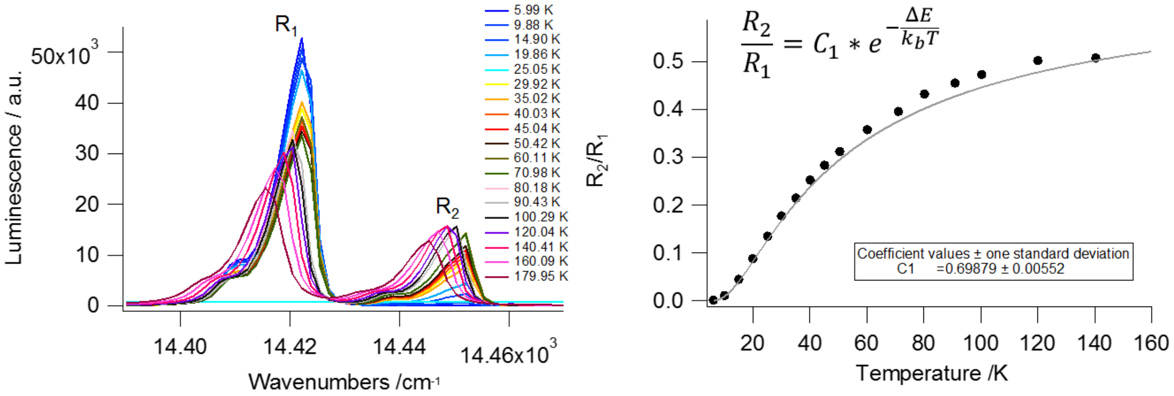

Fig. S16 The R1/R2 intensity ratio dependence with temperature. This relation was used afterward to precisely determine the temperature of the sample when it was placed in the He flow during the photo-irradiation and relaxation experiments.

Appendix 1

Step 1. Obtaining the HS fraction from 2θ

The HS fraction of the mixed phase should be calculated through Vegard's law. Since *a* and *c* are proportional to each other (Figure S11) the unit cell parameter *a* can be used instead of the unit cell volume V_c. Therefore:

$$\gamma_{\mathrm{HS}}^{\mathrm{i}}(t) = \frac{a_i(\mathrm{t}) - a_{LS}}{a_{HS} - a_{LS}} \tag{S1}$$

For a tetragonal system, the d spacing of a reflection (hkl) can be calculated as:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \tag{S2}$$

Then, for a (110) reflexion: $d = \frac{a}{\sqrt{2}}$ (S3)

Using the Bragg law →$a = \frac{\lambda}{\sqrt{2}\,sin\,\theta}$ (S4)

Thus, the variation of the HS fraction with the position θ of the (110) peak is given by equation 3.9.

$$\gamma_{HS} = \frac{1}{(a_{HS} - a_{LS})}\left(\frac{\lambda}{\sqrt{2}\,sin\,\theta} - a_{LS}\right), \tag{S5}$$

where a_{HS} and a_{LS} are the values of the unit cell parameter *a* of the bulk material in the pure HS and pure the LS phases respectively (a_{HS}=7.435 Å and a_{LS}=7.173 Å) , λ is equal to 0.680344 Å.

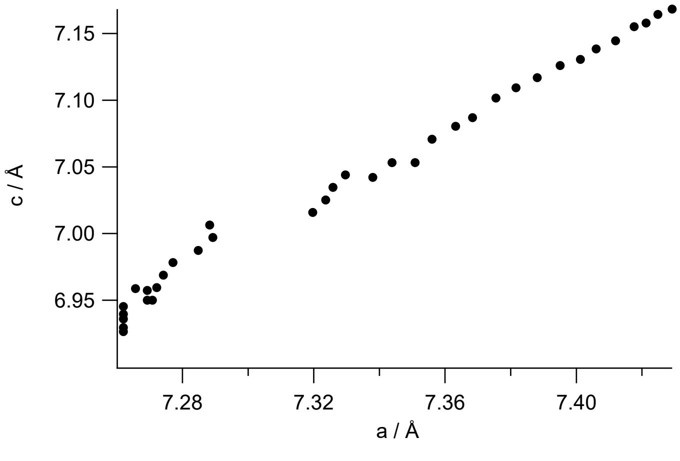

Fig. SA1 Unit cell parameter *c* vs unit cell parameter *a*.

Step 2. Obtaining the intensity *I* at 2θ

From the output by the fitting program TOPAS, we can calculate the profile of the (110) peak alone.

In a pseudo-Voigt profile:

$$I(2\theta) = I_{khl}\,[\eta L(2\theta) + (1-\eta)G(2\theta)], \qquad \text{(S6)}$$

where η is the mixing parameter and $L(2\theta)$ and $G(2\theta)$ are the Lorentzian and Gaussian function used to model the shape of the peak. These two functions are defined as indicated in equations S7 and S8 respectively:

$$L(2\theta) = \frac{a_L}{1+\, b_L\,(2\theta - 2\theta max)^2}, \qquad \text{(S7)}$$

where

$a_L = \frac{2}{\pi H}$ and $b_L = \frac{4}{H^2}$, *H* being the full width at the half maximum,

and

$$G(2\theta) = a_G\, e^{(-b_G\,(2\theta - 2\theta max)^2}, \qquad \text{(S8)}$$

where

$a_G = \frac{2}{H}\sqrt{\frac{Ln2}{\pi}}$ and $b_G = \frac{4Ln2}{H^2}$, *H* being the full width at the half maximum.

Thus, by replacing all the Lorentzian and Gaussian parameters in the pseudo-Voigt function:

$$I(2\theta) = I_{khl}\left[\eta\left(\frac{\frac{2}{\pi H}}{1+\frac{4}{H^2}(2\theta - 2\theta max)^2}\right) + (1-\eta)\left(\frac{2}{H}\sqrt{\frac{Ln2}{\pi}}\; e^{(-\frac{4Ln2}{H^2}(2\theta - 2\theta max)^2}\right)\right] \qquad (S9)$$

A split pseudo-Voigt profile function uses 2 pseudo-Voigt profile functions, one for the left side (parameters I_2, η_2 and H_2), and one for the right side (parameters I_1, η_1 and H_1), as indicated in Figure S12. The total intensity of the peak I_{hkl} being the sum of I_1 and I_2 (Equation 3.14).

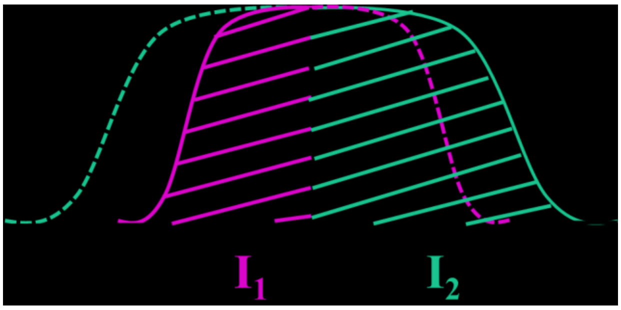

Fig. SA2 The 2 pseudo-Voigt profile function that constitute the split pseudo-Voigt profile.

$$I_{khl} = I_1 + I_2 \tag{S10}$$

The function is continuous at 0 so that I(0)left = I(0)right

$$I_1 \left[\eta_1 \left(\frac{2}{\pi H_1}\right) + (1-\eta_1)\left(\frac{2}{H_1}\sqrt{\frac{Ln2}{\pi}}\right)\right] = I_2 \left[\eta_2 \left(\frac{2}{\pi H_2}\right) + (1-\eta_2)\left(\frac{2}{H_2}\sqrt{\frac{Ln2}{\pi}}\right)\right] \tag{S11}$$

Solving the system of equations S10 and S11 allows to get I_1 and I_2 as a function of the parameters (Equations S12 and S13 respectively) of the peak which are output by our fitting program.

$$I_1 = \frac{I_{khl}\left[\eta_2\left(\frac{2}{\pi H_2}\right)+(1-\eta_2)\left(\frac{2}{H_2}\sqrt{\frac{Ln2}{\pi}}\right)\right]}{\left[\eta_1\left(\frac{2}{\pi H_1}\right)+(1-\eta_1)\left(\frac{2}{H_1}\sqrt{\frac{Ln2}{\pi}}\right)\right]+\left[\eta_2\left(\frac{2}{\pi H_2}\right)+(1-\eta_2)\left(\frac{2}{H_2}\sqrt{\frac{Ln2}{\pi}}\right)\right]}, \tag{S12}$$

and

$$I_2 = \frac{I_{khl}\left[\eta_1\left(\frac{2}{\pi H_1}\right)+(1-\eta_1)\left(\frac{2}{H_1}\sqrt{\frac{Ln2}{\pi}}\right)\right]}{\left[\eta_1\left(\frac{2}{\pi H_1}\right)+(1-\eta_1)\left(\frac{2}{H_1}\sqrt{\frac{Ln2}{\pi}}\right)\right]+\left[\eta_2\left(\frac{2}{\pi H_2}\right)+(1-\eta_2)\left(\frac{2}{H_2}\sqrt{\frac{Ln2}{\pi}}\right)\right]} \tag{S13}$$

Thus, in order to model the split pseudo-Voigt profile, the already described pseudo-Voigt function (Equation S9) is used with an intensity I_1 (Equation S12) if the value of 2θ is lower than the value of 2θ at I_{max} and with an intensity I_2 (Equation S13) if the value of 2θ is higher than the value of 2θ at I_{max}. The full width at the half maximum and the mixing parameters of both contributions to the mixed phase (η_1, η_2, H_1, H_2) as well as the position of the maximum intensity (max) is obtained from the initial split pseudo-Voigt fit.

Step 3. Obtaining $\gamma_{HS}(t)$

Using equation S14, the sum can be made.

$$\gamma_{HS}(t) = \sum_{i=1}^{n} \frac{I_i(t)}{I_{tot}} \gamma_{HS}^{i}(t) \quad \text{(S14)}$$

According to equation S14 the final value of the $\gamma_{HS}(t)$ is obtained by multiplying the values obtained by the function HS (2θ) (Equation S5) by the values obtained for the area ($I(2\theta)\bullet\Delta 2\theta$), where $I(2\theta)$ is obtained in equation S9, and divide by the total intensity. The total intensity is the sum of the mixed phase intensities, ($I(2\theta)\cdot\Delta 2\theta$), and the LS intensity obtained for the second phase in the Pawley fit.