Electronic Supplementary Material (ESI) for Dalton Transactions.

Nanocrystals of the $Fe(phen)_2(NCS)_2$ prototypical compound and the size-dependent spin-crossover characteristics

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Electronic supplementary information

	Selection of Bragg peaks: 2θ (°)
1 (hydrated form)	9.6, 10.1, 10.8, 12.9, 14.8, 18.1, 19.9, 20.0, 21.121.4, 21.7, 21.9, 22.9 and 23.4
1 (dehydrated form)	9.6, 9.7, 10.0, 10.8, 12.6, 12.9, 14.0, 14.3, 14.7, 15.1, 16.2
1c (in PEG)	~9.7, 10.0, 12.9
1d (in PEG)	~9.6, 9.9, 12.8
1e	9.5, 9.9, 10.8 and 12.7
2 (thermolysis)	10.1, 11.0, 12.2, 15.0, 16.8, 17.5, 18.8, 19, 22.0, 22.6 and 23.3
2a	10.2, 11.0, 12.1, 18.8
2b (in PEG)	10.2, 11.1, 12.2
2c, **2d** (in PEG)	~11.0, 12.1

Table S1: Selection of Bragg peaks extracted from powder X-ray diffractograms collected at RT.

$Fe(phen)_2(NCS)_2$ Litterature[1]		$Fe(phen)_2(NCS)_2$ (Bulk) **(2)**		$[Fe(phen)_3](NCS)_2$ (**1**)
HS (300 K)	LS (100 K)	HS (200 K)	LS (150 K)	300 K
				157
188		181	(185)	
				208
224 (νFe-N_{phen})		224		
	251	(251)	255	
262(νFe-N_{NCS})		261		
285		286		
	300		301	301
	312		315	316
	367 (νFe-N_{phen})		370	371
	377 (νFe-N_{phen})		380	
408		407		
422		420		
	431		435	
	459		441	441
	469		465	466
	477		480	
	494		498	499
	728			
				737
				2053 (νNC_{NCS})
2070 (νNC_{NCS})	2114	2074	2119	

Table S2: Raman frequencies of vibrational modes characterizing the low- and high-temperature phases of **2**. For comparison purpose, corresponding frequencies observed for **1** at 300 K (A. Bousseksou et al., *Chem. Phys. Lett.*, 2000, **318**, 409).

Sample	Raman		Infrared	Magnetism	Mössbauer
T (K)	300	200	100	250	300
Bulk	0.95	0.85	-	0.96	0.95
1.4 µm	-	-	-	0.90	0.90
1.4 µm*	0.98	0.85	-	-	-
650 nm*	1	0.95	-	-	-
29 nm*	0.95	0.62	< 0.3	-	-
25 nm*	0.91	0.67	-	-	-

Table S3: Comparison between the HS fraction determined from magnetic and Mössbauer measurements and the normalized areas of the vibrational peaks assigned to HS species.

Magnetic measurement: HS fraction estimated from $x_{HS} \sim \chi_M T/3.26$ (from data in E. König et al *Inorg. Chem.* 1967, **6**, 48); Mössbauer measurement: Normalized area of the HS doublet; Raman or IR measurement: Normalized area of HS vibrational peaks ($A_{HS}/(A_{HS}+A_{LS})$): A_{HS} peaks at 2061/2074 or 2074 cm^{-1}, A_{LS} at 2105, 2113 cm^{-1} or 2119 cm^{-1} from Raman or IR data respectively;. * highly diluted particles in PEG8000;

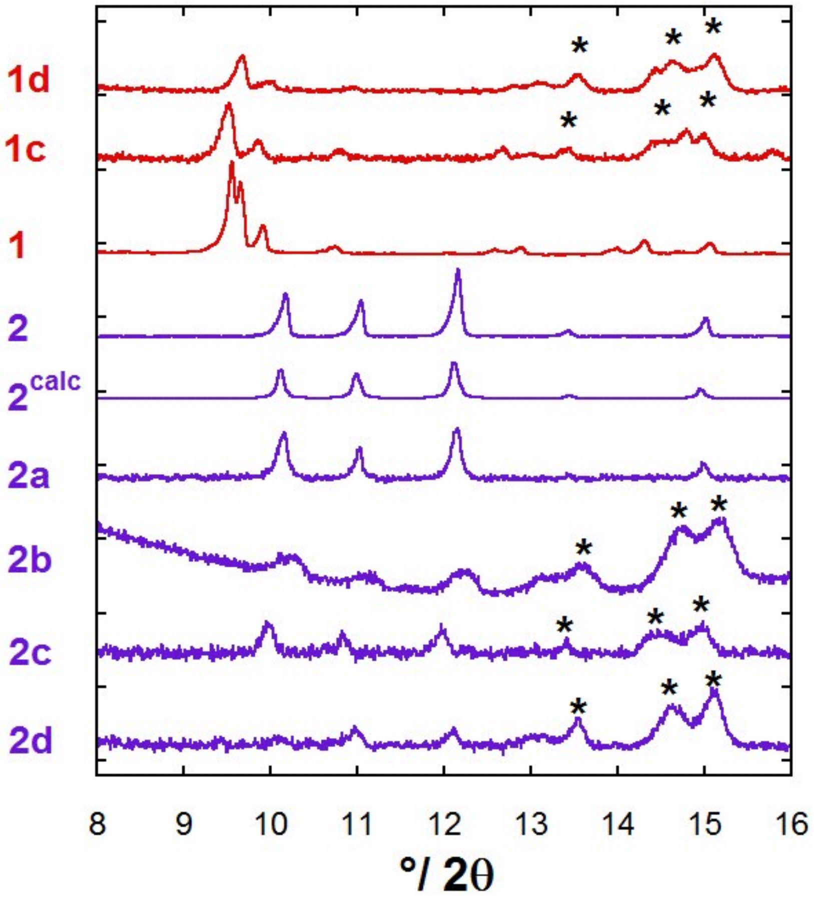


Figure S1: Powder X-ray diffractograms at ambient temperature of polycrystalline powders of **1** (dehydrated form), **2** (prepared by thermolysis) and of micro- and nanoparticles of **1** and **2**: 25 nm (**1c**), 16 nm (**1d**), 1.4 µm (**2a**), 650 nm (**2b**), 29 nm (**2c**), 20 nm (**2d**). The peaks assigned to PEG are marked with (*). $\mathbf{2}^{calc}$: calculated diffractogram of $Fe(phen)_2(NCS)_2$ (polymorph II, 293 K) from B. Gallois et al *Inorg*. *Chem*. 1990, **29**, 1152.

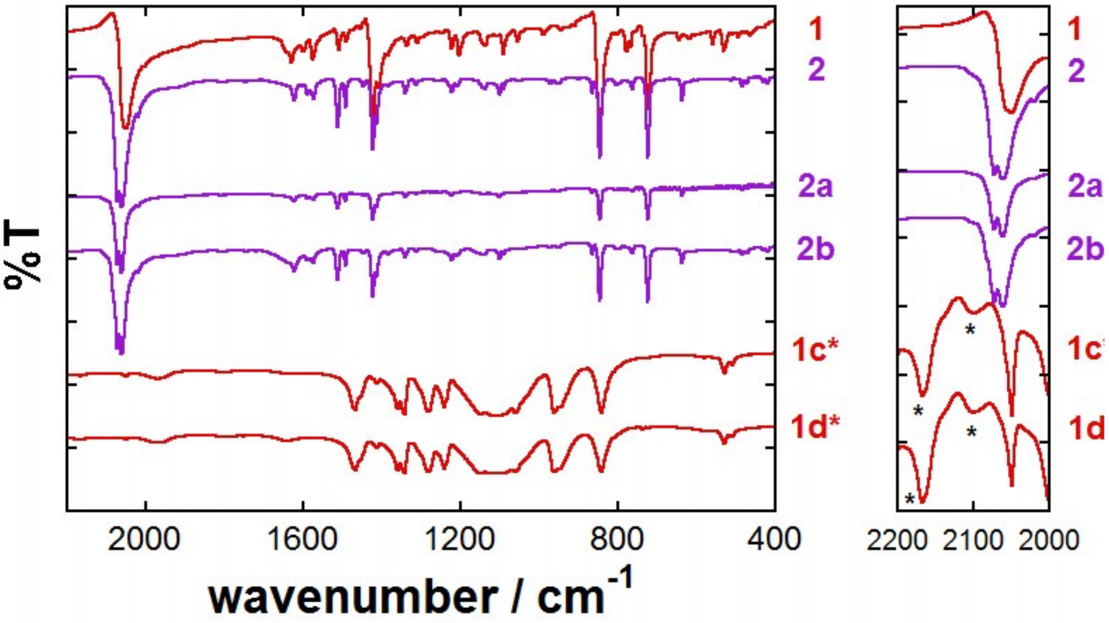
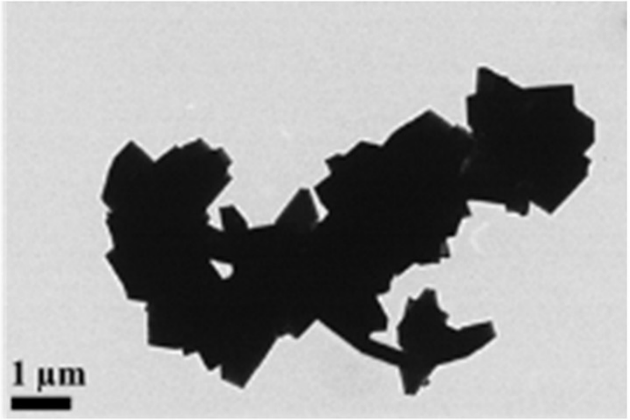


Figure S2: IR spectra at ambient temperature of the polycrystalline powder of **1** before/after thermolysis, micro- and nanoparticles of **1** (inset, 16 (**1d**) and 25 nm (**1c**)) and **2** (1.4 µm (**2a**) and 650 nm (**2b**)). (*) Particles dispersed in PEG, peak assigned to PEG.



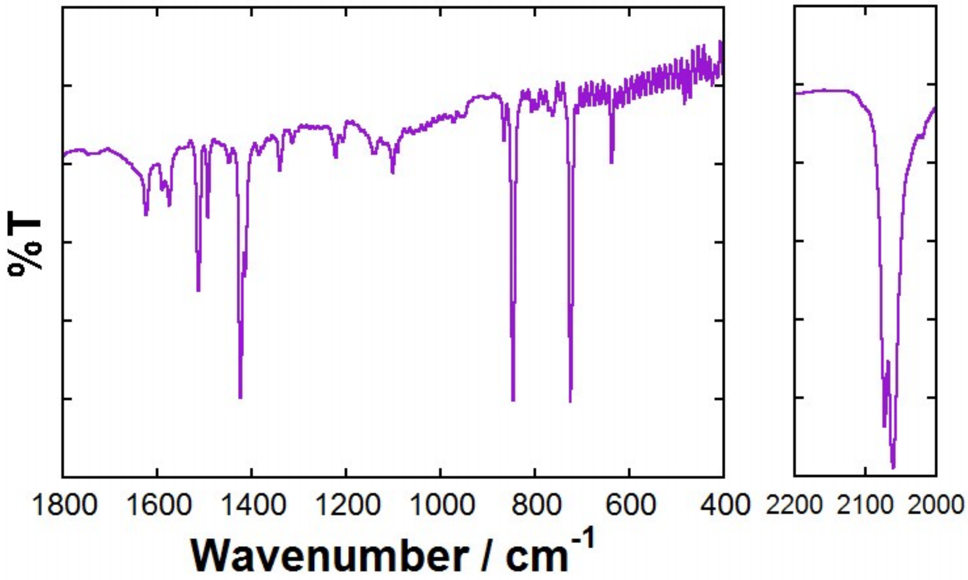


Figure S3: TEM image of the $[1.6\ (0.4)]^2 \times 0.35\ (0.16)\ \mu m^3$ particles of $Fe(phen)_2(NCS)_2$ formed at room temperature by spontaneous precipitation of **1** in methanol ($c = 1.4 \times 10^{-2}$ M). IR spectrum of particles.

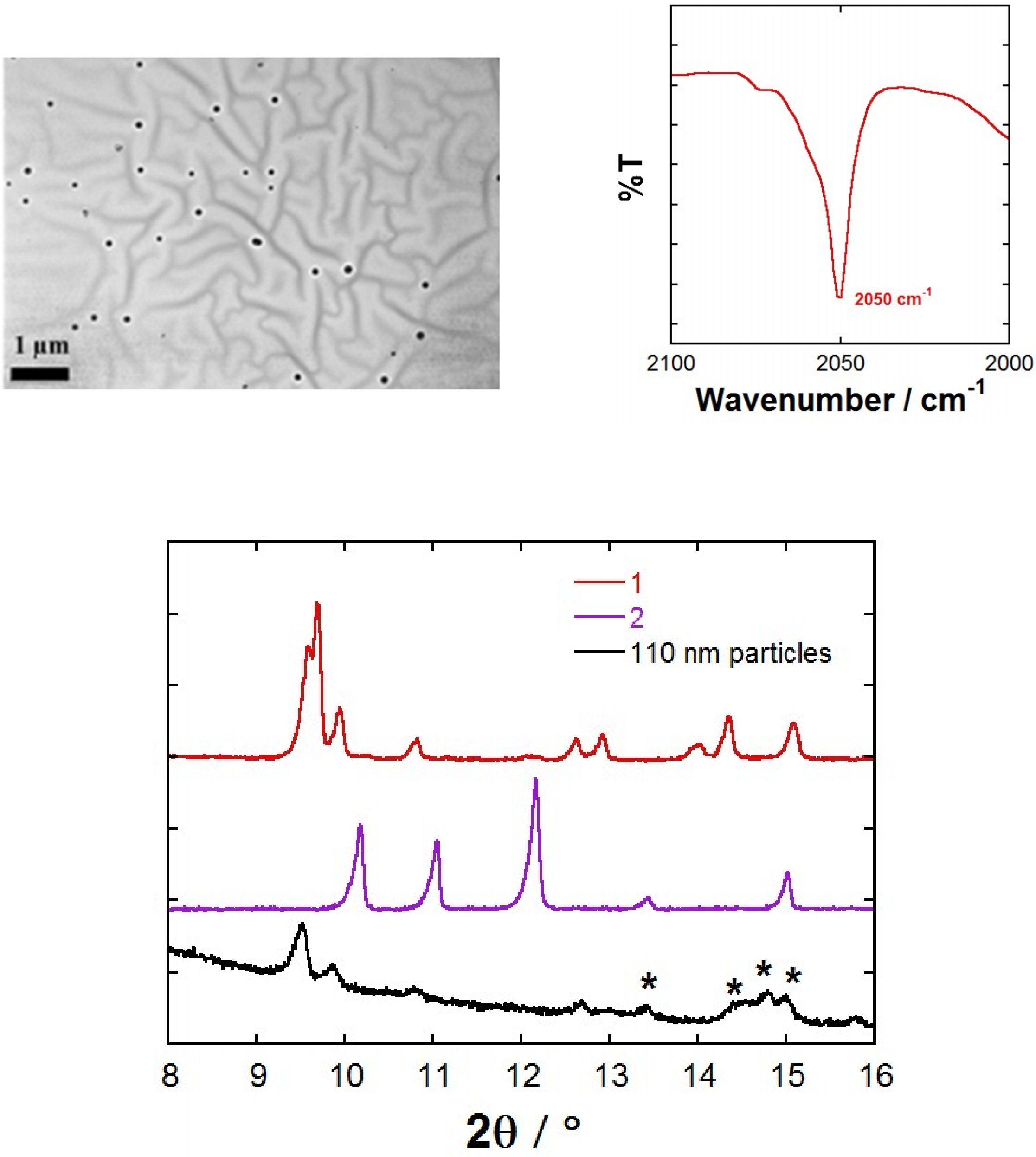


Figure S4: TEM image of the 110 (30) nm spherical particles (**1e**) of $[Fe(phen)_3](NCS)_2$ isolated from the mixture of **1** and an excess of phen in methanol at 20°C. IR spectrum in the 2000-2100 cm^{-1} region and powder X-ray diffractograms of particles at RT. (*) Specific peaks of PEG.

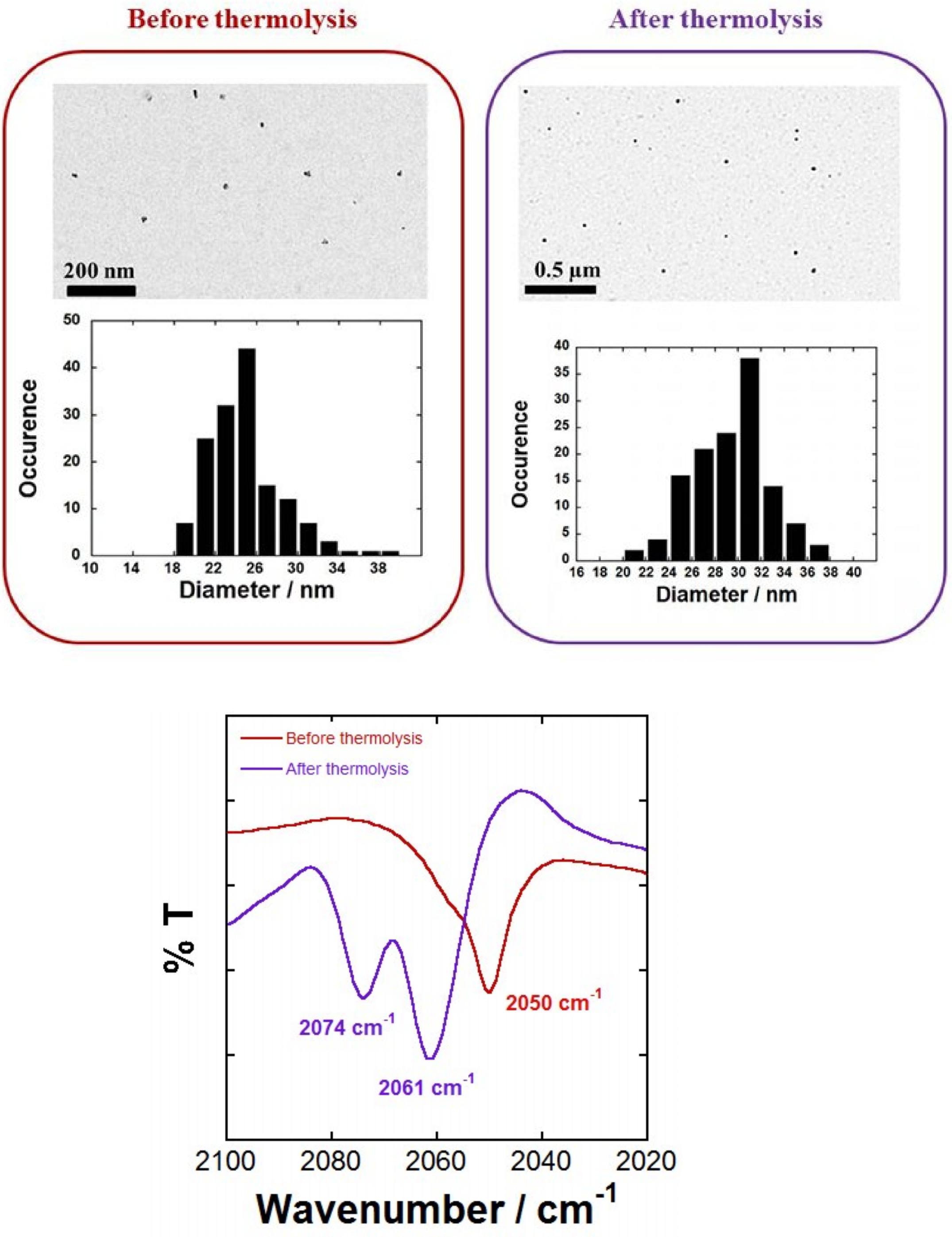


Figure S5: TEM images and related size-distribution of the 25 (3) nm particles of Fe(phen)$_2$(NCS)$_2$ before (**1c**) and after (**2c**) thermolysis and redispersion in butanol. RT IR spectra in the 2060 cm^{-1} region, showing the NC stretching peaks of the NCS groups for both samples. The shift and the splitting of the frequency initially centered at 2050 cm^{-1} for [Fe(phen)$_3$](NCS)$_2$ into 2074 and 2061 cm^{-1} are typical for the coordination of NCS anion in Fe(phen)$_2$(NCS)$_2$.

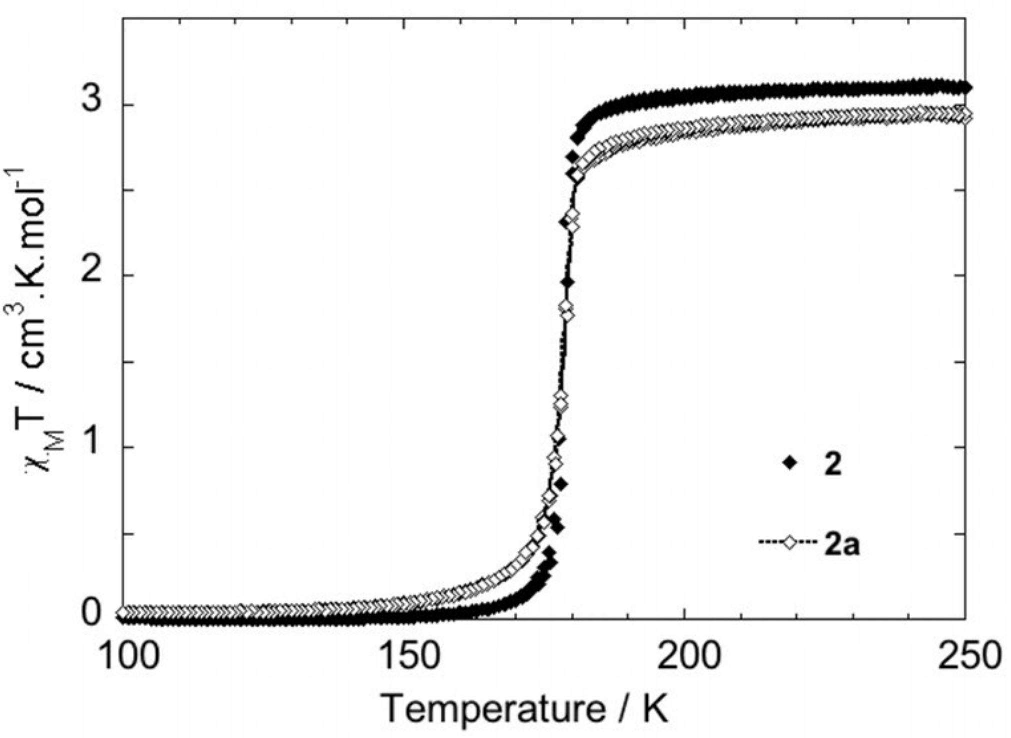


Figure S6: Temperature dependence of χ_MT of the polycrystalline sample of Fe(phen)$_2$(NCS)$_2$ prepared by thermolysis as well as the one of [1.4 (0.4)]^2 x 0.35 (0.14) μm^3 microparticles of Fe(phen)$_2$(NCS)$_2$. The data were collected at a scanning rate of 1 Kmin^{-1}.

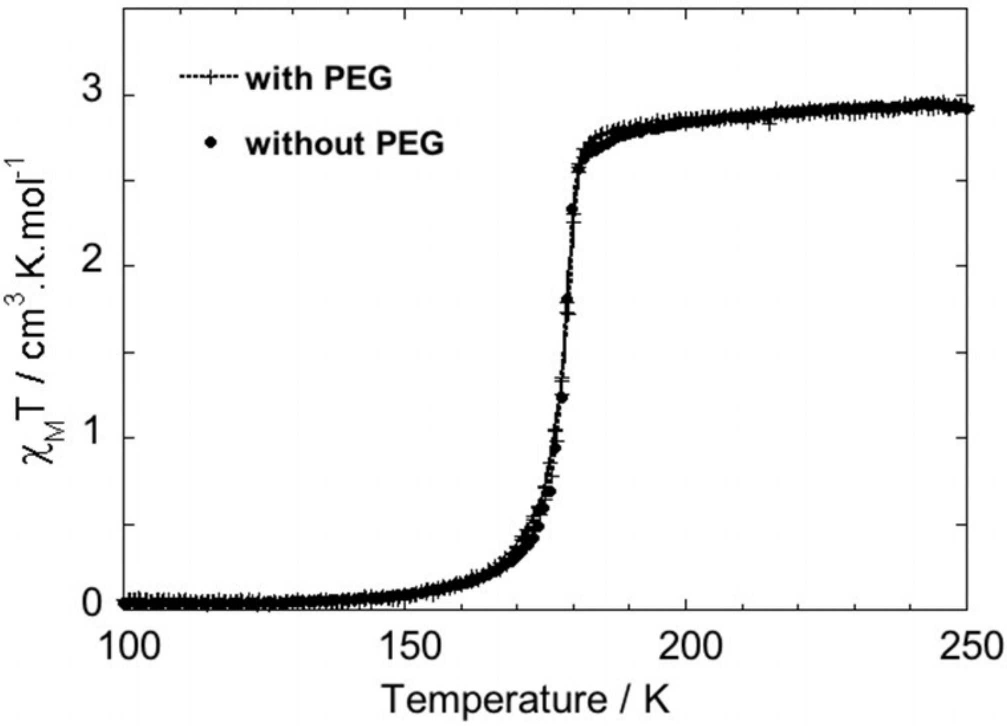


Figure S7: Influence of the polymer (PEG) used for the particles dispersion on the spin-crossover curve of microparticles of Fe(phen)$_2$(NCS)$_2$ (**2a**).

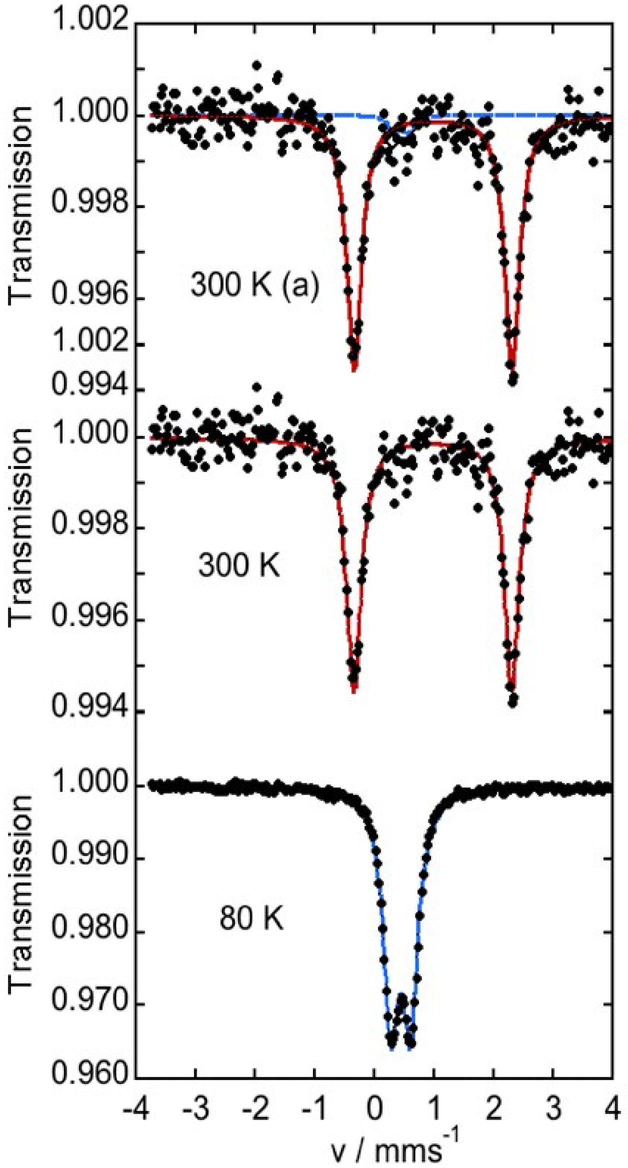
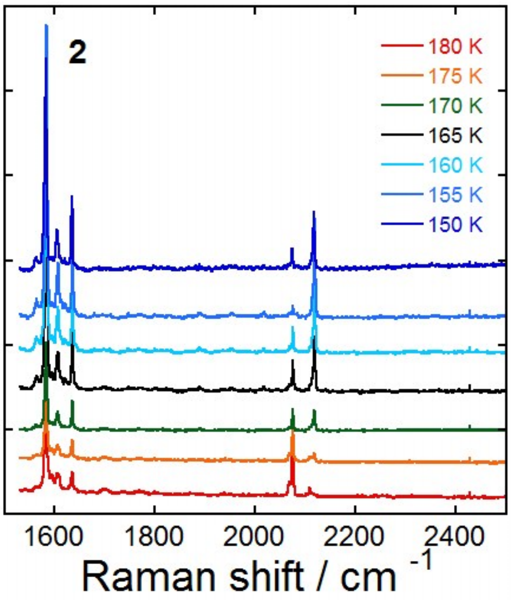
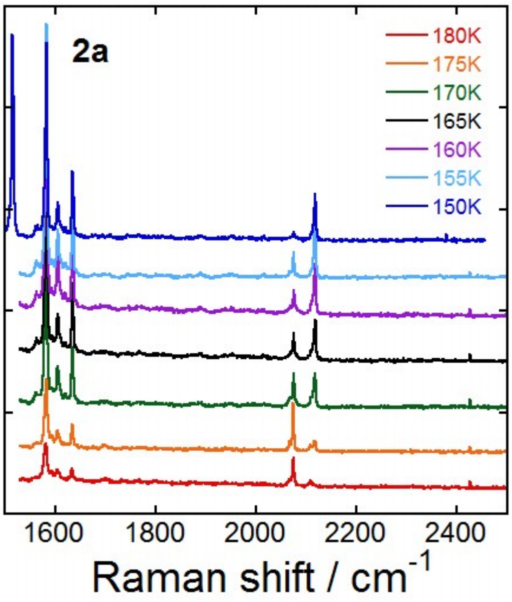
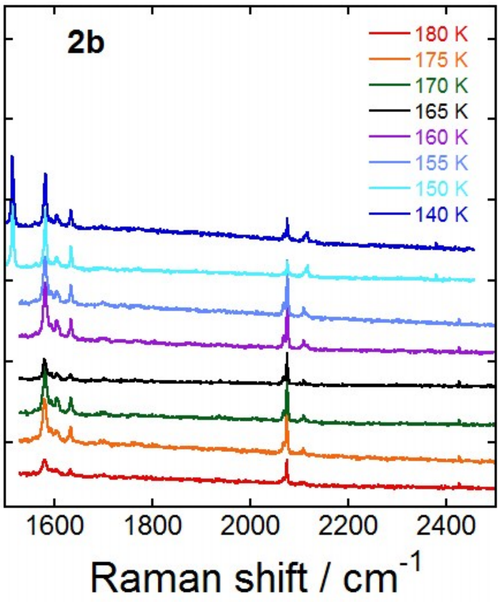
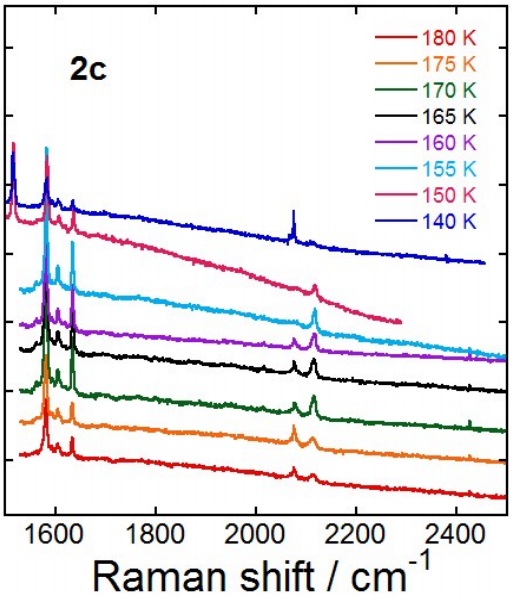


Figure S8: ^{57}Fe Mössbauer spectra of **2** (bulk) collected at 300 and 80 K. The experimental data collected at 300 K were analyzed either with a HS (300 K) or a mixture of HS and LS components (300 K a). Both procedures lead to satisfying R factors.


2
180 K
175 K
170 K
165 K
160 K
155 K
150 K
1600
1800
2000
2200
2400
Raman shift / cm -1


2a
180K
175K
170K
165K
160K
155K
150K
1600
1800
2000
2200
2400
Raman shift / cm-1


2b
180 K
175 K
170 K
165 K
160 K
155 K
150 K
140 K
1600
1800
2000
2200
2400
Raman shift / cm-1


2c
180 K
175 K
170 K
165 K
160 K
155 K
150 K
140 K
1600
1800
2000
2200
2400
Raman shift / cm-1

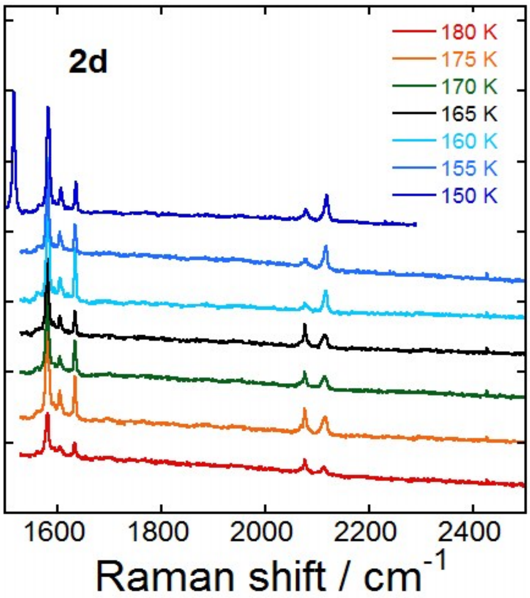

2d
180 K
175 K
170 K
165 K
160 K
155 K
150 K
1600
1800
2000
2200
2400
Raman shift / cm-1

Figure S9 : Expansion in the 1500-2500 cm^{-1} range of the Raman spectra recorded between 180 and 140 K for all the in-PEG dispersed particles of Fe(phen)$_2$(NCS)$_2$.

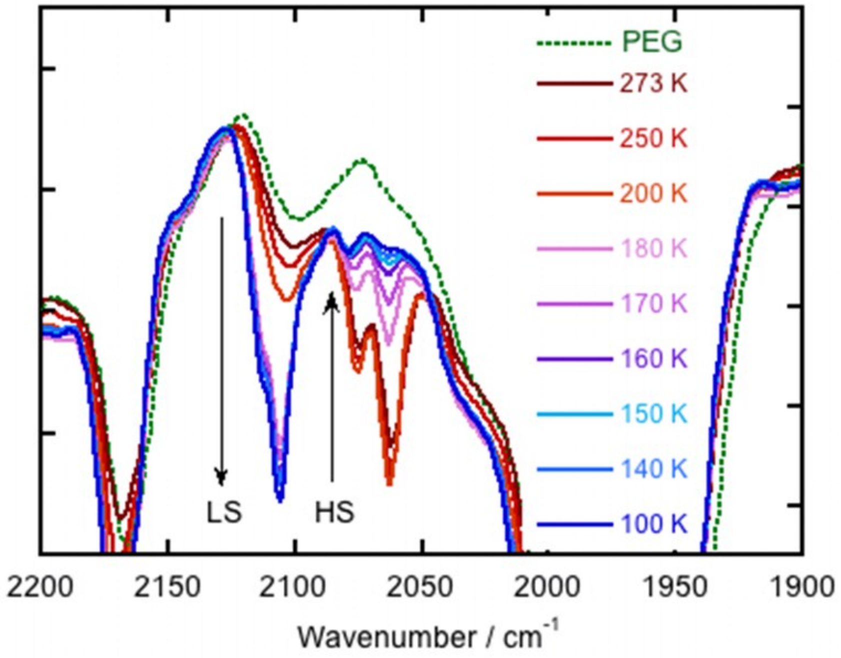


Figure S10: Variable-temperature IR spectra of 29 nm nanoparticles (**2c**) and for comparison purpose, superimposition with the RT spectrum of PEG used as dispersing polymer.