Supplementary Materials

Pressure-induced switching properties of the iron (III) spin transition complex $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$

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Conditions	Pressure (kbar)	$T_{\uparrow}$ (K)	$T_{\downarrow}$ (K)	$T_{1/2}$ (K) = $(T_{\uparrow}+T_{\downarrow})/2$	ΔT (K) = $(T_{\uparrow}-T_{\downarrow})$
Ex-situ	~0[a]	162	160	161	2
oil, ex-situ	~0 [a]	159	155	157	4
oil, in-situ	~0 [a]	157	151	154	6
oil, in-situ	0.5	169	165	167	4
oil, in-situ	2	195	191	193	4
oil, in-situ	3	225	221	223	4
oil, in-situ	4.8	252	247	249	5
oil, in-situ	6.5	-	-	264	2-5

[a], P_{He}~ 400 mm Hg ~ 5x10^{-4} kbar ; Alcatel 100 oil, measurements performed within or out of the pressure cell.

Table S1 – Main characteristics of the M(T) transition curves of an ensemble of small crystals recorded by applying a fixed pressure.

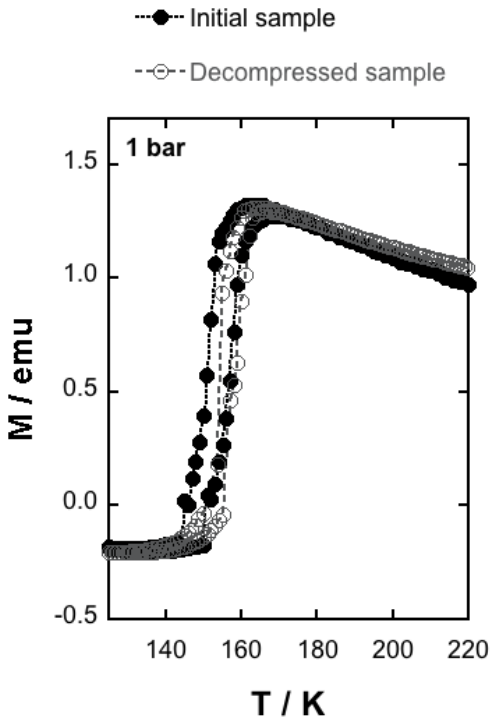

Figure S1 – Magnetization of $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$ recorded as a function of temperature at 1 bar before and after the application of pressure.

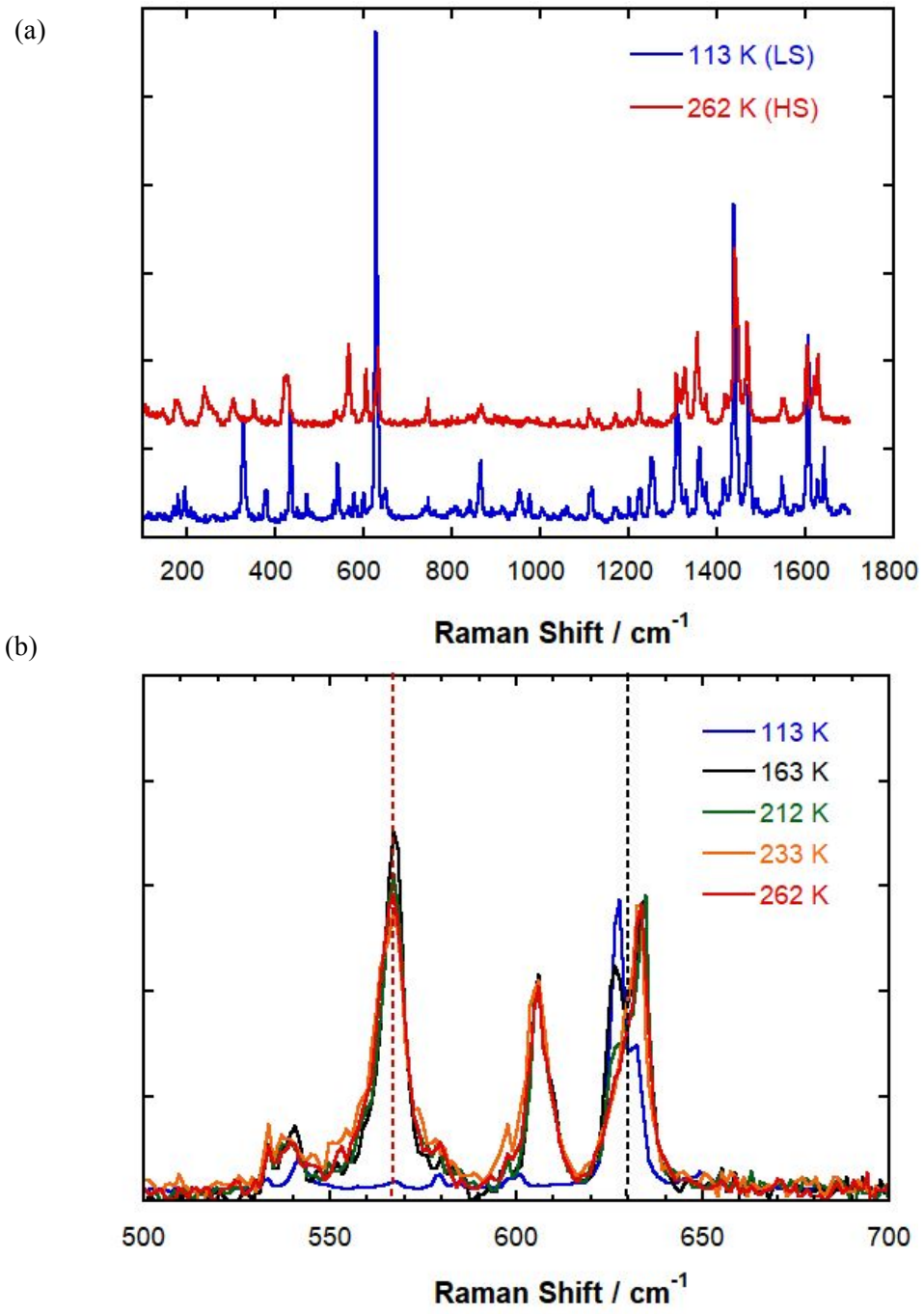

Figure S2 – (a) Raman spectra of $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$ at T = 262 and 113 K (1 bar). (b) Zoom in the 500-700 cm^{-1} area showing the temperature dependence of the 566 cm^{-1} marker normalized with respect to the 630 cm^{-1} double peak.

T = 113 K (LS) P = 1 bar	T = 262 K (HS) P = 1 bar	293 K (HS) P = 1 bar	293 K (LS) P = 12 kbar
195			
	239	240	
	305	300	
328			333
	351	353	
376, 381			376,382
	422,427	421	
434			443
471			
541			546
	565	566	
	605	606	
630 (627,632)	630 (626, 633)	631	629
951			
976			
1252			1254
	1333		
	1356		
1437	1444		1441
1471	1467		1473
1607	1618		1611
1642			

Table S2 - Raman frequencies of vibrational modes characterizing the HS and LS phases of $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$ recorded at variable T (P = 1 bar) and variable P (T = 293 K).

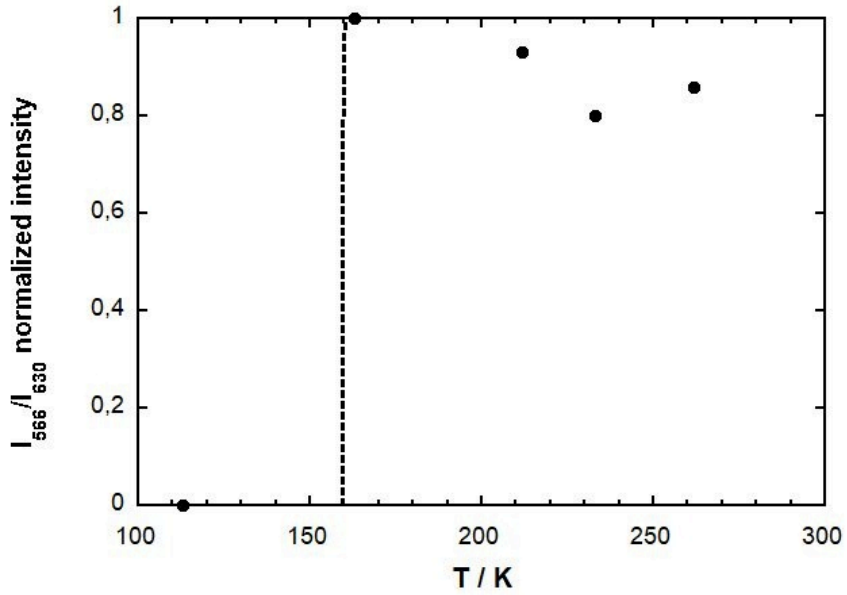

Figure S3 – Plot of the relative intensity ratio I_{566}/I_{630} as a function of temperature showing the change associated to the thermal spin crossover.

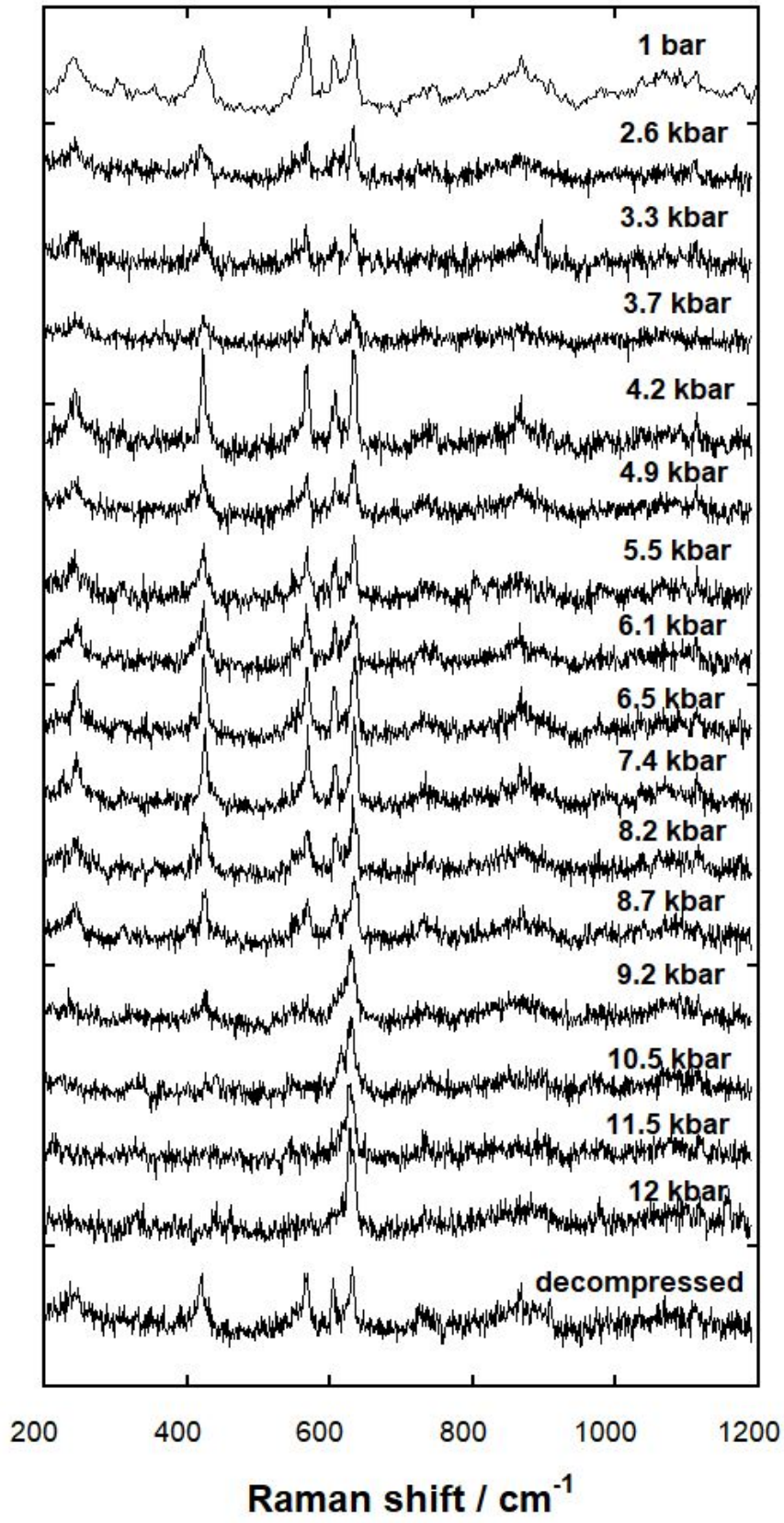

Figure S4 – Set of Raman spectra in the 200-1200 cm^{-1} range of $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$ recorded under pressure.

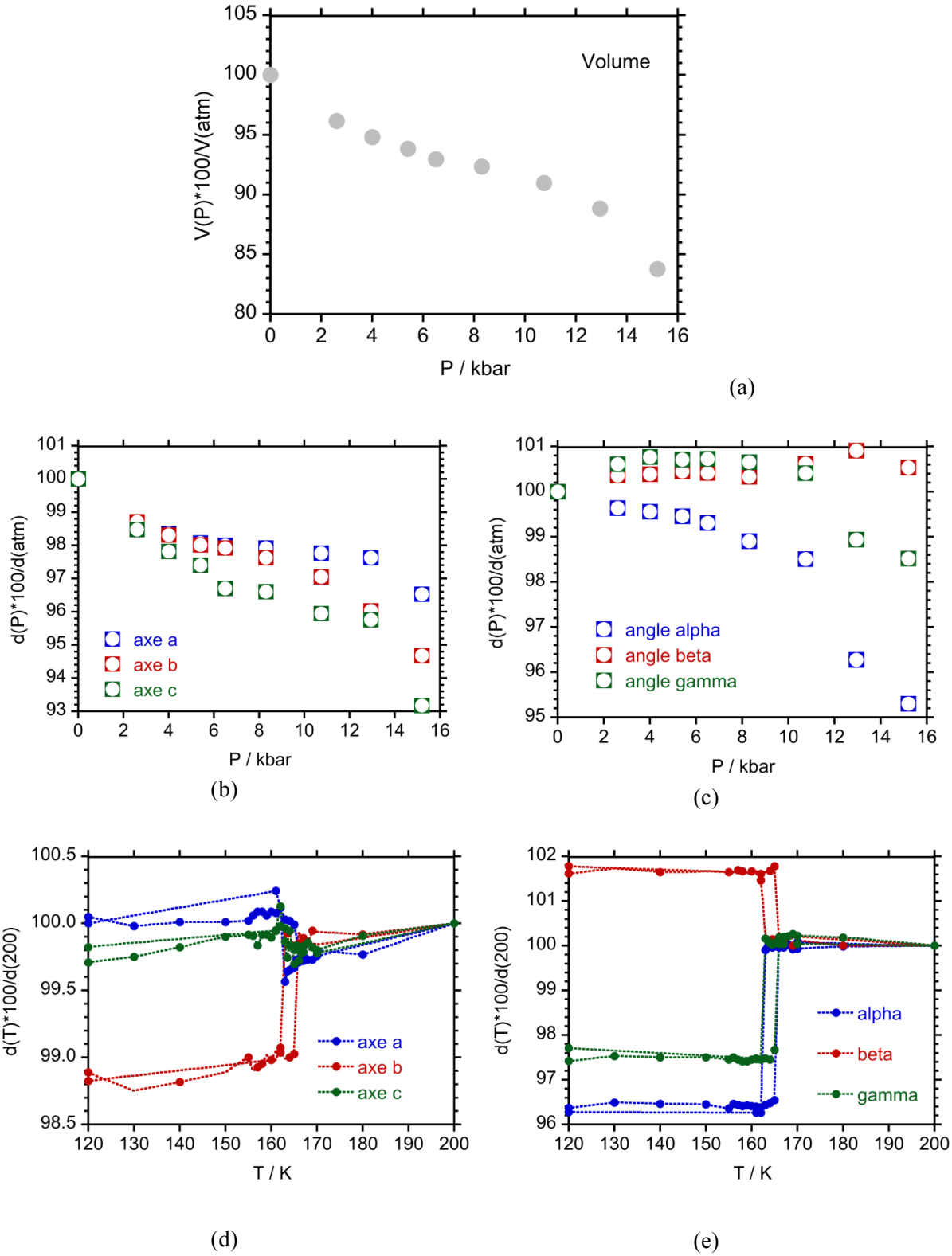

Figure S5 – Relative variation of the lattice parameters of $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$ under the effect of pressure: (a) Lattice volume, (b) *a*, *b* and *c* axes (c) α, β and γ angles. Variation of the *a*, *b* and *c* axes (d) and the α, β and γ angles (e) of the lattice during the thermal transition (see SI in A. Tissot et al, *J. Mater. Chem.*, 2011, **21**, 18347).

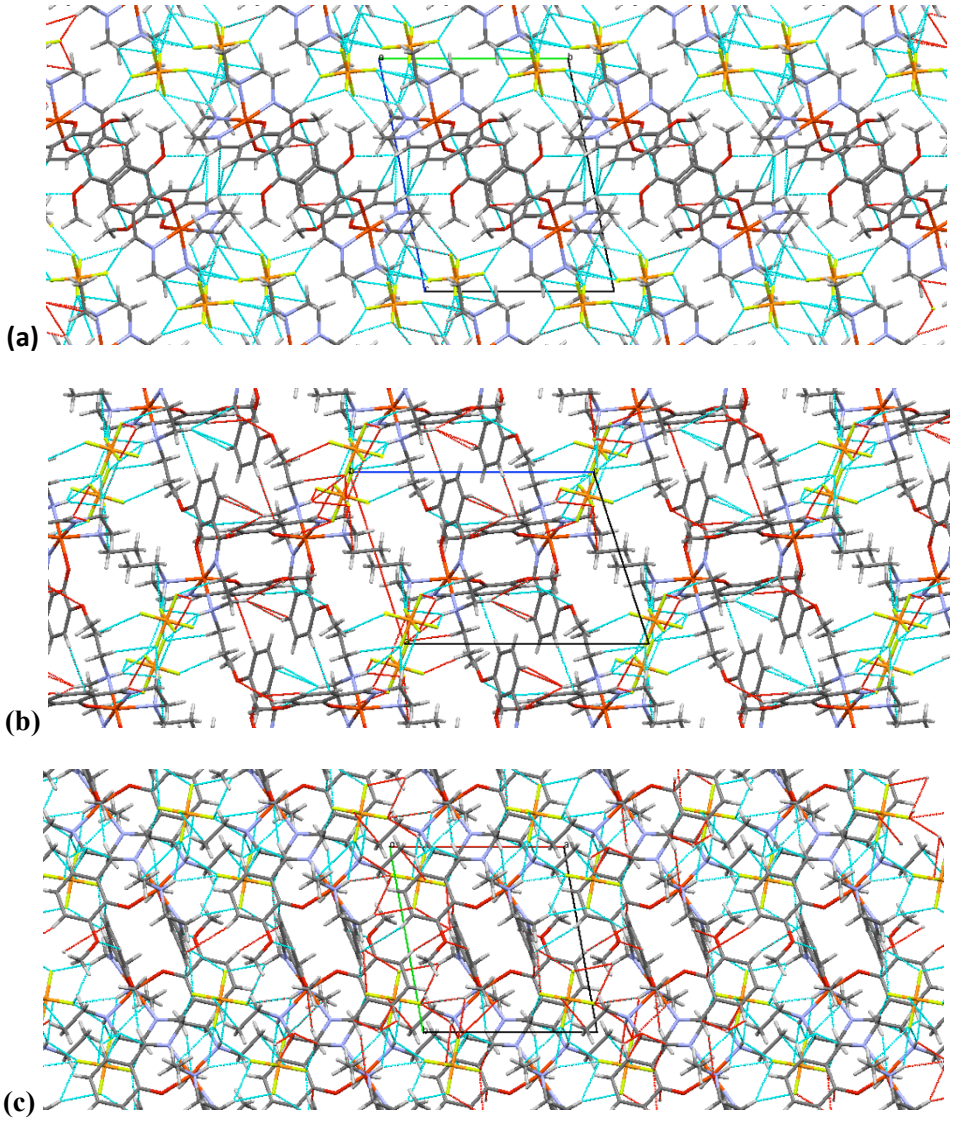

Figure S6 - Crystal packing at 300K of $[Fe^{III}(3\text{-OMeSalEen})_2]PF_6$. View along the *a* axis (a), *b* axis (b) and *c* axis (c). (d) Photography and faces indexation of the platelet-like crystal. The *a* axis is in red, *b* axis in green, *c* axis in blue.

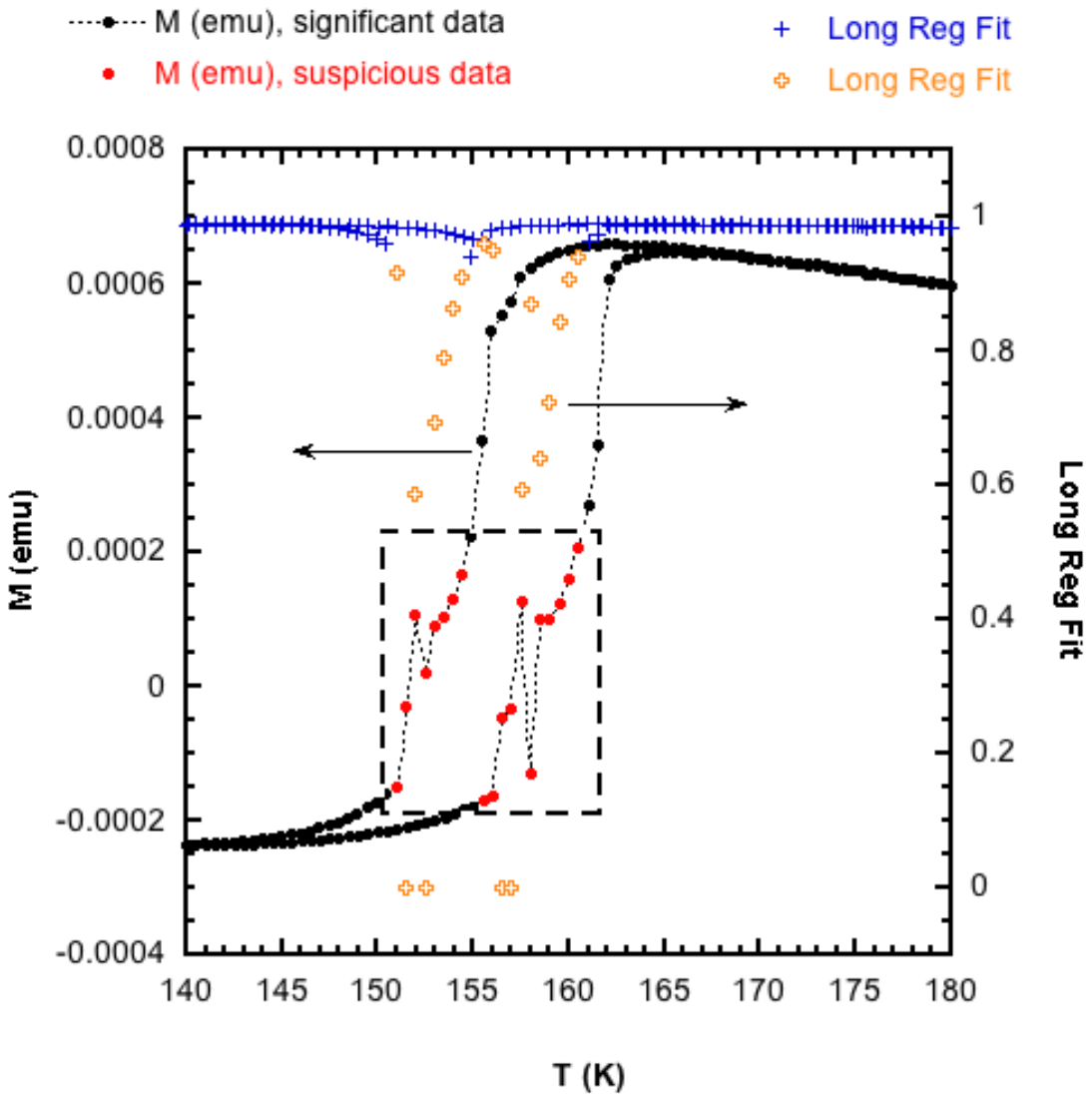

Figure S7 – Magnetization *vs* T plot recorded with the dispersion of crystals of $[Fe^{III}(3\text{-}OMeSalEen)_2]PF_6$ in the Daphne oil (iterative regression algorithm, scanning rate of 0.5 $Kmin^{-1}$). Superimposition with the corresponding response – the longitudinal regression factor - showing artefacts, which can be assigned to suspicious values lower than 0.95 e.m.u. and clearly associated to the distortions in the M(T) plot.

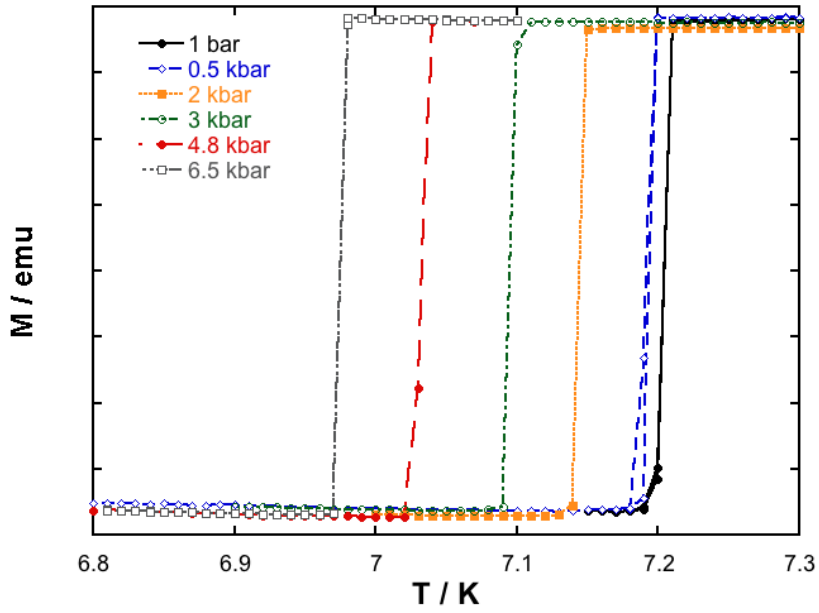

Figure S8– Superconducting transition temperature of Pb as a function of temperature used to calibrate the pressure value in the magnetic measurements.

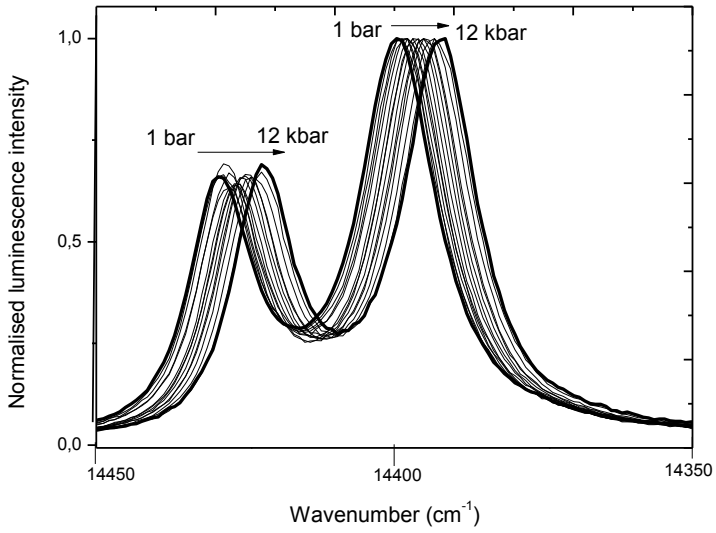

Figure S9– Luminescence spectra of Ruby used for the calibration of the pressure.

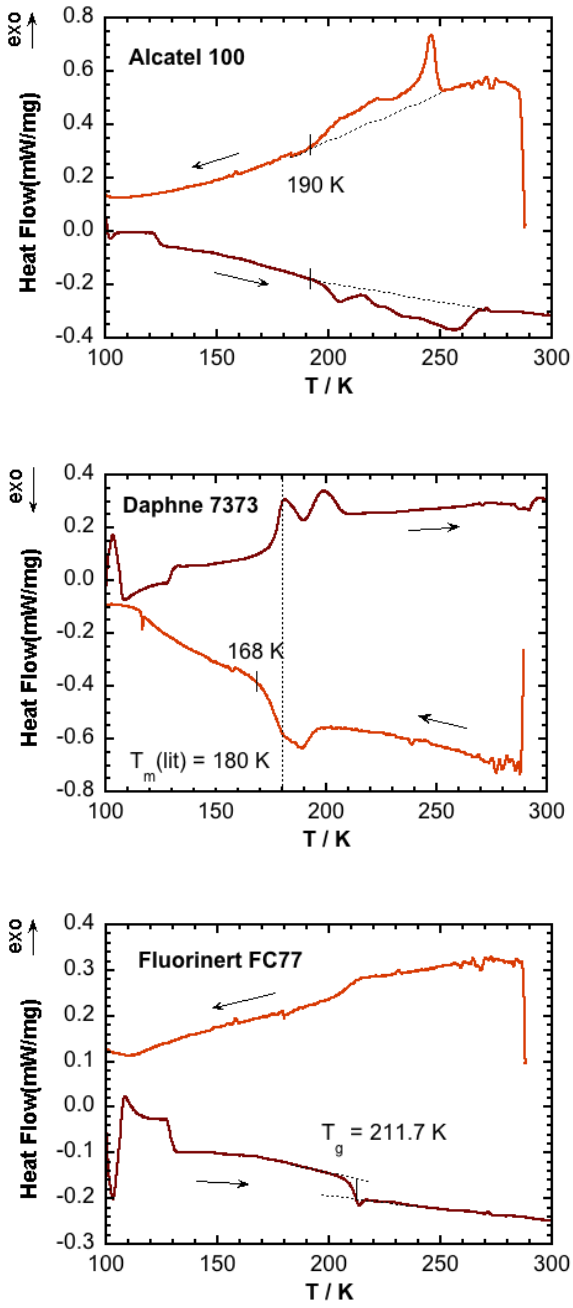

Figure S10– DSC curves of Alcatel 100, Daphne 7373 and Fluorinert FC77 oils recorded at 10 $Kmin^{-1}$. Heating and cooling are indicated by arrows.

The heat flow *vs* temperature plots show exothermic features on cooling corresponding to the multicomponent solidification (vitrification / crystallization) of the media. At atmospheric pressure, the solidification takes place between ca. 250 and 190 K (Alcatel 100), ca. 200 and 170 K (Daphne 7373, in literature[1] T_m = 180 K) or at T_g = 212 K (Fluorinert FC77). Accordingly, all the different matrices used as pressure transmitting media solidify above the transition temperature of the spin-crossover compound under study (ca. $T_{1/2}$ = 164 K).

1- K. Yokogawa et al *Jpn J. Appl. Phys*. 2007, **46**, 3636.