# Supporting Information

**Figure S1.** Thermal Analysis of **1·(1.5MeOH)**.

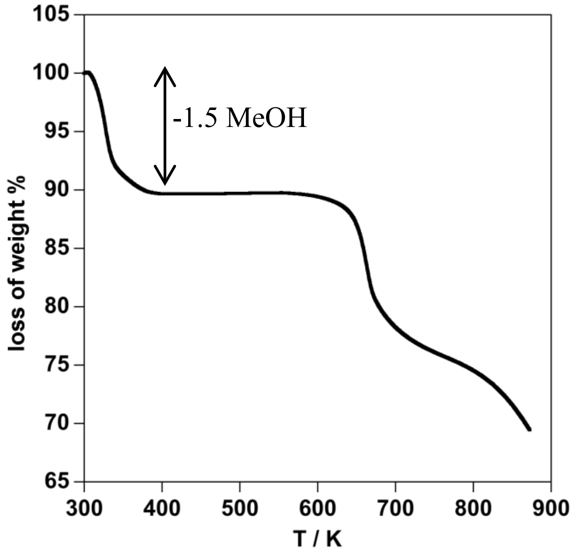


**Figure S2.** Magnetic behaviour of **1** (annealing).

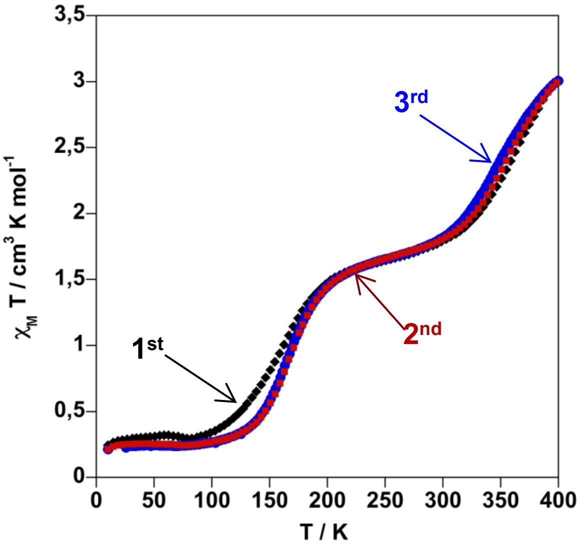
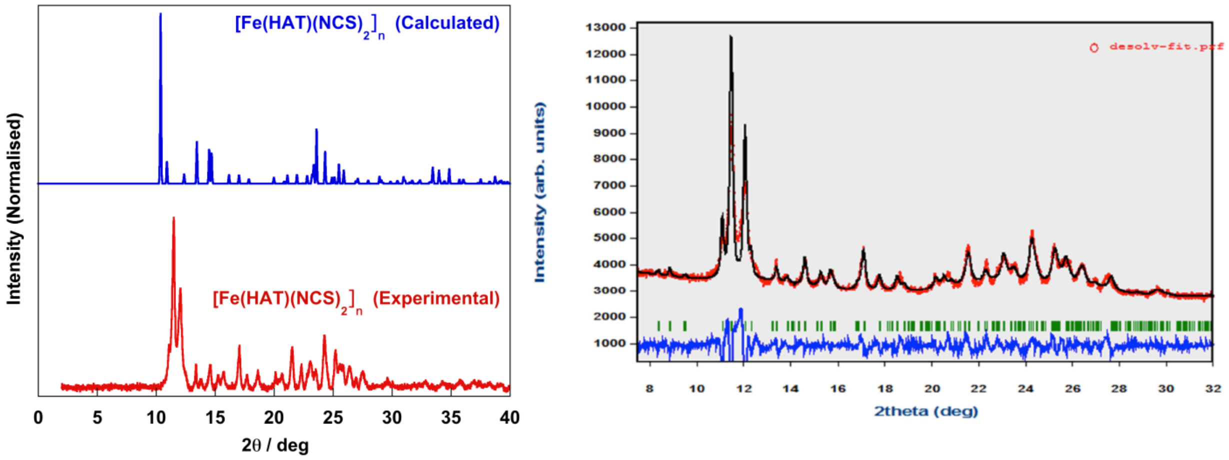


**Figure S3.** (Left) Comparison between experimental and calculated powder X-ray diffraction pattern of $[Fe(HAT)(NCS)_2]$. (Right) Simulation of the experimental pattern with a = 14.6918 Å, b = 12.1399 Å, c = 14.3851 Å, α = 90.00°, β = 93.31° and γ = 90.00°.



The loss of the methanol molecules in $[Fe(HAT)(NCS)_2]\cdot1.5MeOH$ seriously deteriorates the quality of the single crystals, making impossible to obtain single crystal diffraction data. The Powder X-Ray Diffraction (PXRD) pattern of the resulting de-solvated compound has been registered and compared to the calculated one from the single crystal data of $[Fe(HAT)(NCS)_2]\cdot1.5MeOH$ after removing the molecules of methanol from the model (see Figure S3, left). There are two main effects, which make rather difficult a structural analysis of the data: i) the differences between the two patterns are quite important; and ii) the experimental PXRD pattern displays too wide peaks. The large difference between both patterns is an expected result because the distance between the $[Fe(HAT)(NCS)_2]_n$ chains in the de-solvated system must decrease. The wideness of the peaks results from the loss of quality of the crystallites and usually hides important information (additional peaks). Nevertheless, we have simulated the experimental data (Figure 1, right) and proposed a possible indexation, as follows: a = 14.6918 Å, b = 12.1399 Å, c = 14.3851 Å, α = 90.00°, β = 93.31° and γ = 90.00°. However, we have not been able to find the position of the atoms from this pattern.

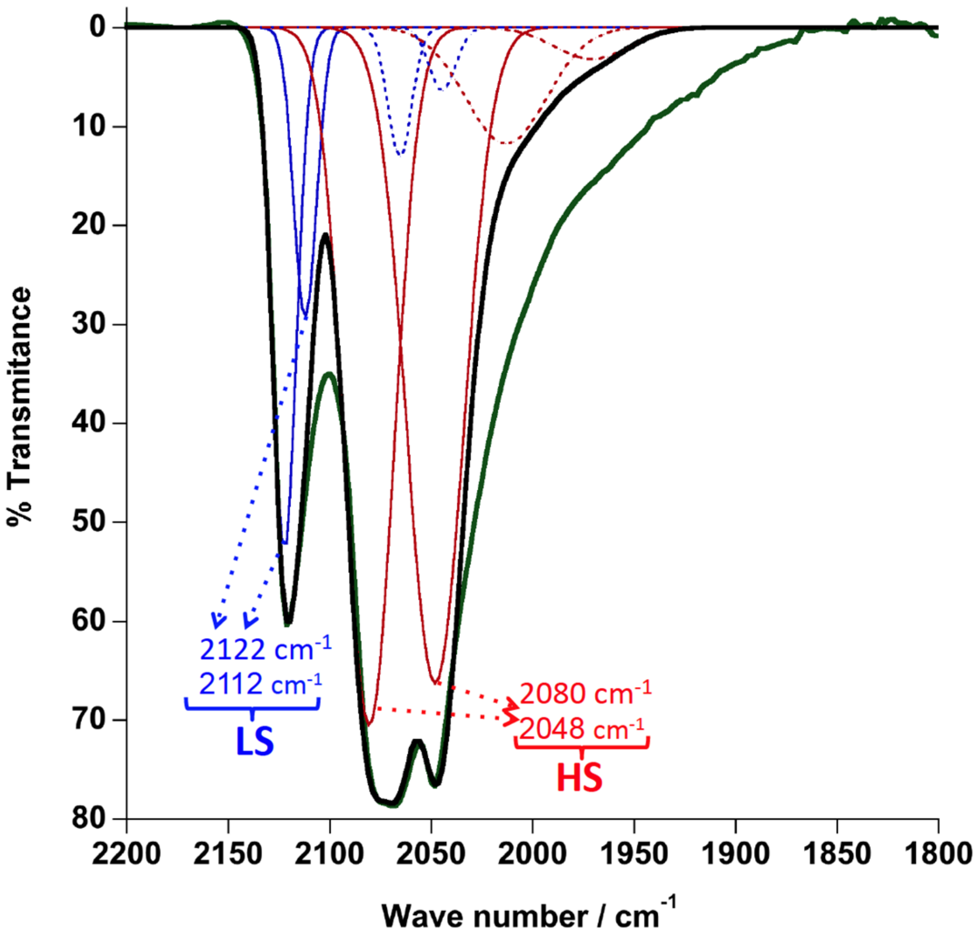


**Figure S4.** IR spectrum of $Fe(HAT)(NCS)_2$ at 300 K.

Experimental IR spectrum of $Fe(HAT)(NCS)_2$ at 300 K in the interval 2200-1800 $cm^{-1}$ at 298 K (Fig.1, green line). This spectrum is composed of several absorption peaks, one centred at 2120 $cm^{-1}$ and two additional peaks (doublet) centred at 2080 and 2048 $cm^{-1}$. Compared with IR spectrum of the prototypal spin crossover complex $[Fe(phen)_2(NCS)_2]$ in the high-spin (HS) and low-spin (LS) states reported by König and Sorai and coworkers[1], it is safe to ascribe the peak around 2120 $cm^{-1}$ to the CN stretching mode of the NCS groups in the LS state whereas the doublet 2080-2048 $cm^{-1}$ to the same group in the HS state. In the mentioned reports the high-resolution IR spectra show two doublets associated with the LS and HS states. Taking this into account, we have simulated reasonably well the experimental CN stretching band of $Fe(HAT)(NCS)_2$ at 300 K (Fig. 1, black line). This simulation has been carried out using four Gaussian functions, namely two for the LS state and two for the HS state (see Fig. 1, blue and red continuous lines, respectively). The obtained values for the LS doublet $\nu(CN)^{LS}$ equal to 2122 and 2112 $cm^{-1}$ and for the HS doublet $\nu(CN)^{HS}$ equal to 2080 and 2046 $cm^{-1}$ agree well with the data found in the literature. According to the previously reported spectra for $[Fe(phen)_2(NCS)_2]$ we have also included four very weak doublets corresponding to the $C^{13}N$ stretching (dotted lines) [$\nu(C^{13}N)^{LS}$ = 2080, 2048 $cm^{-1}$ (blue dotted line); $[\nu(C^{13}N)^{HS}$ = 2013, 1971 $cm^{-1}$ (red dotted line)].

1- a) König, K. Madeja "*Infra-red spectra at the $^5T_2$-$^1A_1$ cross-over in iron(II) complexes*" *Spectrochim. Acta* 1967, *23A*, 45-54; b) M. Sorai, S. Seki "*Phonon coupled cooperative low-spin $^1A_1 \leftrightarrow ^5T_2$ transition in $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$*", *J. Phys Chem. Solids* 1974, *33*, 555-570).