Supplementary Information

Temperature dependence of desolvation effects in hydrogen-bonded spin crossover complexes

Verónica Jornet-Mollá, Carlos Giménez-Saiz, Bruno J. C. Vieira, João C. Waerenborgh and Francisco M. Romero*

Table S1 Summary of crystal data of **1** at 298 K and 120 K.

	1 (298 K)	**1** (120 K)
Formula	$C_{28}H_{26}FeN_{10}O_4$	$C_{28}H_{26}FeN_{10}O_4$
Formula weight	622.44	622.44
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a/ Å	18.4520(2)	18.3091(5)
b/ Å	20.1395(3)	20.1160(4)
c/ Å	15.0697(2)	14.9144(3)
α/ º	-	-
β/ º	94.2540(10)	93.730(2)
γ/ º	-	-
V/ Å^3	5584.68(13)	5481.4(2)
Z	8	8
T/ K	298.00(10)	119.9(2)
D_{calcd}/ g·cm^{-3}	1.481	1.508
λ/ Å	0.71073	0.71073
θ-range/ º	2.435-29.992	3.012-29.792
No. of rflns collected	68072	65272
No. of indep. rflns/ R_{int}	7758/ 0.0449	7476/ 0.0739
Restraints/ parameters	174/ 498	294/ 498
*R*1/ *wR*2 ($I > 2\sigma(I)$)[a]	0.0393/ 0.0888	0.0541/ 0.1014
*R*1/ *wR*2 (all data)[a]	0.0650/ 0.1029	0.0747/ 0.1093
$\Delta\rho_{max}$ and $\Delta\rho_{min}$/ e·Å^{-3}	0.276/ – 0.345	0.501/ – 0.579

[a] $R1 = \Sigma (F_o - F_c) / \Sigma (F_o)$; $wR2 = [\Sigma [w(F_o^2 - F_c^2)^2 / \Sigma [w(F_o^2)^2]]^{1/2}$.

Table S2 Fe–N bond distances of **1** at 298 K and 120 K.

	1 (298 K)	**1** (120 K)
Fe1–N2	2.1772(15)	2.058(2)
Fe1–N3	2.111(2)	2.002(3)
Fe1–N5	2.1849(15)	2.069(2)
Fe1–N6	2.117(2)	2.006(3)
Fe2–N8	1.9638(14)	1.9663(18)
Fe2–N9	1.9154(13)	1.9161(19)
Fe2–N10	1.9671(14)	1.9613(18)

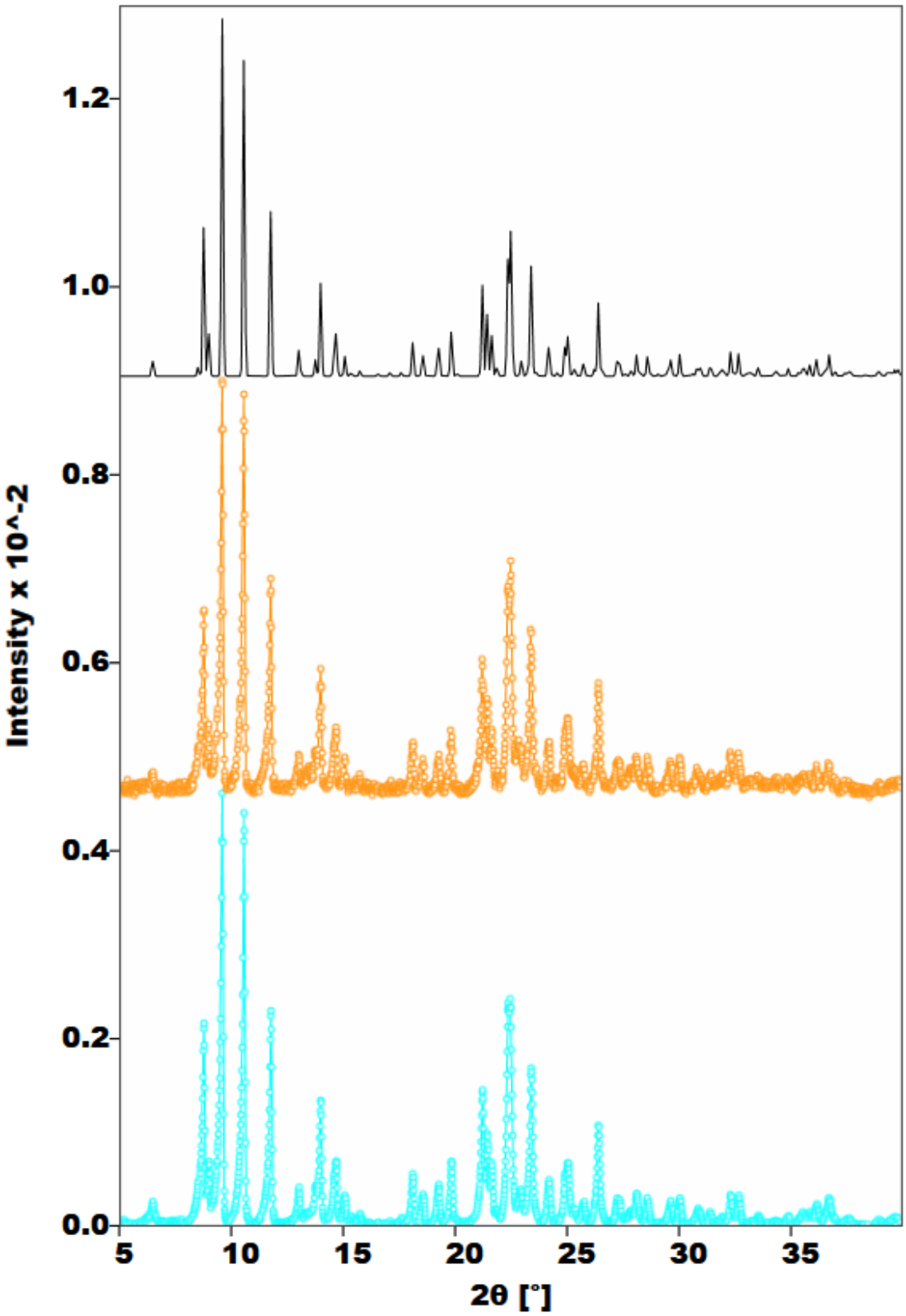

Fig. S1. Room temperature powder X-ray diffractogram of anhydrous **1** registered just after dehydration (orange), and after exposure to ambient humidity during 6 h (blue). The simulation obtained from single-crystal data at 298 K (black line) is shown for comparison.

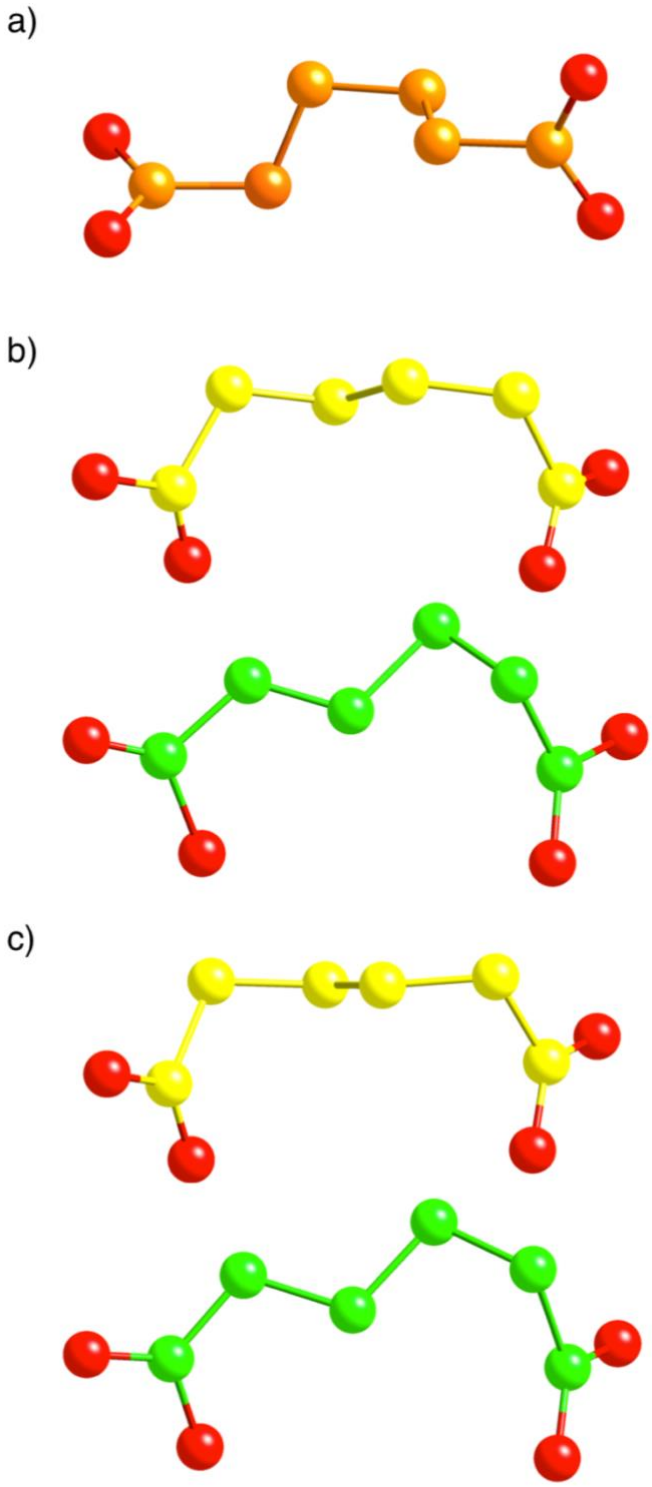

Fig. S2. View of the different adipate anions found in the X-ray crystal structures of **1**·4H_2O (a) and **1** at 298 K (b) and 120 K (c). Yellow and green colours refer to adipates A and B, respectively.

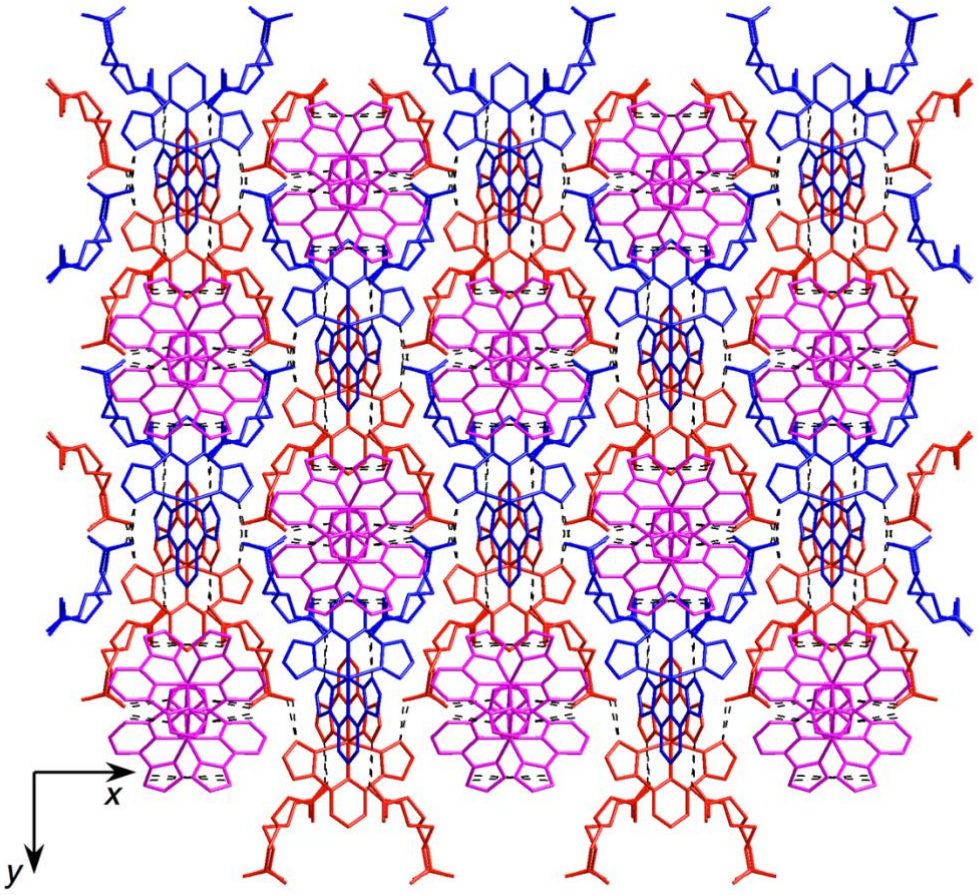

Fig. S3. View of the X-ray crystal structure of **1** at 298 K along the *c* axis. The plot shows two adjacent layers (red and blue coloured) of high-spin Fe1 sites connected by adipate anions. The void within these layers is occupied by stacks of Fe2 sites (depicted in magenta).

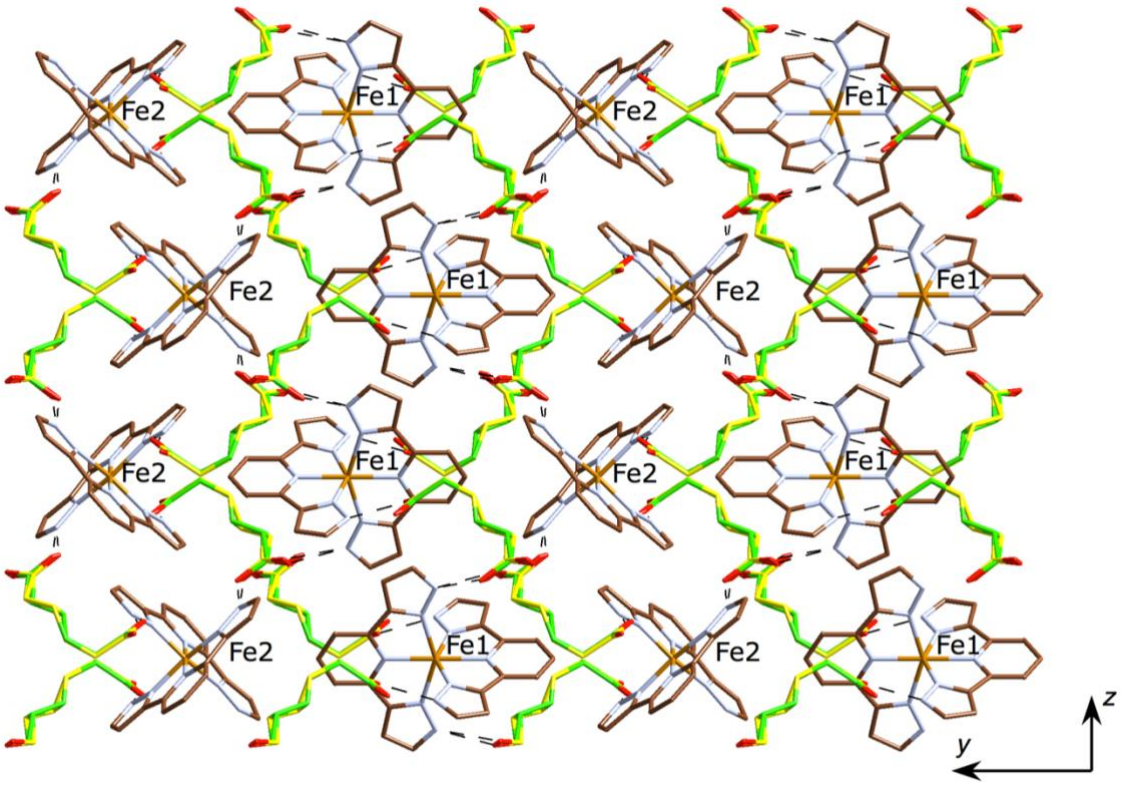

Fig. S4. Partial view of the X-ray crystal structure of **1** at 298 K showing the two crystallographically independent Fe sites forming separate stacks running along the *c* axis. Disordered adipate anions (in yellow and green) occupy the space between the stacks. Dashed lines refer to H bonds.

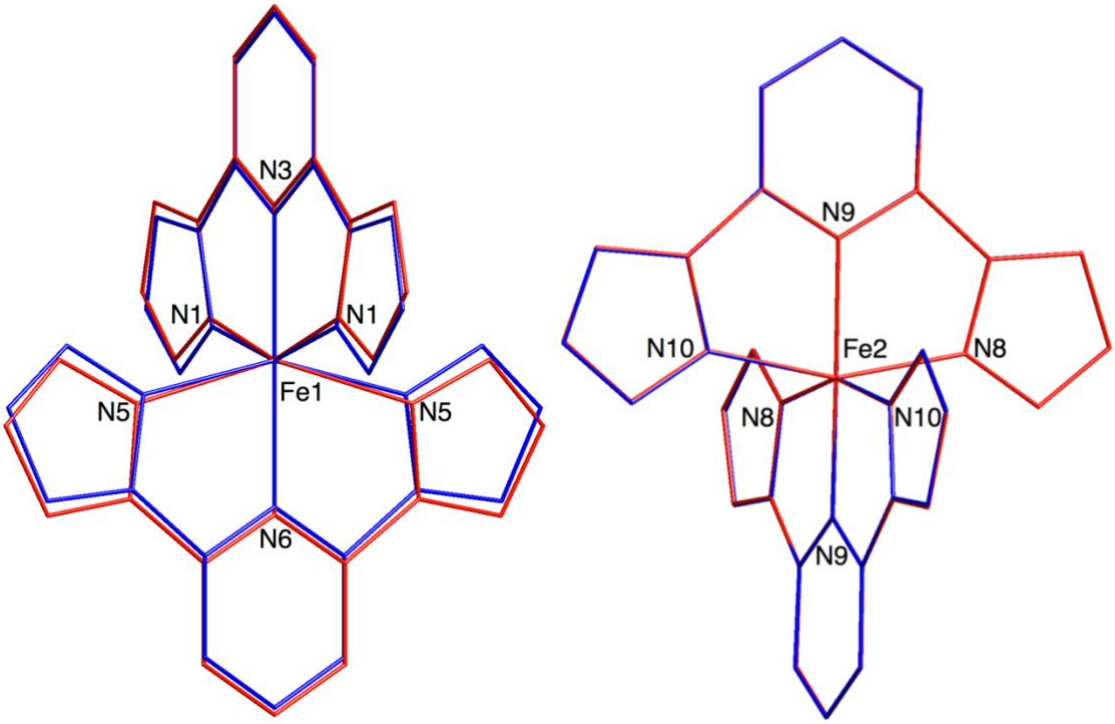

Fig. S5. Superposition of the X-ray crystal structures of **1** at 298 K (red sticks) and 120 K (blue sticks), showing the coordination environment of Fe1 (left) and Fe2 (right) sites.

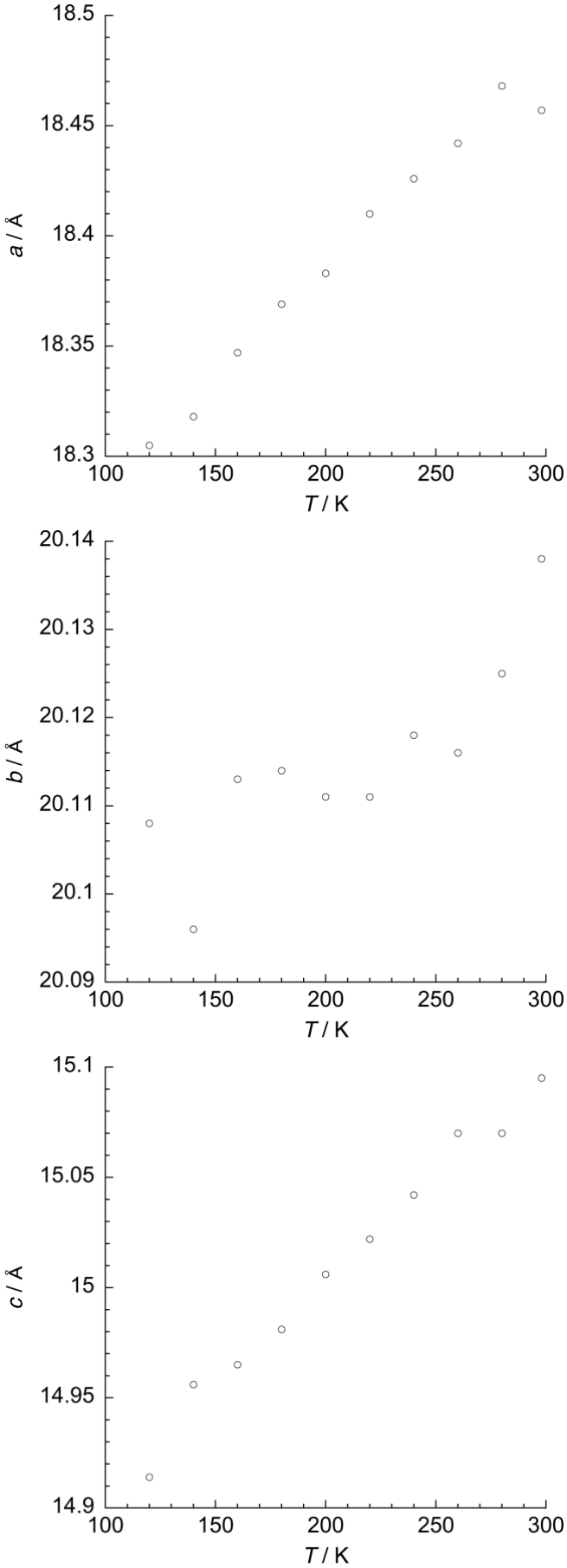

Fig. S6. Thermal dependence of unit cell parameters of **1**.

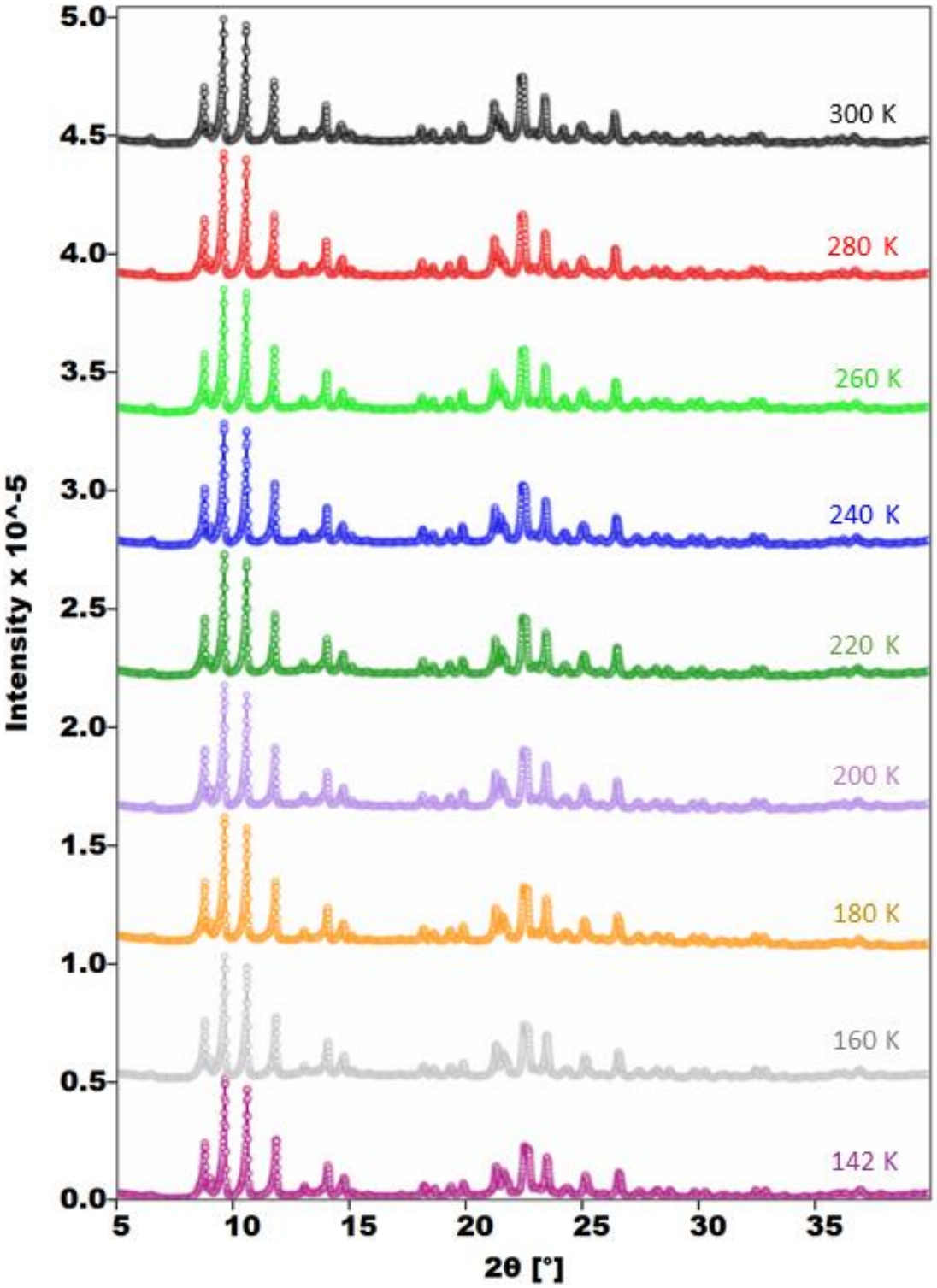

Fig. S7. Powder X-ray diffractograms of **1** at different temperatures.

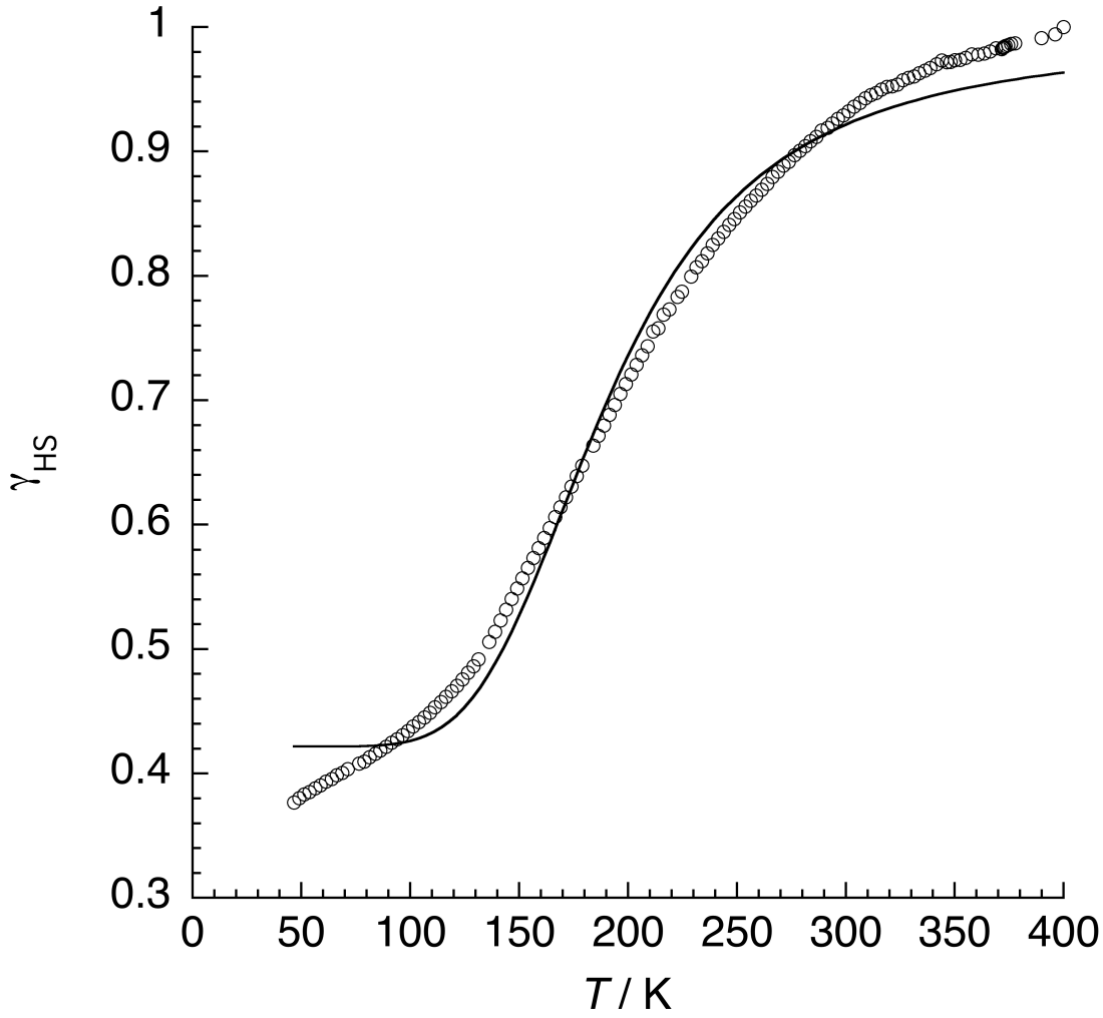

Fig. S8. Temperature dependence of the fraction of high-spin (HS) centers corresponding to the Fe1 site of compound **1**. The line corresponds to the best fit to a Boltzmann distribution with thermodynamic parameters ΔH = 8.4 ± 0.2 kJ·mol^{-1} and ΔS = 30 ± 1 J·K^{-1}·mol^{-1}. The residual fraction of Fe1 HS centers present at low temperatures is γ_{res} = 0.42.

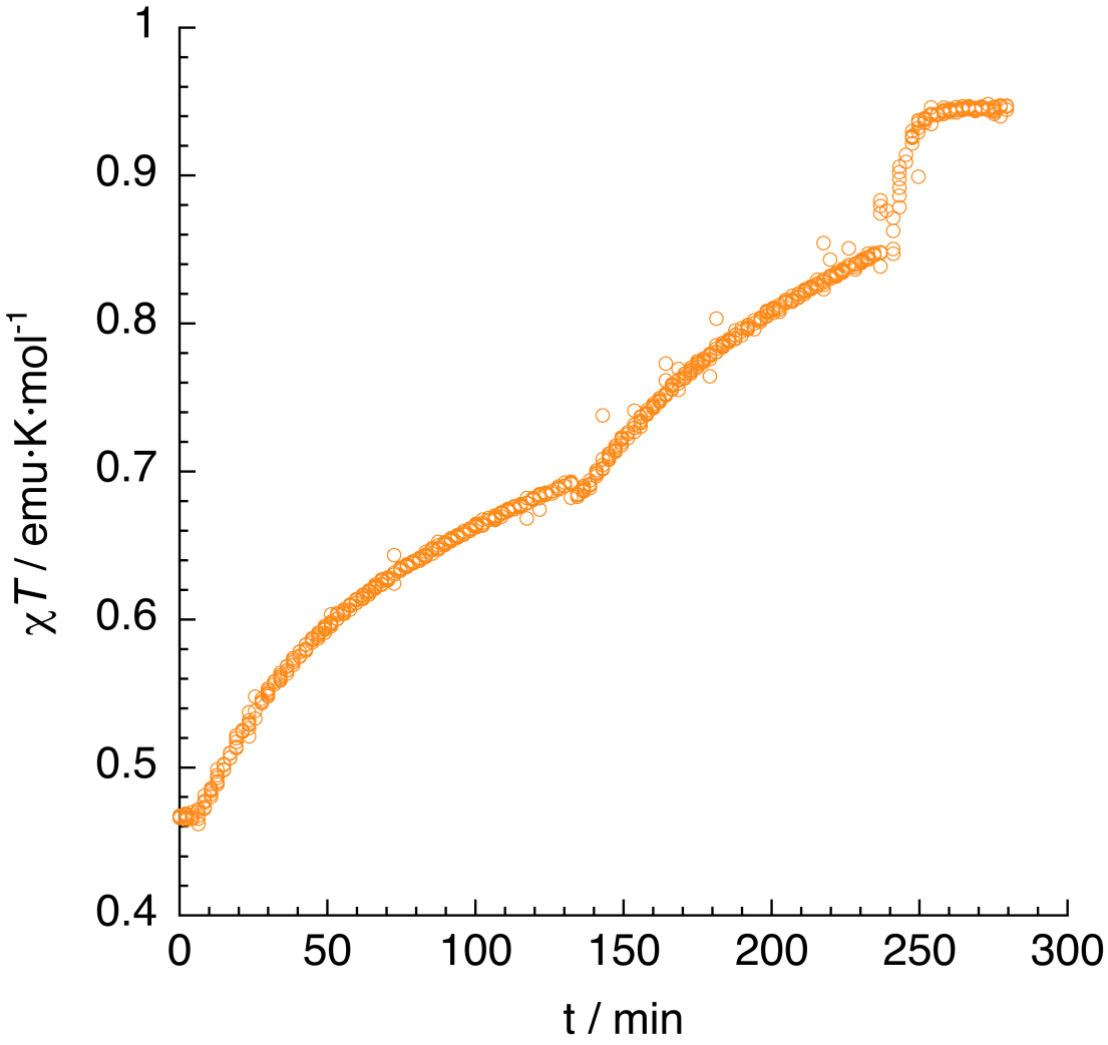

Fig. S9. Time dependence of the χT product of compound **1** during irradiation (λ = 532 nm) at 10 K.