Supplementary materials

Photoinduced HS state in the first spin-crossover chain containing a cyanocarbanion as bridging ligand by *G. Dupouy, M. Marchivie, S. Triki, J. Sala-Pala, C. J. Gómez-García, S. Pillet, C. Lecomte and J.-F. Létard*

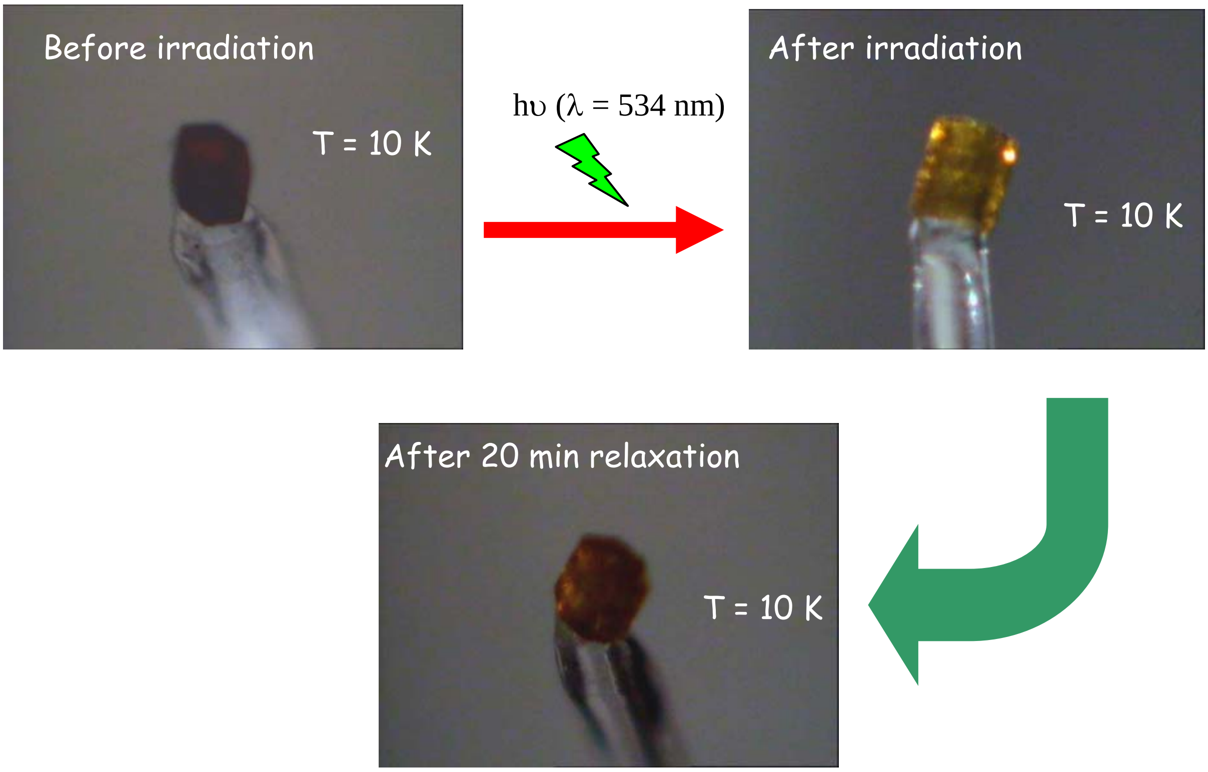
S1 – Synthesis and IR spectroscopy of 1

Chemicals (Aldrich, Fluka) were used without further purification. K_2(tcpd) was prepared as reported.[1] To an aqueous solution (10 mL) of K_2(tcpd) (0.070 g, 0.25 mmol) was added, under vigorous stirring, 1 mL of tetramethoxysilane (TMS). The gel was formed on standing one day at room temperature. A methanolic solution (10 mL) containing $FeCl_2.4H_2O$ (0.050 g, 0.25 mmol) and abpt (0.015 g, 0.063 mmol) was carefully added onto the gel. Yellow prismatic single crystals of **1** were grown within the gel at room temperature after several weeks. They were manually separated, washed with cold water and dried in air (yield 32 %). Four absorption bands assigned to the ν_{CN} stretching vibrations are observed in the IR spectrum (2122, 2168, 2175, 2187 cm^{-1}). The first three absorption bands are in the range of those observed for the tetrabutylammonium salt ($[(C_4H_9)_4N]_2$(tcpd)) containing the uncoordinated cyanocarbanion (2094-2174 cm^{-1}), while the fourth strongest absorption band (2187 cm^{-1}) is significantly shifted to higher wave-numbers. This is in good agreement with the presence of both coordinated and uncoordinated CN groups in **1** as confirmed by the X-ray structures. Single-crystal X-ray diffraction data of **1** were collected at 293, 100 and 10 K (flash cooled and light induced structures). Elemental analysis (%) for **1**: Found: C, 55.7; H, 2.6; N, 34.1; Fe, 7.4. $C_{34}H_{20}N_{18}Fe$ requires C, 55.5; H, 2.7; N, 34.2; Fe, 7.6 %. IR absorptions (KBr) ν/cm^{-1}: 3426br, 3281w, 3199w, 2925w, 2187s, 2175m, 2168m, 2122m, 1653w, 1635w, 1602w, 1591w, 1570w, 1490w, 1458w, 1451w, 1431s, 1413s, 1296w, 1254w, 1035w, 792w, 748w, 701w.

[1] (a) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.* 1958, **80**, 2775; (b) W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.* 1958, **80**, 2788. (c) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.* 1958, **80**, 2795. (d) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.* 1958, **80**, 2804.

S2 – Crystallographic and photocrystallographic studies of 1

1 – Photocrystallographic study, crystal data and detailed description of the molecular chain of **1**.



Scheme S2. Photocrystallographic experiment at 10 K

The crystal structure of the title compound has been solved at 293 K, 100 K, 10 K after a thermal trapping and 10 K in the light induced metastable high spin state. Crystals used for XRD provided a low diffraction pattern what limit the resolution especially at room temperature. The 10K experiments were performed using a He open flow cryosystem (Helijet®, Oxford Diffraction), which restricts the available angular range of the goniometer and the detector to crystal distance and prevents reaching completeness in low symmetry system. However, 70 % completeness could be reached in both cases what lead to relatively good quality crystal structures (see X-ray data collection and refinement parameters gathered in table S2).

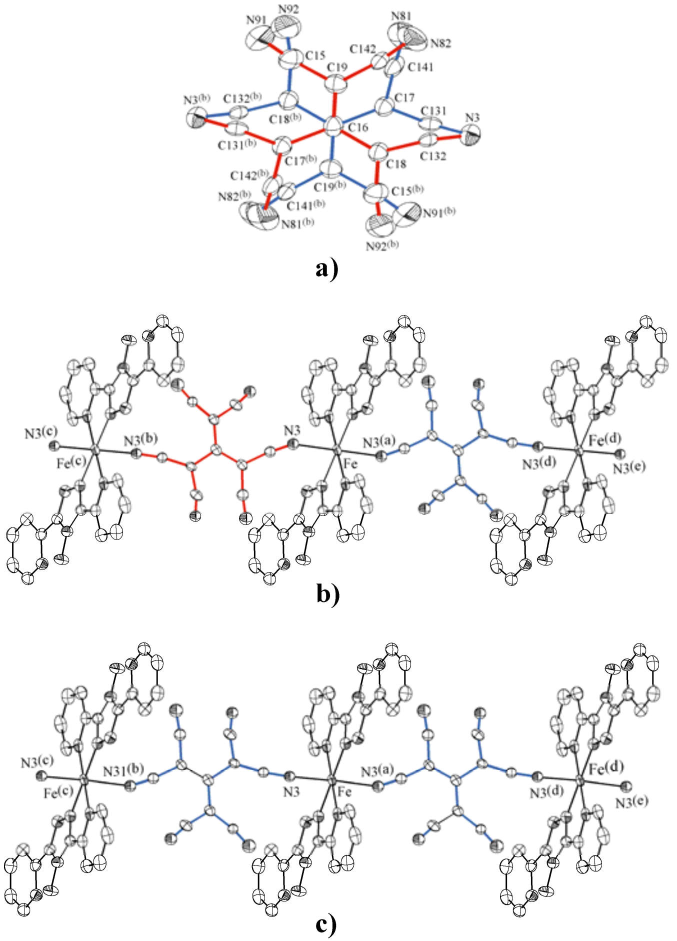
2 - Table S2. X-ray data collection and refinement for [Fe(abpt)$_2$(tcpd)] (**1**) in the temperature range 293-10 K.

Temperature	***293 K***	***100 K***	***10 K*** ***“flash cooled”***	***10 K*** ***“light induced”***
Color				
Formula	$C_{34}H_{20}N_{18}Fe$			
Fw (g.mol^{-1})	736.53			
cryst syst	monoclinic			
space group	$P2_1/n$ (no. 14)			
a (Å)	11.3762(3)	11.2359(3)	11.2071(8)	11.3894(8)
b (Å)	12.4222(3)	12.2079(2)	12.1518(6)	12.1165(4)
c (Å)	11.8683(3)	11.8655(2)	11.8916(5)	11.8384(4)
β (°)	92.031(2)	91.703(2)	91.495(5)	92.832(4)
V (Å^3)	1676.14(7)	1626.83(6)	1618.9(2)	1631.70(14)
Z	2			
ρ_{calcd}	1.459	1.504	1.511	1.499
μ(mm^{-1})	5.07	5.22	5.25	5.20
F_{000}	752			
crystal size (mm)	0.33 x 0.09 x 0.09		0.24 x 0.12 x 0.12	
Refl. Measured	18122	21459	7010	6258
2θ range	5.88-46.50	5.94-52.74	5.96-52.96	5.90-52.72
refl. Unique / R_{int}	2390 / 0.0275	3234 / 0.0311	2474 / 0.0457	2337 / 0.0267
refl. with $I>2\sigma(I)$	1858	2353	1514	1747
N_v	332	322	297	288
$^bR1$ / $^cwR2$	0.0353 / 0.0747	0.0417 / 0.0839	0.0485 / 0.0810	0.0483 / 0.0892
^dGooF	1.112	1.110	1.040	1.144
$\Delta\rho_{\text{max, min}}$ / eÅ^3	0.202/-0.137	0.285/-0.250	0.333/-0.296	0.423/-0.288

$^bR1 = \sum|Fo\text{-}Fc|/Fo$. $^cwR2 = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/\ \Sigma[w(F_o^2)^2]\}^{1/2}$. $^dGOF = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/\ (N_{\text{obs}}\text{-}N_{\text{var}})\}^{1/2}$

Compound **1** crystallises in the monoclinic P2$_1$/n space group and does not show any structural transition within this temperature range. The asymmetric unit is built from one Fe^{II} cation one abpt ligand and one tcpd^{2-} anion presenting an orientation disorder. Both orientations appear in the asymmetric unit as two half of tcpd^{2-} anion in a 0.5 / 0.5 ratio. The atom C15 belongs to both orientations and has, that way, an occupancy factor of 1. Application of symmetry leads to a monodimensional chain where Fe cations are bridged by the disordered organic dianion. Two abpt ligands complete the iron octahedral environment in an equatorial position (Fig. S2A).

3 - Additional description of the molecular chain of 1



a)

b)

c)

Fig. S2A. (a) Ortep structure of the disordered bridging tcpd^{2-} anion showing the two orientations (red and blue orientations); **(b)** and **(c)** structure of two possible portions of the chain of **1** involving the red and/or the blue orientations of the disordered (tcpd)$^{2-}$ anion. Code of equivalent positions: (a) 1-x,2-y,-z; (b) 2-x,2-y,-z; (c) 1+x,y,z; (d) -1+x,y,z; (e) -x,2-y,-z.

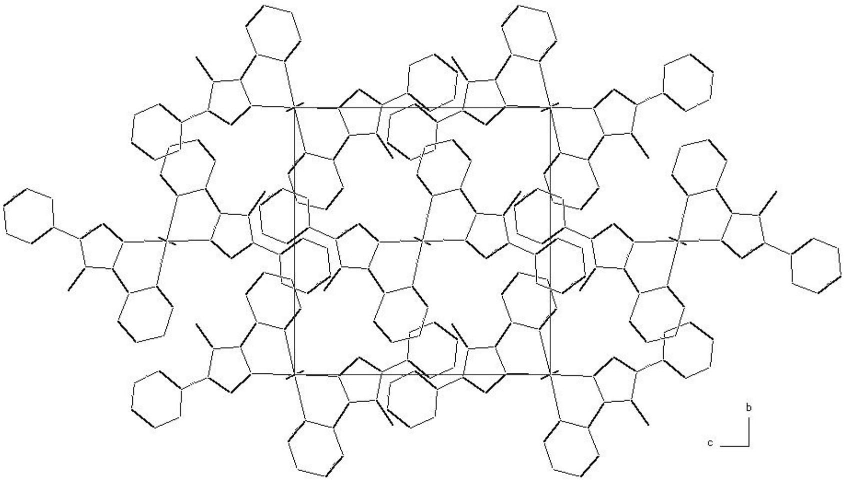


Fig. S2B. View of the packing of the title compound in the *bc* plane showing the π-π interactions between abpt ligands of adjacent chains.

As clearly depicted in Figure S2B, such π-π interactions between abpt ligands of adjacent molecular chains are similar to those observed in parent discrete complexes of the $[Fe(abpt)_2(A)_2]$ series (A = cyanocarbanion) which we have reported recently (see G. Dupouy, M. Marchivie, S. Triki, J. Sala-Pala, J.-Y. Salaün, C. J. Gómez-García and P. Guionneau, Inorg. Chem., 2008, **47**, 8921). The efficiency of theses interactions is the same than in the $[Fe(abpt)_2(A)_2]$ complexes that undergo a spin transition (more than 5 short C-C or C-N contacts in the range 3.26–3.55 Å) and confirm the influence of abpt-abpt π interactions in the presence of the spin crossover.

S3 – Magnetic properties

Variable temperature magnetic susceptibility measurements were carried out on a polycrystalline sample in the temperature range 2-300 K with a Quantum Design MPMS-XL-5 SQUID susceptometer.

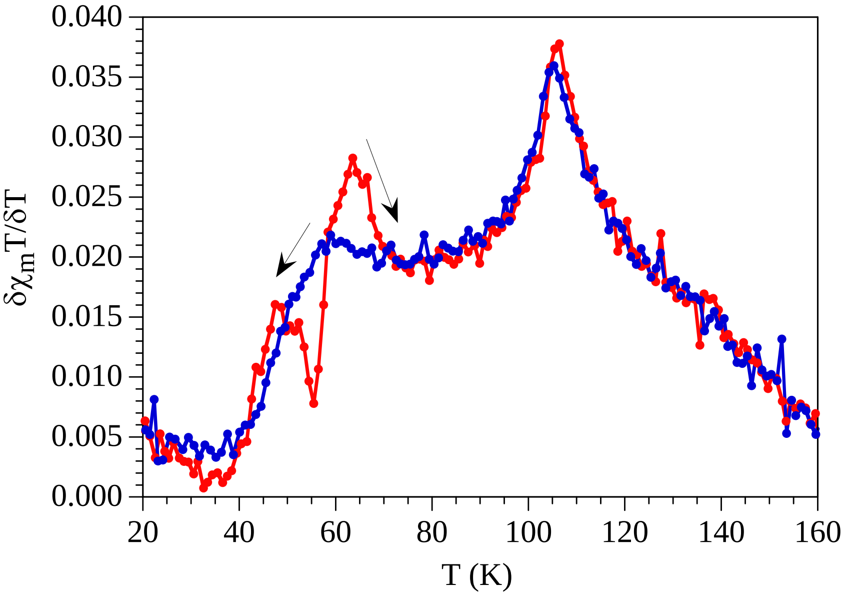


Fig. S3A. Derivative of the $\chi_m T$ product as a function of temperature for the title compound showing the presence of two maxima in the cooling (blue points) and warming (red points) scans.

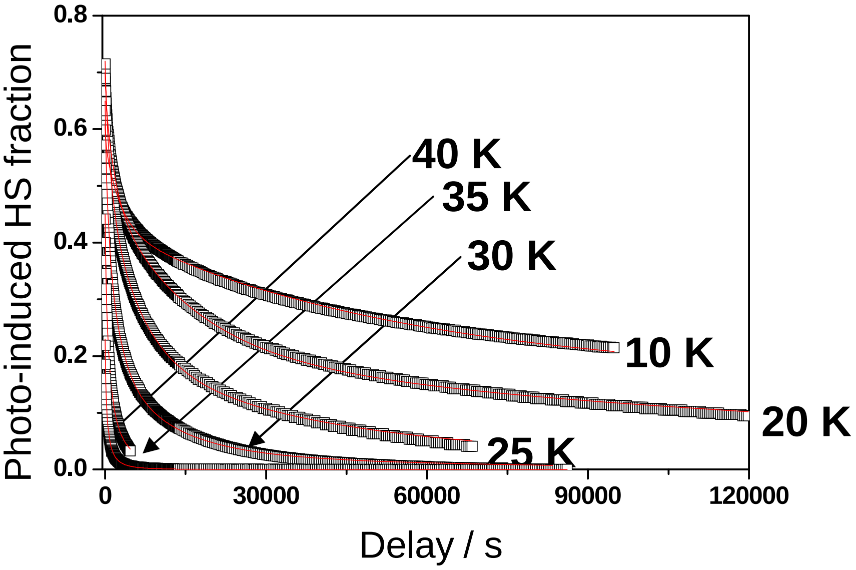


Fig. S3B. Relaxation kinetics of the HS fraction vs. time at different temperatures for the title compound.