

Supporting information

Direct crystallographic evidence of the reversible photo-formation and thermo-rupture of a coordination bond inducing spin-crossover phenomenon

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Methods, materials and physical measurements:

All experiments were carried out under anaerobic conditions using commercial grade degassed solvent. $[\text{Fe}^{\text{II}}_{\text{LS}}(\text{LN}_5)(\text{CN})_2] \cdot \text{MeOH}$ (**1LS-MeOH**) was synthesized as a purple crystalline powder following the reported procedure using Schlenk techniques.¹ Single crystals of the compound were obtained as previously described.² Surface reflectivity measurements were carried out using a home-built system at different temperatures between 10 and 280 K. Due to the dark color of the compound, the sample was previously grounded and diluted in BaSO_4 before the experiments. The spectra were collected using white spectroscopic light (Leica CLS 150 XD, $P = 1 \text{ mW cm}^{-2}$). The measurements were calibrated by comparing the spectra to a white reference obtained with a NIST traceable reflectance standard (SphereOptics, ref. SG3054). As the compound is potentially very photosensitive, the light exposure time was minimized in the experiments during cooling and heating modes keeping the samples in the dark except during the spectra measurements when white light is shined on the sample surface ($P = 1 \text{ mW cm}^{-2}$). For all the excitation/de-excitation experiments performed at 80 K, the sample was initially placed at this temperature keeping it in the dark to avoid any excitation. Heating and cooling measurements were carried out at 4 K min^{-1} . For white light irradiation, the same white light source described above was used, but in a continuous manner with a power of 1 mW cm^{-2} . Light Emitting Diodes (LEDs) operating between 385 and 940 nm (from Thorlabs) were used for excitation and de-excitation experiments.

Single crystal X-Ray crystallography:

A single crystal of **1LS-MeOH** was mounted on a 50 mm MicroMountsTM using CargilleTM NHV immersion oil at 82 K. The crystals were selected and mounted only one day after their formation to avoid crystal damage as previously observed.² The crystallographic data were collected with a Bruker APEX II Quasar diffractometer with a graphite monochromator Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The program SAINT was used to integrate the data (corrected for absorption using SADABS).³ The structures were solved by direct methods and refined by a full-matrix least-squares method on F^2 using SHELXL-2013.⁴ All non-hydrogens were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined isotropically using a riding model, except for those on nitrogen atoms

which were localized on the difference Fourier map, and refined using DFIX constraints. The crystal structure of **1LS·MeOH** contains two crystallographically disordered methanol molecules (one bearing O1b and C18b, and the other one bearing O1c and C18c atoms) which were refined over two positions using EADP and EXYZ constraints. Hydrogen atoms on these disordered solvent molecules were not introduced but are taken into account in the compound formula. The doubling of the unit cell along the *b* axis does not improve the quality of the crystal structure. In addition, examination of the precession images do not show any indication of a doubling of the unit cell.

Crystal structure of **1HS·MeOH** was obtained by irradiating the same single crystal using a 455-nm LED bought from Thorlabs ($P \approx 84 \text{ mW cm}^{-2}$). In order to avoid damaging of the detector, the crystal was left under irradiation for two hours without collecting the diffraction pattern. Unit cell parameters were then measured, exhibiting a new diffraction pattern, and the crystal structure was collected. The crystal structure of **1LS·MeOH** at 250 K was obtained after gently increasing the temperature of the same crystal with a sweep rate of 4 K min^{-1} . The two crystallographically disordered methanol molecules (one bearing O1b and C18b, and the other one bearing O1c and C18c atoms) were again refined over two positions using EADP and EXYZ constraints. Hydrogen atoms on these disordered solvent molecules were not introduced but are taken into account in the compound formula. The crystal structure of **1HS·MeOH** was also obtained by irradiating a new crystal using white light (Leica LED5000 SLI, $P \approx 1 \text{ W cm}^{-2}$) at 82 K. The irradiation was maintained while collecting the crystal in a fixed position to assess the evolution of the diffraction pattern (5 minutes of irradiation). Still with the white light irradiating the crystal, the full collection was obtained. The CIF files have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1521743-1521746.

Table S11. Crystallographic data and structural refinement for **1LS·MeOH** (82 and 250 K) and **1HS·MeOH** (455-nm LED and white light irradiation)

	1LS·MeOH		1HS·MeOH	
Formula	'C36 H54 Fe2 N14 O2'		'C18 H27 Fe N7 O'	
<i>M</i> / g mol⁻¹	826.63		413.32	
Crystal system	monoclinic		monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>		<i>P</i> 2 ₁ / <i>c</i>	
Colour, shape	purple plate		purple plate	
Wavelength / Å	0.71073		0.71073	
Crystal size / mm³	0.09 x 0.09 x 0.02		0.09 x 0.09 x 0.02	0.06 x 0.06 x 0.02
Temperature / K	82(2)	250(2)	82(2)	82(2)
Light irradiation source	-	-	455-nm LED	white light
<i>a</i> / Å	10.8084(4)	10.8708(8)	10.8410(17)	10.8196(19)
<i>b</i> / Å	23.0976(11)	23.2716(18)	11.5544(18)	11.5806(18)
<i>c</i> / Å	15.5032(9)	15.6275(14)	15.814(3)	15.777(3)
<i>β</i> / °	94.329(2)	94.751(3)	94.199(5)	94.491(7)
<i>V</i> / Å³	3859.3(3)	3939.9(5)	1975.6(6)	1970.7(6)
<i>d</i>_{calc} / g cm⁻³	1.423	1.394	1.390	1.393
<i>Z</i>	4	4	4	4
Unique reflections	7896	7095	3624	3593
Parameters; Restraints	505; 4	503; 4	254; 8	254; 2
<i>R</i>₁^a [all data]	0.0873	0.1423	0.0785	0.1132
<i>wR</i>₂^b [all data]	0.1447	0.2836	0.1493	0.1549
<i>R</i>₁^a [<i>I</i> > 2σ(<i>I</i>)]	0.0563	0.0866	0.0534	0.0587
<i>wR</i>₂^b [<i>I</i> > 2σ(<i>I</i>)]	0.1269	0.2340	0.1349	0.1306
GOF on <i>F</i>²	1.035	0.999	1.034	1.012
^a <i>R</i> ₁ = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o . ^b <i>wR</i> ₂ = (Σ[<i>w</i> (<i>F</i> _o ² - <i>F</i> _c ²) ²]/Σ[<i>w</i> (<i>F</i> _o ²) ²]) ^{1/2}				

Table S12. Selected interatomic distances (Å) and angles (°) for **1LS·MeOH** (82 and 250 K) and **1HS·MeOH** (at 82 K after 455 nm LED and white light irradiations)

	1LS·MeOH (82 K)	1LS·MeOH (250 K)	1HS·MeOH (after 455 nm LED irradiation, at 82 K)	1HS·MeOH (after white light irradiation, at 82 K)
Fe1-N1	1.854(3)	1.839(6)	2.154(3)	2.147(4)
Fe1-N2	1.906(3)	1.902(5)	2.276(3)	2.252(3)
Fe1-N3	2.115(3)	2.116(5)	2.330(3)	2.320(4)
Fe1-N4	-	-	2.327(3)	2.339(4)
Fe1-N5	2.031(3)	2.014(5)	2.250(3)	2.275(3)
Fe1-C16	1.941(4)	1.941(7)	2.168(4)	2.173(5)
Fe1-C17	1.958(4)	1.949(6)	2.185(4)	2.191(5)
Fe1b-N1b	1.851(3)	1.846(6)	-	-
Fe1b-N2b	1.901(3)	1.917(5)	-	-
Fe1b-N3b	2.111(3)	2.112(5)	-	-
Fe1b-N4b	-	-	-	-
Fe1b-N5b	2.041(3)	2.024(5)	-	-
Fe1b-C16b	1.961(4)	1.948(7)	-	-
Fe1b-C17b	1.947(4)	1.939(6)	-	-
N1-Fe1-N2	80.38(12)	80.9(2)	70.79(11)	71.60(12)
N1-Fe1-N5	79.66(12)	79.5(2)	71.54(11)	70.88(12)
N1-Fe1-N3	162.61(12)	163.1(2)	141.79(11)	143.57(12)
N1-Fe1-N4	-	-	143.50(11)	142.00(12)
N2-Fe1-N3	82.96(12)	82.4(2)	71.36(11)	71.99(12)
N2-Fe1-N5	159.72(13)	160.1(2)	142.32(12)	142.47(13)
N5-Fe1-N3	117.22(12)	117.2(2)	145.89(11)	145.54(12)
N2-Fe1-N4	-	-	145.69(11)	145.60(12)
N3-Fe1-N4	-	-	74.55(11)	74.25(12)
N5-Fe1-N4	-	-	71.99(11)	71.49(12)
N1-Fe1-C17	97.93(13)	96.5(2)	94.76(13)	94.65(15)
N2-Fe1-C17	93.28(13)	93.3(2)	91.93(13)	90.73(14)
N1-Fe1-C16	89.31(14)	90.0(3)	98.06(14)	98.71(15)
N2-Fe1-C16	92.47(13)	92.4(2)	92.83(13)	93.69(14)
N3-Fe1-C16	86.45(13)	87.7(3)	88.81(14)	82.43(15)
N3-Fe1-C17	87.93(13)	87.4(3)	81.44(13)	86.98(15)
C16-Fe1-N5	90.82(13)	91.2(2)	93.28(14)	92.84(14)
C17-Fe1-N5	85.97(13)	85.4(2)	90.21(13)	91.30(14)
C16-Fe1-N4	-	-	82.59(14)	88.19(15)
C17-Fe1-N4	-	-	86.77(13)	81.09(14)
C16-Fe1-C17	171.41(16)	171.9(3)	167.17(15)	166.64(17)
N1b-Fe1b-N2b	80.59(12)	80.4(2)	-	-

N1b-Fe1b-N3b	163.47(12)	163.2(2)	-	-
N1b-Fe1b-N5b	79.37(12)	79.5(2)	-	-
N2b-Fe1b-N3b	83.21(12)	82.9(2)	-	-
N2b-Fe1b-N5b	159.28(13)	159.4(3)	-	-
N5b-Fe1b-N3b	117.05(12)	117.3(2)	-	-
N1b-Fe1b-C16b	90.66(14)	90.7(2)	-	-
N1b-Fe1b-C17b	96.75(14)	96.2(2)	-	-
N2b-Fe1b-C16b	93.56(14)	92.7(2)	-	-
N2b-Fe1b-C17b	92.46(13)	92.2(2)	-	-
N3b-Fe1b-C16b	87.06(13)	87.5(2)	-	-
N3b-Fe1b-C17b	87.19(13)	87.1(2)	-	-
N5b-Fe1b-C16b	91.86(13)	92.0(2)	-	-
N5b-Fe1b-C17b	84.75(13)	85.5(2)	-	-
C16b-Fe1b-C17b	171.13(16)	172.1(3)	-	-

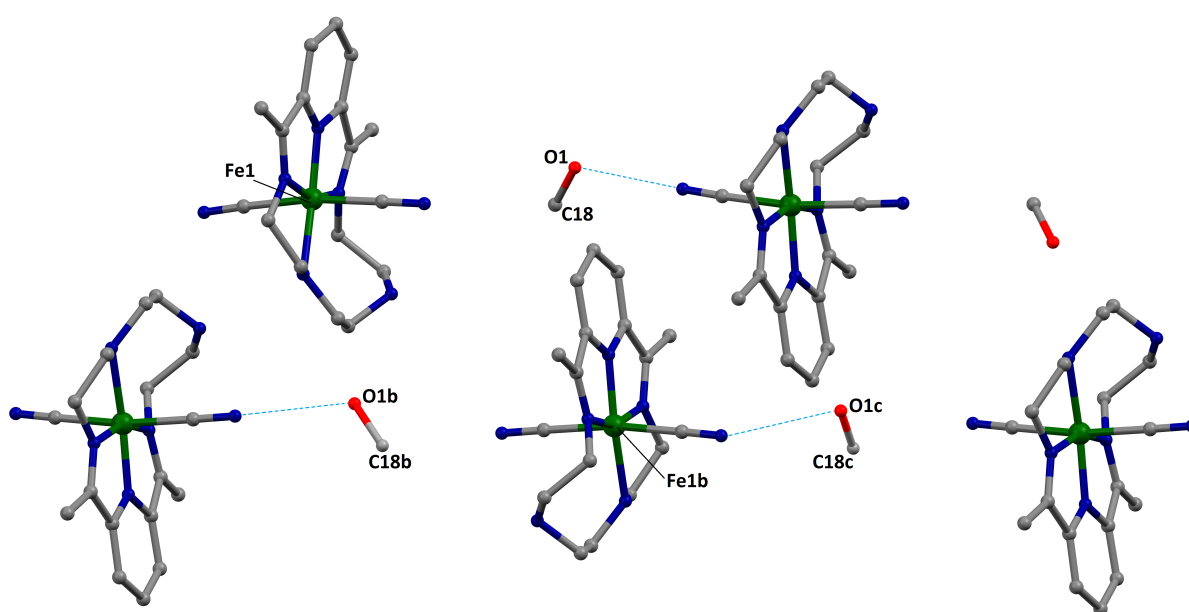


Figure S11. Packing arrangement and hydrogen bonding interactions (dashed light blue lines) between $[\text{Fe}^{\text{II}}_{\text{LS}}(\text{LN}_5)(\text{CN})_2]$ and methanol molecules in **1LS·MeOH** at $T = 82$ K. For clarity, only one of the two positions for O1b-C18b and O1c-C18c methanol molecules are shown. Fe, N, C and O atoms are indicated in green, blue, grey and red, respectively.

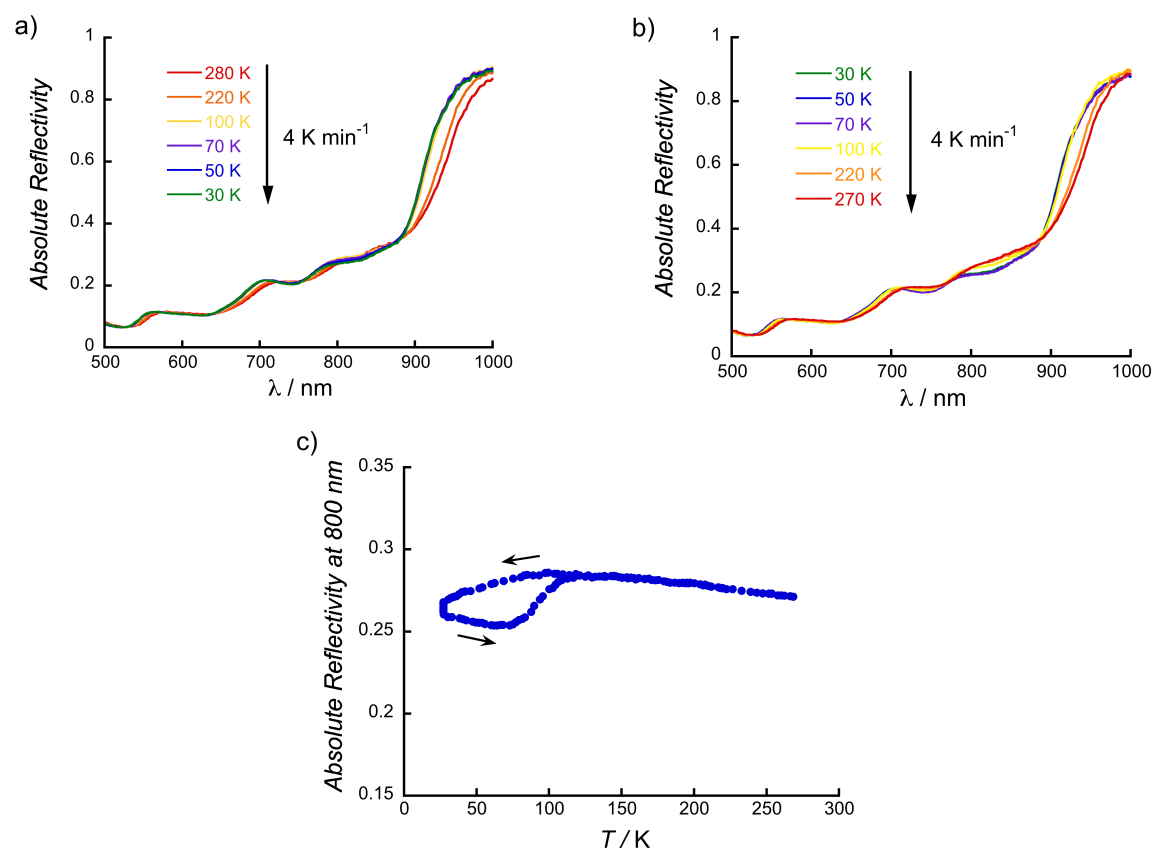


Figure S12. Optical reflectivity spectra (500 - 1000 nm spectral range, spectroscopic white light $P = 1$ mW cm⁻²) of **1LS·MeOH** at selected temperatures in the: (a) cooling mode, (b) heating mode. (c) Thermal dependence of the absolute reflectivity at 800 nm (4 K min⁻¹).

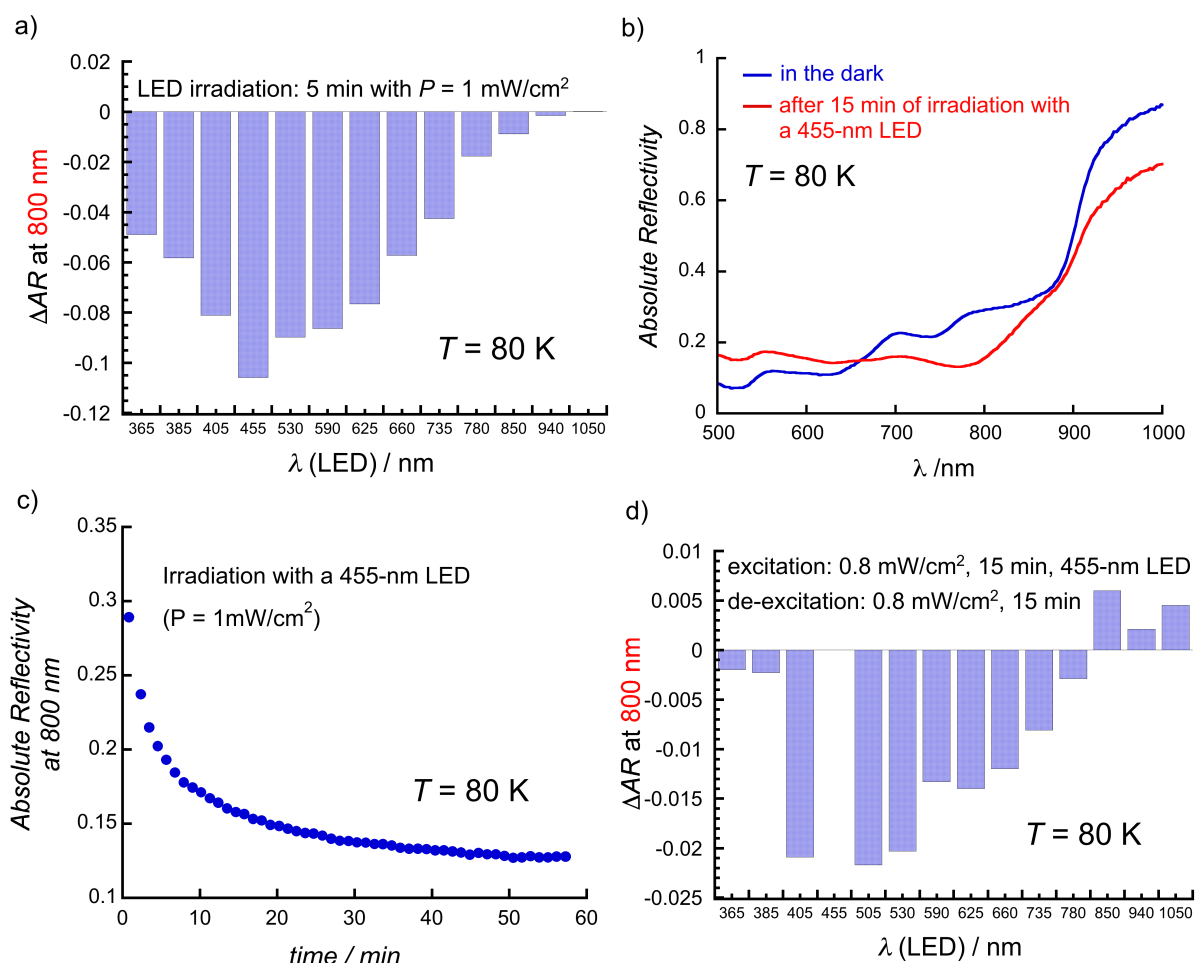


Figure S13. (a) Variation of the relative optical reflectivity ΔAR of **1LS-MeOH** at 800 nm as a function of the LED wavelength ($\Delta AR = R_{\text{after}} - R_{\text{before}}$ with R_{before} being the initial absolute optical reflectivity value at 80 K and R_{after} the absolute optical reflectivity value at 80 K after a LED irradiation of 5 minutes with $P = 1$ mW cm⁻²). (b) Optical reflectivity spectra before and after 15 minutes of irradiation with a 455-nm LED at 80 K. (c) Time evolution of the absolute optical reflectivity at 800 nm under irradiation with a 455-nm LED at 80 K. (d) Variation of the relative optical reflectivity ΔAR of **1LS-MeOH** ($\Delta AR = R_{\text{after}} - R_{\text{before}}$ with R_{before} being the absolute optical reflectivity value at 80 K after 15 minutes of irradiation with a 455-nm LED, $P = 0.8$ mW cm⁻² and R_{after} the absolute optical reflectivity value after a consecutive second LED irradiation of 15 minutes with $P = 0.8$ mW cm⁻²) at 800 nm as a function of the LED wavelength.

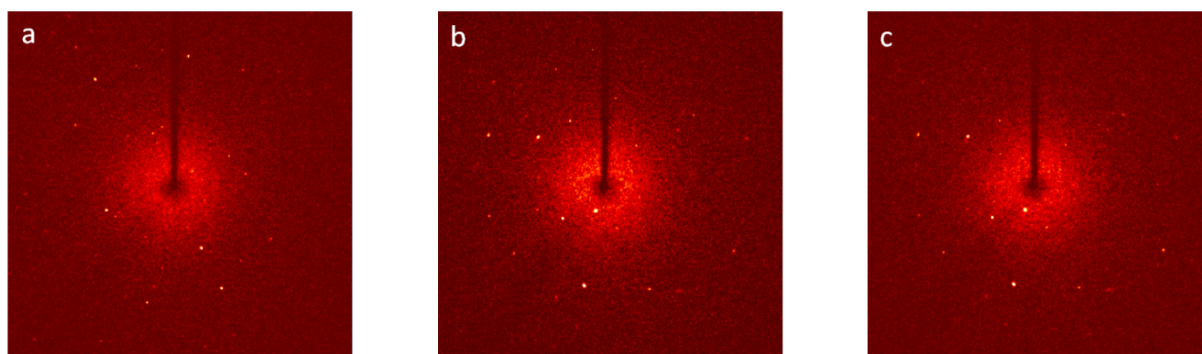


Figure SI4. Evolution of the X-ray diffraction pattern of **1LS-MeOH** towards **1HS-MeOH** under white light irradiation (with a power of a few W cm^{-2}) with the single crystal in a fixed position (a) before irradiation, (b) after 30 seconds of irradiation, and (c) after 5 minutes of irradiation, showing no evolution of the pattern between 30 second and 5 minutes and thus demonstrating the fast generation of the photo-induced state with these conditions.

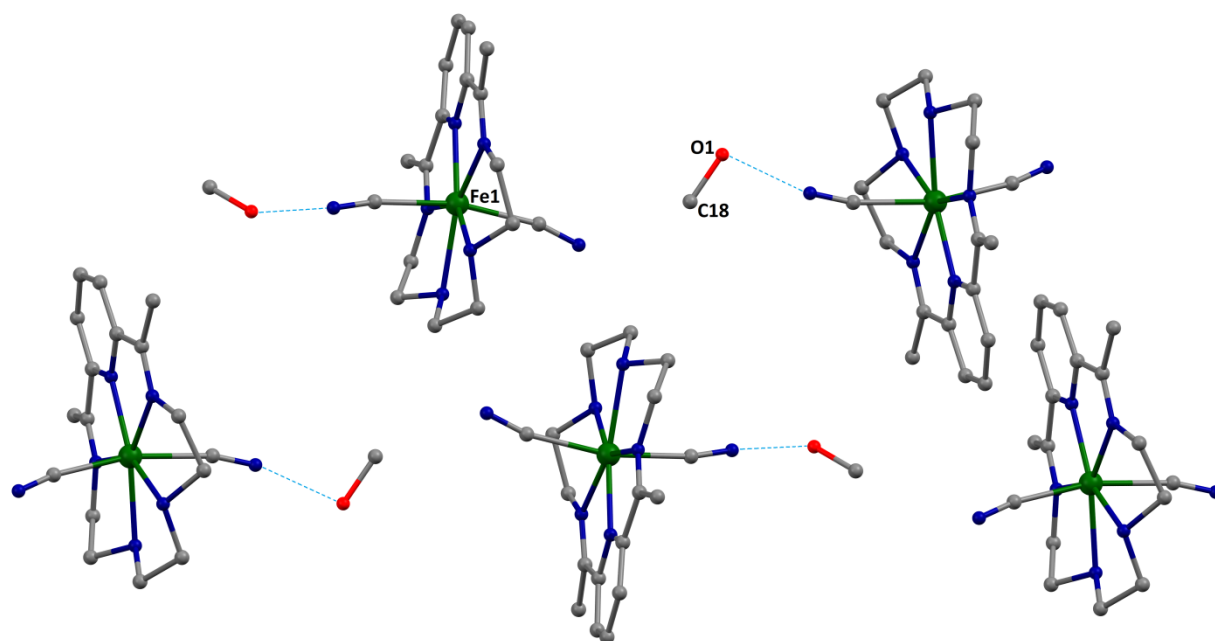


Figure SI5 Packing arrangement and hydrogen bonding interactions (dashed light blue lines) between $[\text{Fe}^{\text{II}}_{\text{HS}}(\text{LN}_5)(\text{CN})_2]$ and methanol molecules in **1HS-MeOH** at $T = 82 \text{ K}$. Fe, N, C and O atoms are indicated in green, blue, grey and red, respectively.

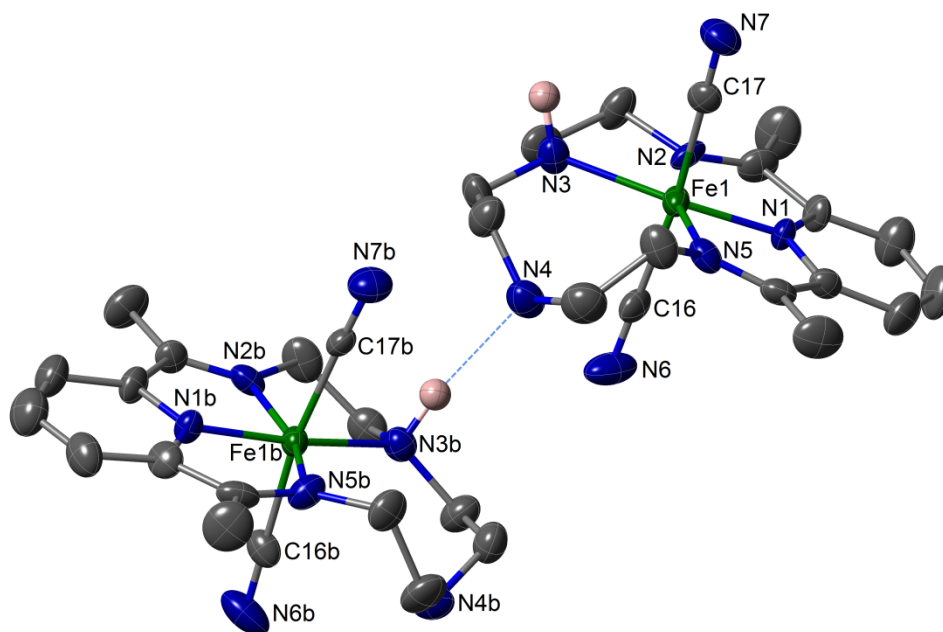


Figure SI6. Crystal structure of **1LS·MeOH** at $T = 250$ K after the thermal relaxation of the photo-induced **1HS·MeOH** phase (with thermal ellipsoids fixed at 60%). Fe, N and C atoms are shown in green, blue and grey, respectively. Methanol molecules and H atoms are omitted for clarity. Only H atoms bonded to N3 and N3b are shown, in order to evidence the hydrogen bonding (dashed light blue line).

¹ S. M. Nelson, P. D. A. McIlroy, C. S. Stevenson, E. König, G. Ritter and J. Waigel, *J. Chem. Soc. Dalton Trans.*, 1986, 991.

² R. Ababei, C. Pichon, O. Roubeau, Y.-G. Li, N. Bréfuel, L. Buisson, P. Guionneau, C. Mathonière and R. Clérac, *J. Am. Chem. Soc.*, 2013, **135**, 14840.

³ G. M. Sheldrick, SADABS, version 2.03, Bruker Analytical X-Ray Systems, Madison, WI, 2000.

⁴ G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.