Electronic Supplementary Information for:

Photoinduced reversible spin-state switching of an Fe^{III} complex assisted by a halogen-bonded supramolecular network

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Table of Contents

Experimental Section	S2
Table S1: Crystallographic data for 1, view along the crystallographic b axis	S4
Table S2: Selected bond distances and angles at the Fe centers of 1 at 298, 250 and 100 K	S5
Figure S1: Crystal packing in 1 and 2 at 298 K, view along the crystallographic c axis	S6
Figure S2: Crystal packing in 1 at 298 K, view along the crystallographic c axis	S7
Figure S3: Temperature dependence of the unit-cell parameters	S8
Figure S4: Reconstructed diffraction intensity of the reciprocal space	S9
Figure S5: Thermal evolution of the diffraction intensity of satellites ($Q = 1/2a^* + 1/2b^*$)	S10
Figure S6: X-ray crystal structure of [Fe(qsal) ₂] ⁺ in 1 at 298, 250, and 100 K	S11
Figure S7: X-ray crystal structure of 1, collected at 100 K	S12
Figure S8: Crystal packing in 1 at 298 and 100 K, view along the crystallographic <i>a</i> axis	S13
Figure S9: Variable-temperature dc magnetic susceptibility data for 1 with a fit	S14
Figure S10: Variable-temperature dc magnetic susceptibility data for 1 in heating and cooling	S15
Figure S11: Difference in absolute reflectivity (ΔR) at 850 nm for 1	S16
Figure S12: Reflectivity spectra for 1	S16
Figure S13: χT versus T and χT versus time plots of 1 at 53 K	S17
References	S18

Experimental Section

General Considerations. The manipulations described below were performed under ambient atmosphere. 1,3,5-trifluoro-2,4,6-triiodobenzene ($C_6F_3I_3$) and [Fe(qsal)₂]Cl·MeOH·H₂O were prepared according to reported literature procedures.^{1,2} All reagents were purchased from commercial vendors and used without further purification.

 $[Fe(qsal)_2][(C_6F_3I_3)I]$ (1). To a MeOH solution (36 mL) of $[Fe(qsal)_2]Cl \cdot MeOH \cdot H_2O$ (0.048 g, 0.077 mmol) was added a MeOH solution (96 mL) of $C_6F_3I_3$ (0.60 g, 1.18 mmol) and KI (0.012 g, 0.072 mmol) to give a dark brown solution. The resulting solution was left undisturbed for 3 days to afford 0.038 g of 1 as dark brown elongated plate-shaped crystals (42 %) suitable for X-ray analysis. Anal. Calcd. for $C_{38}H_{22}F_3FeI_4N_4O_2$ C 38.4, H 1.87, N 4.72 %. Found: C, 38.4; H, 1.70; N, 4.79 %.

X-ray Structure Determination. The crystallographic data of 1 at 298 K were collected on a Bruker D8 venture diffractometer equipped with MoK α microsource and PHOTON100 detector at the Centre de Diffractométrie (CDIFX, Université de Rennes 1, France). Raw data were integrated and corrected for Lorentz and polarization effects using Bruker APEX3 v. 2015.³ Absorption corrections were applied using SADABS.⁴ Space group assignments were determined by examination of systematic absences, Estatistics, and successive refinement of the structures. Structures were solved and refined with SHELXT and SHELXL operated with the OLEX interfaces.⁵⁻⁷ The crystallographic data at 250 and 100 K were collected with an Oxford Diffraction X calibur3 diffractometer, using monochromated Mo-K α radiation (λ = 0.71073 Å). The diffractometer was fitted with a liquid nitrogen Oxford Cryosystems 700 series lowtemperature device for measurements down to 100K. A data scaling and empirical or analytical correction were performed with CrysAlisPro 1.171.38.46 software by Rigaku Oxford Diffraction. The structures were solved by dual-space direct methods using SHELXT⁵ and refined by full-matrix least-squares on F^2 using SHELXL-97⁶ with the OLEX-2 interfaces.⁷ Thermal parameters were refined anisotropically for all non-hydrogen atoms. All hydrogen atoms were placed at calculated positions using suitable riding models and refined using isotropic displacement parameters derived from their parent atoms. Crystallographic data and the details of data collection are listed in Table S1. In addition, the changes of the unit cell volume and cell parameters have been investigated by short omega-scans during sample cooling and heating modes for two crystals of 1 at the scanning rate of ~0.1 K/min; the best results are presented here on figure S3. CCDC 1568816, 1550127 and 1550128 contain the supplementary crystallographic data for 1 respectively at 298K, 250K and 100K. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Magnetic Measurements. Magnetic measurements were performed with a MPMS-XL Quantum Design SQUID magnetometer. Reproducible measurements were performed on polycrystalline samples of 1 (12.80 mg), that are introduced in a sealed polypropylene bag ($3 \times 0.5 \times 0.02$ cm of 17.40 mg). Prior to measurements, the field-dependent magnetization was measured at 100 K in order to confirm the absence of any bulk ferromagnetic impurities. Dc susceptibility data were corrected for diamagnetic contributions from the sample holder and for the core diamagnetism of each sample.⁸

Photomagnetic Measurements. Photomagnetic experiments were carried out at Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB) and utilized a Quantum Design SQUID magnetometer MPMS-7S and a set of photodiodes coupled to an optical fiber that was directed into the magnetometer cavity. A polycrystalline sample of 1 (0.8 mg) was introduced into a preformed straw at a distance of 3 cm from the optical fiber end (incident light flux = 12.6 mW/cm^2 (830 nm) and 3.7 mW/cm^2 (650 nm)).

The temperatures have been corrected to take into account the light-induced heating (an average +2 K has been observed with 830 nm irradiation).

Optical Measurements. Surface reflectivity measurements were performed on a home built system, housed at the Centre de Recherche Paul Pascal, at temperatures ranging between 10 and 270 K. A tungsten-halogen light source was used (Leica CLS 150 XD, adjustable up to 1 W/cm²) at wavelengths between 400 and 1000 nm. This set-up collects the light reflected by the sample (that is the sum of direct and diffuse reflected light). To limit photoexcitation effects, the power of the spectroscopic white light is fixed at 0.8 mW/cm², and the light is only switched on for 1 second to record the reflectivity spectrum at a given temperature, and then the light is switched off during the next temperature step. To investigate the photoexcitation effect with specific wavelength, the white light is used as a light probe for spectroscopy and a set-up of 14 different LEDs was used for irradiations with the following protocol: the compound is placed at 10 K after cooling at 10 K/min in the dark, and a spectrum is first collected. Then the compound is irradiated with one LED for 10 minutes with a power of 2 mW/cm², and a new spectrum is recorded. To recover the low temperature phase, the compound is reheated at 270 K and then placed again in the dark at 10 K/min, before finally being irradiated with another LED. This procedure is repeated for each LED. To further investigate the photoreversibility, the compound was first irradiated with the 940 nm-LED (for 10 minutes at 2 mW/cm²), which is the most efficient wavelength for the photoexcitation, and successively irradiated with other LEDs (each for 10 minutes at 2 mW/cm²).

Other Physical Measurements. Elemental analysis was performed by microanalysis service at the Institut de Chimie des Substances Naturelles (CNRS UPR 2301, France).

	1					
Empirical formula		$C_{38}H_{22}F_3FeI_4N_4O_2$				
Formula weight, g.mol ⁻¹	1187.04					
Crystal system	Monoclinic					
Wavelength, Å		0.71073				
Temperature, K	298	250	100			
Space group	Pc	Pc	Сс			
<i>a</i> , Å	8.447(3)	8.3692(2)	16.7237(2)			
<i>b</i> , Å	11.738(5)	11.5822(2)	22.9833(2)			
<i>c</i> , Å	19.660(6)	19.5061(5)	19.4485(2)			
α, °	90	90	90			
β , °	107.207(12)	106.785(2)	107.484(1)			
γ, °	90	90	90			
$V, Å^3$	1862.2(12)	1810.24(7)	7129.98(13)			
Ζ	2	2	8			
$\rho_{\rm calcd}$, g cm ⁻³	2.121	2.178	2.212			
μ , mm ⁻¹	3.777	3.884	3.945			
Reflections coll./unique	24899/5343	28715/6751	60010/12446			
$R_{\rm int}$	0.0984	0.0434	0.0527			
${}^{a}R_{1}\left(I > 2\sigma(I)\right)$	0.0471	0.0287	0.0330			
$^{b}wR_{2}$ (all)	0.0735	0.0438	0.0452			
GoF	0.972	0.977	0.946			

 Table S1 | Crystallographic data of 1 at 298, 250 and 100 K.

 ${}^{a}R_{1} = \Sigma ||F_{O}| - |F_{C}|| / \Sigma |F_{O}|, \text{ and } {}^{b}wR_{2} = [\Sigma w (F_{O}{}^{2} - F_{C}{}^{2})^{2} / \Sigma w (F_{O}{}^{2})^{2}]^{1/2}$

	298 K	250 K	100 K	
	Fe1	Fe1	Fe1	Fe2
Fe1-O1/Fe2-O3	1.913(7)	1.892(4)	1.913(7)	1.871(6)
Fe1–O2/Fe2–O4	1.909(8)	1.906(5)	1.900(7)	1.866(6)
Fe–O _{avg}	1.911	1.899	1.907	1.869
Fe1-N1/Fe2-N5	2.178(9)	2.145(6)	2.153(7)	1.967(8)
Fe1-N2/Fe2-N6	2.123(8)	2.106(5)	2.113(8)	1.946(8)
Fe1-N3/Fe2-N7	2.155(8)	2.136(5)	2.160(8)	1.988(8)
Fe1-N4/Fe2-N8	2.133(8)	2.100(6)	2.122(7)	1.941(7)
Fe-N _{avg}	2.147	2.122	2.137	1.961
N1-Fe1-N3	166.1(3)	166.2(2)	165.7(3)	175.4(3)

 Table S2 | Selected bond distances (Å) and angles (°) at the Fe centers of 1 at 298, 250 and 100 K.^a

^aSee Figure S6 for atom labels



Figure S1 | Crystal packing in 1 (top) and 2 (bottom) at 298 K, view along the crystallographic *b* axis. Brown, purple, red, blue, and grey spheres represent Fe, I, O, N, and C atoms, respectively, with highlighting C and F atoms in $C_6F_3I_3$ in lilac; H atoms are omitted for clarity, and halogen bonding and π interactions are highlighted in purple and red dashed lines, respectively.



Figure S2 | Crystal packing in 1 at 298 K, view along the crystallographic *c* axis, highlighting 1D organization of Fe^{III} molecules. Brown, red, blue, and grey spheres represent Fe, O, N, and C atoms, respectively. H atoms are omitted for clarity, and halogen bonding and π interactions and hydrogen bond interactions are highlighted in red dashed lines.



Figure S3 | Temperature dependence of the lattice parameters for the unit cell of the higher symmetry.



Figure S4 | Reconstructed diffraction intensity of the reciprocal space in the *0kl*, *h0l*, and *hk0* planes for **1** at 250 (top) and 100 K (middle), and *0.5kl*, *h0.5l*, and *hk0.5* planes at 100 K (bottom). The satellite reflections at $Q = 1/2a^* + 1/2b^*$ are highlighted by arrows.



Figure S5 | Thermal evolution of the averaged diffraction intensity of 10 satellites ($Q = 1/2a^* + 1/2b^*$).



Figure S6 | X-ray crystal structure of $[Fe(qsal)_2]^+$ in 1, collected at 298 K (top, left), 250 K (top, right), and 100 K (bottom). Brown, red, blue, and grey elipsoids, shown at the 50% probability level, represent Fe, O, N, and C atoms, respectively; H atoms are omitted for clarity.



Figure S7 | X-ray crystal structure of 1, collected at 100 K (right), highlighting alternating Fe1 molecules (high-spin) and Fe2 molecules (low-spin) shown in red and blue, respectively. Two independent Γ ions are also differentiated by purple and green spheres.



Figure S8 | Crystal packing in 1 at 298 (top) and 100 K (bottom), view along the crystallographic *a* axis, highlighting the imperfect superposition between layers at 100 K.



Figure S9 | Variable-temperature dc magnetic susceptibility ($\chi = M/H$ per mole of compounds) data for 1 shown as a plot of $\chi T vs. T$, collected under an applied field of 1 T from 400 to 100 K and 0.1 T below 100 K at a temperature sweeping rate of 0.7 K/min. The red line corresponds to a fit based on an ideal solution model.⁹



Figure S10 | Variable-temperature dc magnetic susceptibility ($\chi = M/H$ per mole of compounds) data for 1 shown as a plot of $\chi T vs. T$, collected under an applied field of 1 T at a temperature cooling (blue) and heating (red) rate of 0.7 K/min (right). Experimental sequences: heating up to 400 K and then cooling (top); cooling before irradiation, 3 cycles of photoswitching experiments (successive 830 and 650 nm-irradiations), and then heating after the last photo-excitation with 830 nm irradiation (bottom). See the experimental section for the details of photo-irradiation conditions.



Figure S11 | Difference in absolute reflectivity (ΔR) at 850 nm for 1, obtained at 10 K: (left) difference between before irradiation and after 10 min. of irradiation with the 14 different LEDs ($P = 2 \text{ mW/cm}^2$); (right) difference between 10 min. of irradiation with the 940 nm-LED ($P = 2 \text{ mW/cm}^2$) and 10 min. of irradiation with the 12 different LEDs ($P = 2 \text{ mW/cm}^2$).



Figure S12 | (Left) reflectivity spectra at 10 K before irradiation (blue), after 10 min. of irradiation with the 940 nm-LED (brown) and after successive 10 min. of irradiation with the 625 nm-LED (orange) for 1; (right) reflectivity spectra at 850 nm under an 940 nm-irradiation (for 10 min., $P = 2 \text{ mW/cm}^2$) and a 650 nm-irradiation (for 10 min., $P = 10 \text{ mW/cm}^2$), successively, at 10 K.



Figure S13 | χT versus *T* plots for a polycrystalline sample of **1** collected under an applied field of 1 T upon heating after the photoexcitation with the 830 nm-LED at 10 K (40 min., *P* = 3.7 mW/cm²): (black) constant heating at 0.4 K/min and (red) heating at 2 K/min before staying at a constant temperature at 53 K. Inset: Time-dependence of the χT product at 53 K.

References

- (1) D. T. Rosa, R. A. Reynolds, S. M. Malinak and D. Coucouvanis, Inorg. Synth., 2002, 33, 112.
- (2) I.-R. Jeon, O. Jeannin, R. Clérac, M. Rouzières and M. Fourmigué, Chem. Commun., 2017, 53, 4989.
- (3) APEX2, v. 2015 ; Bruker Analytical X-Ray Systems, Inc: Madison, WI, 2015.
- (4) G. M. Sheldrick, SADABS, version 2.03, Bruker Analytical X-Ray Systems, Madison, WI, 2000.
- (5) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3.
- (6) G. M. Sheldrick, Acta. Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.
- (7) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, **42**, 339; Farrugia, L. J. J. Appl. Crystallogr., 1999, **32**, 837.
- (8) G. A. Bain and J. F. Berry, J. Chem. Ed., 2008, 85, 532.
- (9) P. Atkins and J. de Paula, *Physical Chemistry*, Oxford University Press: Oxford, UK, 2006, Chapter 5.