Persistent bidirectional optical switching in the 2D high-spin polymer $[Fe(bbtr)_3](BF_4)_2$

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X-ray crystallography

Diffraction data were collected on the Oxford Diffraction KM6 Kappa diffractometer at the Swiss Norwegian Beamline of the ESRF using a wavelength of 0.69412 Å. The crystal was mounted inside a modified version of a Cryovac KONTI-cryostat as shown in Figure S1. Although the cryostat was nominally cooled to 9 K, due to the low efficiency of the heat conduction between the crystal and the cryostat plate and the low heat conductivity of the crystal itself, the estimated temperature at the crystal was about 70K, based on comparison with the spectroscopic measurements.

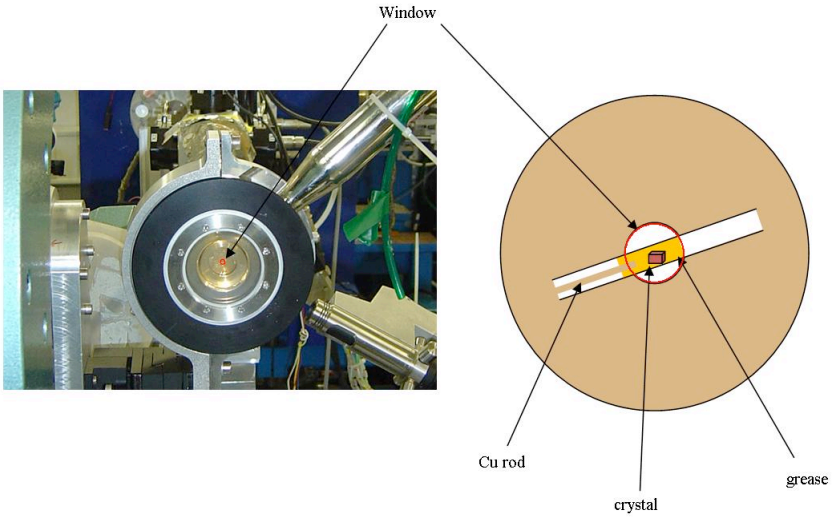

Figure S1. The cryostat used for the crystallographic experiment. The crystal is mounted inside a capillary, which is open on both sides and contacted to the copper plates of the cryostat. To improve the thermal contacts, the crystal was embedded in Apiezon N grease and a copper rod was put inside the capillary with one end inside the grease, close to the crystal, and the other contacted to the copper plate of the cryostat with silver paste.

Due to the cryostat, only a small fraction of the reciprocal space was reachable so that the completeness of the dataset is low. Moreover, some reflections had to be excluded from the refinement due to shading of the cryostat in some positions. For each dataset, about 400 reflections were finally usable. Nevertheless, we were able to solve the structure using direct methods (SIR 2004 R1)[1] and to refine it to acceptable R-values (Table S1). To keep the number of refined parameters reasonable, only the Fe atom was refined anisotropically.

Initially, data were collected at ~70 K before and after irradiation for 15 minutes at 12050 cm^{-1} (830 nm). The structure before irradiation is trigonal and corresponds to the HS structure, with the typical Fe-N bond length of the HS species of 2.19(1) Å. After irradiation, the c-axis is doubled, with diffuse scattering also appearing along the ***c**** axis (Figure S2). Moreover, splitting of the reflections is observed (Figure S3) and the unit-cell seems no longer to be trigonal but to undergo a phase transition to a triclinic crystal system. As the crystal goes back to the HS state, either by heating to above 120 K or by irradiating at 21186 cm^{-1} (472 nm), the splitting of the diffraction peaks completely disappears. We believe therefore that this splitting is associated to a twinning of the crystal due to a lowering of the symmetry from $P\bar{3}$ to $P\bar{1}$. Such a symmetry change was also observed in the perchlorate derivative, preceding the spin transition, but in that case without doubling of the unit-cell.[2] This transition was accompanied by a shift of the 2D layers, relative to each other. Since those 2D layers are perpendicular to the c-axis, such a shift could also produce the doubling of the unit-cell that we observed here. However, the data collected here did not allow full elucidation of the structure of the LS phase. An average structure could nevertheless be refined in the small unit-cell using the $P\bar{3}$ symmetry (Table S1). This refinement gives an average distance of 1.99(2) Å compatible with a full conversion to the LS state.

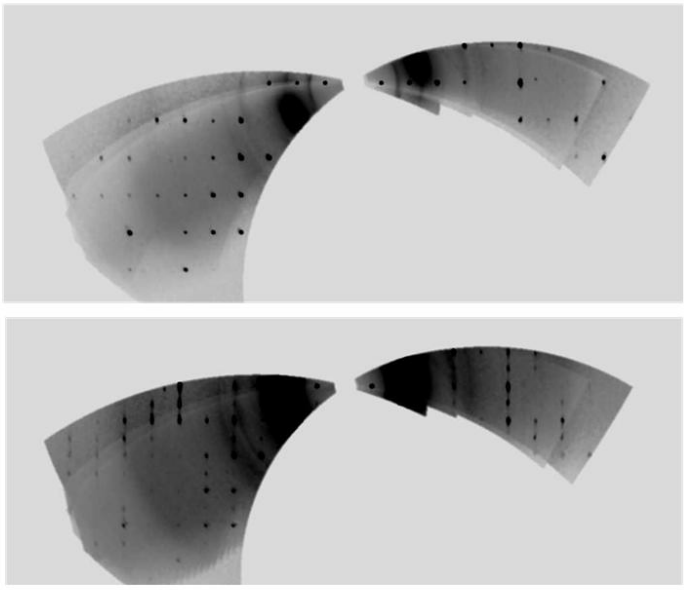

Figure S2. Reconstruction of the h0l layer (***a**** horizontal, ***c**** vertical) before and after irradiation.

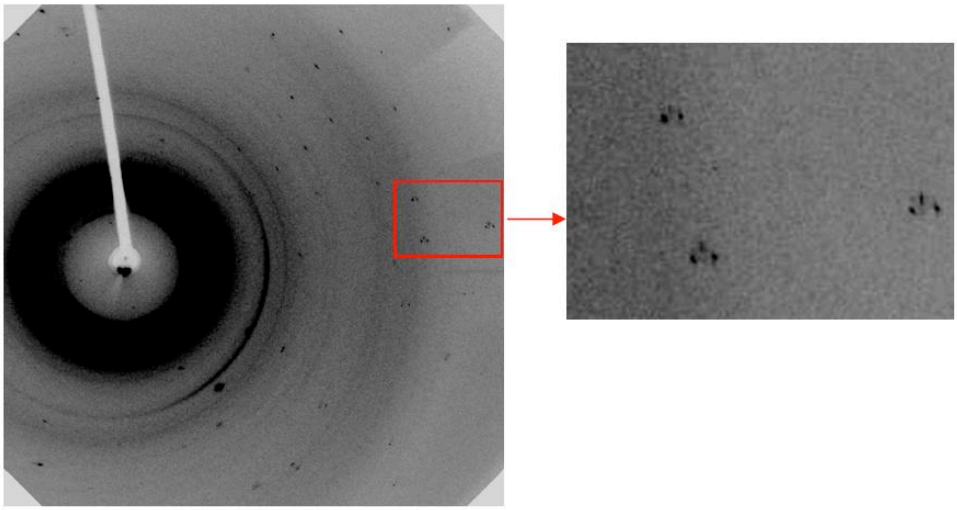

Figure S3. Diffraction image after the irradiation with an enlargement showing the splitting of the peaks.

Table S1. Crystallographic data for the refinement of the structure before irradiation and the average structure after irradiation at 830 nm for 15 minutes and at a temperature of ~70 K. The average structure was solved and refined in $P\bar{3}$ without taking into account neither the doubling of the c-axis nor the lowering of the symmetry.

	Before Irradiation	After irradiation
Formula	$C_4H_6B_{0.33}F_{1.33}Fe_{0.17}N_3$	$C_4H_6B_{0.33}F_{1.33}Fe_{0.17}N_3$
Z	6	6
Unit cell parameters a (Å) b (Å) c (Å) α (°) β (°) γ (°)	 11.5803(18) 11.5803(18) 7.4811(18) 90 90 120	 11.333(6) 11.254(7) 7.652(4) 91.31(5) 89.98(4)) 119.85(6)
V ($Å^{3)}$	868.8 (3)	839.1(9)
Reflections (measured/independent/I>2σ)	843/474/367	1133/494/331
Completeness at θ = 17.6 °	0.616	0.781
$R[F^2 > 2\sigma(F^2)]$	0.071	0.186
$wR(F^2)$	0.148	0.470
S	1.07	1.23
Reflections/parameter/restrains	414/39/0	494/39/0
$\Delta\rho_{min}$ / $\Delta\rho_{max}$ ($Å^{-3}$)	-0.54/0.57	-0.72/1.11
Average d(Fe-N) (Å)	2.19(1)	1.99(2)

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) before irradiation

	x	y	z	U_{iso}*/U_{eq}
Fe1	1.0000	0.0000	1.0000	0.0107
F9	0.3333	−0.3333	0.8357 (12)	0.011 (2)*
F10	0.4404 (5)	−0.3464 (5)	0.5893 (7)	0.0151 (13)*
N1	0.8526 (7)	0.0139 (8)	0.8324 (11)	0.012 (2)*
N2	0.8099 (7)	0.0948 (8)	0.8800 (11)	0.011 (2)*
N3	0.7003 (8)	0.0607 (8)	0.7850 (11)	0.0101 (19)*
C4	0.6695 (10)	−0.0438 (9)	0.6756 (14)	0.014 (2)*
C7	0.4907 (10)	0.0273 (9)	0.9146 (12)	0.010 (2)*
B8	0.3333	−0.3333	0.650 (2)	0.004 (4)*
C5	0.7706 (9)	−0.0728 (9)	0.7095 (12)	0.008 (2)*
C6	0.6196 (9)	0.1239 (9)	0.8244 (14)	0.013 (2)*
H41	0.5978	−0.0860	0.5968	0.0160*
H72	0.4409	0.0724	0.9375	0.0120*
H71	0.4403	−0.0464	0.8332	0.0121*
H51	0.7805	−0.1407	0.6569	0.0101*
H62	0.6696	0.1966	0.9055	0.0151*
H61	0.6023	0.1571	0.7145	0.0150*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0064 (14)	0.0064 (14)	0.019 (3)	0.0032 (7)	0.0000	0.0000

Table S3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) after irradiation

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	1.0000	0.0000	1.0000	0.069 (3)
F9	0.3333	−0.3333	0.823 (3)	0.064 (6)*
N1	0.8612 (16)	0.0072 (16)	0.847 (2)	0.050 (5)*
N2	0.811 (2)	0.090 (2)	0.891 (3)	0.077 (6)*
F10	0.4387 (14)	−0.3524 (14)	0.563 (2)	0.089 (5)*
C4	0.683 (2)	−0.043 (2)	0.668 (3)	0.063 (6)*
H4	0.6168	−0.0828	0.5799	0.075*
N3	0.7059 (17)	0.0582 (18)	0.782 (3)	0.066 (5)*
C7	0.490 (2)	0.025 (2)	0.909 (3)	0.067 (6)*
H7A	0.4345	−0.0543	0.8345	0.081*
H7B	0.4401	0.0737	0.9272	0.081*
C6	0.623 (2)	0.121 (2)	0.810 (4)	0.075 (7)*
H6A	0.6001	0.1431	0.6977	0.090*
H6B	0.6753	0.2061	0.8767	0.090*
C5	0.784 (2)	−0.074 (2)	0.717 (3)	0.073 (7)*
H5	0.7956	−0.1426	0.6641	0.087*
B8	0.3333	−0.3333	0.633 (7)	0.069 (14)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.065 (4)	0.065 (4)	0.077 (7)	0.0324 (19)	0.000	0.000

Optical spectroscopy

Single crystals of $[Fe(bbtr)_3](BF_4)_2$ of dimensions ~300x300x75 μm^3 was mounted to cover a small aperture and inserted into a closed cycle cryostat capable of reaching 5 K with the sample in He exchange gas for efficient cooling (Janis-Sumitomo). Variable temperature high-quality single crystal absorption spectra were recorded on a dual beam spectrometer (Cary 5000). For irradiation experiments the light of a diode laser (830 nm) or a DPSS laser (472 nm) was used. Kinetic experiments were performed using a home-built system consisting of a W-lamp as light source, a 28 cm single monochromator (Spex 280M) for light dispersion and a cooled CCD (Jobin Yvon) for detection and software which allowed recording full spectra between 400 and 850 nm at fixed time intervals of 1 s or longer.

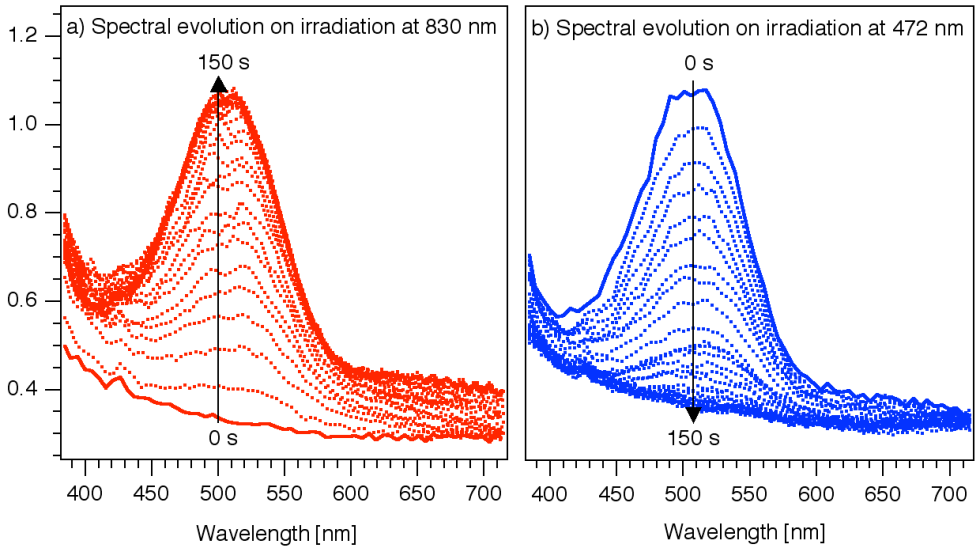

Figure S4. Evolution of the single crystal absorption spectrum in the region of the $^1A_1 \rightarrow {}^1T_1$ transition at 65 K for (a) irradiation at 830 nm with 10 mW/mm^2 followed by (b) irradiation at 472 nm with 1.2 mW/mm^2 recorded at 5 seconds intervals using the setup with the CCD.

References

(1) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2005**, *38*, 381.

(2) Kusz, J; Bronisz, R.; Zubko, M; Bednarek, G. *Chem. Eur. J.* **2011**, *17*, 6807.