Light-induced spin-state switching in the mixed crystal series of the 2D coordination network {[Zn_{1-x}Fe_x(bbtr)₃](BF₄)₂}_∞: optical spectroscopy and cooperative effects

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Supporting Information

X-ray diffraction data for the structure $\{[Zn_{1-x}Fe_x(bbtr)_3](BF_4)_2\}_{\infty}$ with x=0.01,0.31,0.67

All data were collected at the Swiss Norwegian Beamline BM1A using a Pilatus2M detector. The sample was placed in the helium flow of an Oxford Diffraction Helijet and the temperature was fixed to 10K during all the measurements. A phi scan was made (This limited the covered reciprocal space but, due to the high symmetry of the structure, the data quality is still acceptable). For x=0.67, three-fold twinning occurred while going through the $P\bar{3}$ to $P\bar{1}$ phase transition, as reflected in the triangular shape of the spot in the hk5 layer of the reciprocal space reconstruction (Fig S9). The doubling of the c-axis is visible in the 0kl layer. The split reflections were too close to each other to be successfully integrated separately and attempt to take care of the twinning of the overlapping reflections during the structure refinement of the triclinic structure was not satisfactory even though the twinning matrices are known. As a result, an average structure was refined in $P\bar{3}$ to give an average value for the Fe-N bond length.

For all mixed compound, the composition was fixed to the nominal composition, as the difference in scattering power for Fe/Zn is low. The refined composition gave slightly higher composition in Fe.

Refinement were carried out in SHELXL using full matrix least square on F^2 . Details of the refinement are given in Table 1.



Fig S1 : View of the structure along the a-axis showing the stacking of the layers around c

Table 1 :	X-ray dat	a collection	and refine	ment details
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Compound	x=0.01	x=0.67 before	x=0.67 after	x=0.31 before	x=0.31 after
_		irradiation	irradiationª	irradiation	irradiation
	1005050	1005050	4005054	4005050	1005050
ССДС	1007069	1007070	1007071	1007072	1007073
Formula	$C_{24}H_{36}B_2F_8N_{18}Zn$	$C_{24}H_{42}B_2F_8Fe_{0.67}N_{18}$	$C_{24}H_{36}B_2F_8Fe_{0.67}N_{18}$	$C_{24}H_{36}B_2F_8Fe_{0.31}N_{18}$	$C_{24}H_{36}B_2F_8Fe_{0.31}N_{18}$
		Zn _{0.33}	Zn _{0.33}	Zn _{0.69}	Zn _{0.69}
$D_{calc.}$ / g cm ⁻³	1.544	1.544	1.554	1.539	1.547
μ/mm^{-1}	0.745	0.575	0.583	0.666	0.670
Formula Weight	815.70	815.38	809.33	812.75	812.75
Crystal System	trigonal	trigonal	trigonal	trigonal	trigonal
Space Group	P-3	P-3	P-3	P-3	P-3
a/A	11.5868(6)	11.5937(3)	11.4601(16)	11.5915(3)	11.5302(3)
b/A	11.5868(6)	11.5937(3)	11.4601(16)	11.5915(3)	11.5302(3)
c/A	7.5429(5)	7.5357(4)	7.602(3)	7.5372(2)	7.5779(3)
$\alpha/^{\circ}$	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	120	120	120	120	120
V/Å ³	876.99(10)	877.20(7)	864.6(4)	877.04(5)	872.47(6)
Z	1	1	1	1	1
$\Theta_{min}/^{\circ}$	1.982	1.981	2.004	1.981	1.992
$\Theta_{max}/^{\circ}$	24.094	24.268	24.380	24.090	24.052
Measured Refl.	3296	3342	2689	3555	3567
Independent Refl.	950	913	902	969	963
Reflections Used	816	884	809	928	906
R _{int}	0.0720	0.0261	0.0286	0.0418	0.0479
Parameters	81	81	81	81	81
Restraints	0	0	0	0	0
Largest Peak	2.101	0.787	2.29	0.493	0.466
Deepest Hole	-1.410	-0.355	-0.55	-0.797	-0.680
GooF	1.178	1.057	1.117	1.112	1.164
wR_2 (all data)	0.2397	0.0831	0.2033	0.1186	0.1181
wR_2	0.2312	0.0789	0.1966	0.1162	0.1169
R_1 (all data)	0.0847	0.0345	0.0770	0.0420	0.0416
R_1	0.0801	0.0325	0.0722	0.0410	0.0403

^a effective space group $P\overline{1}$, refinement performed in $P\overline{3}$.



Fig S2 : Reconstruction of the 0kl layer before irradiation for x=0.31



Fig S3 : Reconstruction of the 0kl layer after irradiation for x=0.31



Fig S4 : Reconstruction of the hk5 layer before irradiation for x=0.31



Fig S5: Reconstruction of the hk5 layer after irradiation for x=0.31



Fig S6: Reconstruction of the 0kl layer before irradiation for x=0.67



Fig S7: Reconstruction of the 0kl layer after irradiation for x=0.67



Fig S8: Reconstruction of the hk5 layer before irradiation for x=0.67



Fig S9: Reconstruction of the hk5 layer after irradiation for x=0.67