**Supporting Information for** 

## Ultrafast spin-state photoswitching in a crystal and slower consecutive processes investigated by femtosecond optical spectroscopy and picosecond X-ray diffraction

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**Fig. S1.** UV-vis-NIR spectra of the monoclinic (left) and orthorhombic (right) polymorphs were recorded as a function of temperature for crystalline samples dispersed in KBr pellets. The spectra exhibit several temperature dependent spinallowed charge transfer transitions which can be assigned from the TD-DFT calculations performed for a close analogue [Fe(TPA)Cat]BPh<sub>4</sub> (see Simaan et al, Chem. Eur. J., 2005, 11, 1779). As previously reported by Enachescu et al (Chem. Phys. Chem., 2006, 7, 1127), the low-temperature structured band is typical for a low-energy catecholate to iron(III) charge transfer absorption (LMCT) of LS species (ca. 11 200 cm<sup>-1</sup> /  $\approx$  890 nm) with a vibronic progression of ca. 560 cm<sup>-1</sup>. At room temperature, we note the presence of the two broad LMCT absorption bands in the vis range around 12900 cm<sup>-1</sup> ( $\approx$  775 nm) and 18900 cm<sup>-1</sup> ( $\approx$  530 nm) for the monoclinic and around 13860 cm<sup>-1</sup> ( $\approx$  720 nm) and 18600 cm<sup>-1</sup> ( $\approx$  540 nm) for the orthorhombic. These bands characterize this class of compounds mimicking catechol-dioxygenases. Comparison of these measurements performed for crystalline samples dispersed in KBr pellets and single crystal transmission measurements with light polarized in the direction yelding maximum transmission in Fig. 1 (long crystalline axis **a**) indicates an anisotropic response for the monoclinic polymorph. At 600 nm (16666 cm<sup>-1</sup>) transmission increases between LS and HS states for light polarized along **a** axis and decreases for the other polarizations.

SORTAV					Filtering	
Fime delev	No. of reflections		Completeness / 9/	D mong / 9/	No. of reflections	
time delays	not merged	merged	Completeness / %	K merg / %	$I/\sigma(I) > 4$	η/σ(η) > 1
-1ns	18473	4095	65.8	6.03		
500ps	18488	4099	65.8	5.90	2455	408
50us	18473	4119	65.4	8.25	2265	1340

**Table S1** Details of the SORTAV merging and data filtering of the monoclinic polymorph. Outliers were downweighted by the use of the robust/resistant Tukey biweighted criterion in SORTAV (Blessing R. H. 1997, J. Appl. Cryst. 30, 421-426).

**Table S2** Details of the LASER refinement of the 50 $\mu$ s data of the monoclinic polymorph. Only intensities with  $\eta/\sigma(\eta) > 1$  were considered.

Time delays	50µs	
damping factor	0.2	
<b>θ</b> / °	25	
goodness of fit	1.164	
final number of refined parameters	25	
population / %	10.5(16)	
$k_B$ estimated from the Wilson plot	1.143	
$k_B$ after the refinement	1.169(4)	
final $R(\eta) / \%$	42.1	
final R(R) / %	9.63	
$R(R)/R(\eta)$ / %	22.9	



Fig. S2 Variation of the agreement factor R(R) for 500ps data of the monoclinic polymorph with an increase of the excited state population. Geometry of the excited state molecule was taken from the LASER refinement of 50µs data.