

Metal-to-metal communication during the spin state transition of a [2x2] Fe(II) metallogrid at equilibrium and out-of-equilibrium conditions

Jose de Jesus Velazquez-Garcia^{a*}, Krishnayan Basuroy^a, Darina Storozhuk^a, Joanne Wong^b, Serhiy Demeshko^b, Franc Meyer^b, Robert Henning^c and Simone Techert^{a,d}

^aPhoton Science - Structural Dynamics in Chemical Systems, Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, Hamburg, 22607, Germany

^bInstitut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4, Göttingen, 37077, Germany

^cCenter for Advanced Radiation Sources, The University of Chicago, Argonne National Laboratory, 9700 South Cass Ave, Lemont, Illinois, 90439, USA

^dInstitut für Röntgenphysik, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, Göttingen, 37077, Germany

Synthesis

The complex grid **FE4** and its ligand were synthesized following the procedure reported in literature¹. The crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Deposition numbers:

FE4 from 100 K to 390 K: 2126240, 2127042-2127051, 2127052-2127057 and 2127059-2127064.

Time resolved: 2127311-2127319.

Vibrational spectroscopy

The infrared spectra in the 2000-2500 cm^{-1} range of the original and desolvated **FE4** grid are shown in Figure S6. The presence of acetonitrile in the original **FE4** sample is confirmed by the appearance of two distinctive signals: $\nu(\text{C}\equiv\text{N})$ at 2249 cm^{-1} and a combined band of $\nu(\text{C}-\text{C})+\delta(\text{CH}_3)$ at 2293 cm^{-1} ²⁻⁵. In contrast, the desolvated **FE4** grid did not display the aforementioned bands, which indicate a complete desolvation.

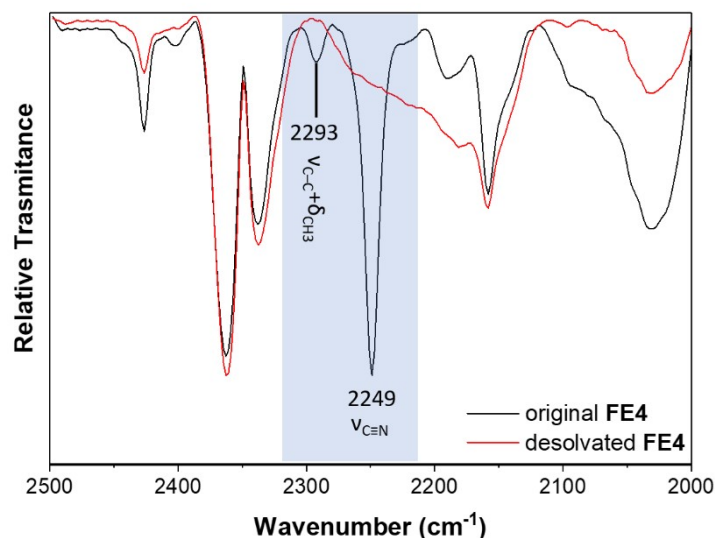


Figure S1. FTIR spectra for original and desolvated **FE4** grid.

Characterization

Table S1. Crystal data and structure refinement parameters of **FE4** at 100 K.

Temperature	100 K
Empirical Formula	C100 H74 B4 F16 Fe4 N26
Crystal color/habit	Black/block
Crystal size (mm)	(0.090x0.120x0.050)
Crystallizing solvent	Acetonitrile
Crystal system/ Space group	Monoclinic/ C2/c
<i>a</i> (Å)	30.680 (6)
<i>b</i> (Å)	12.780 (3)
<i>c</i> (Å)	26.810 (5)
α (°)	90
β (°)	120.76 (3)
γ (°)	90
Volume (Å ³)	9107.0 (4)
Z/Z'	4/0.5
Molecular Weight	2210.49
Calculated density (g/cm ³)	1.625
F(000)	4496
Radiation	Synchrotron ($\lambda=0.61990$ Å)
θ range (°)	1.902/31.355
Scan type	φ
Measured reflections	48052
Unique reflections	14709
Observed reflections	13786
[F > 4 σ (F)]	
Final R (%)	5.03
wR2 (%)	14.88
Good-of-fit on F ² (S)	1.086
$\Delta\rho$ max (e. Å ⁻³)	0.794
$\Delta\rho$ min (e. Å ⁻³)	-0.696
No of restraints/parameters	90/751
Data [F > 4 σ (F)]-to-parameter ratio	18.35:1

Table S2. Selected bond lengths and bond angles for compound **FE4** at 100K.

Bond lengths (Å)		Bond angles (°)			
Fe(A)-N2	1.9030(12)	N2-Fe(A)-N5	172.81(5)	N7-Fe(B)-N10	100.60(5)
Fe(A)-N5	1.9036(12)	N2-Fe(A)-N00	80.53(6)	N7-Fe(B)-N11	129.94(5)
Fe(A)-N00	1.9893(14)	N5-Fe(A)-N00	95.49(6)	N10-Fe(B)-N11	76.23(5)
Fe(A)-N3	1.9898(13)	N2-Fe(A)-N3	80.08(6)	N7-Fe(B)-N8	76.59(6)
Fe(A)-N4	1.9949(12)	N5-Fe(A)-N3	103.96(6)	N10-Fe(B)-N8	128.36(5)
Fe(A)-N6	1.9953(11)	N00-Fe(A)-N3	160.55(5)	N11-Fe(B)-N8	143.82(6)
Fe(B)-N7	2.1203(14)	N2-Fe(A)-N4	94.07(5)	N7-Fe(B)-N12	90.50(5)
Fe(B)-N10	2.1327(13)	N5-Fe(A)-N4	80.37(5)	N10-Fe(B)-N12	146.11(5)
Fe(B)-N11	2.1331(13)	N00-Fe(A)-N4	96.60(5)	N11-Fe(B)-N12	72.20(5)
Fe(B)-N8	2.1413(13)	N3-Fe(A)-N4	86.31(5)	N8-Fe(B)-N12	85.27(5)
Fe(B)-N12	2.2799(14)	N2-Fe(A)-N6	105.09(5)	N7-Fe(B)-N9	147.01(5)
Fe(B)-N9	2.3278(17)	N5-Fe(A)-N6	80.30(5)	N10-Fe(B)-N9	92.69(6)
		N00-Fe(A)-N6	84.10(5)	N11-Fe(B)-N9	82.44(5)
		N3-Fe(A)-N6	99.48(5)	N8-Fe(B)-N9	71.53(6)
		N4-Fe(A)-N6	160.64(5)	N12-Fe(B)-N9	95.07(6)

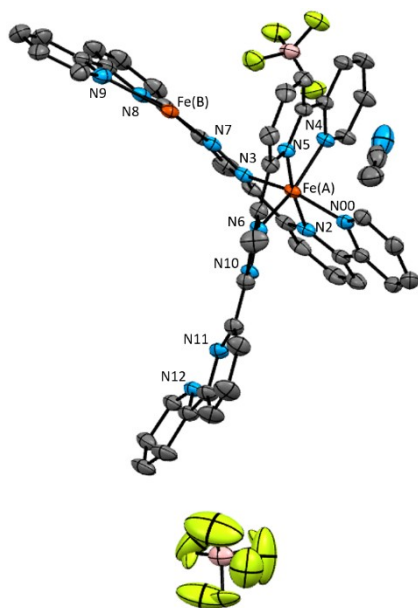


Figure S2. Asymmetric unit of the **FE4** grid at 100K. Hydrogen were omitted for clarity.

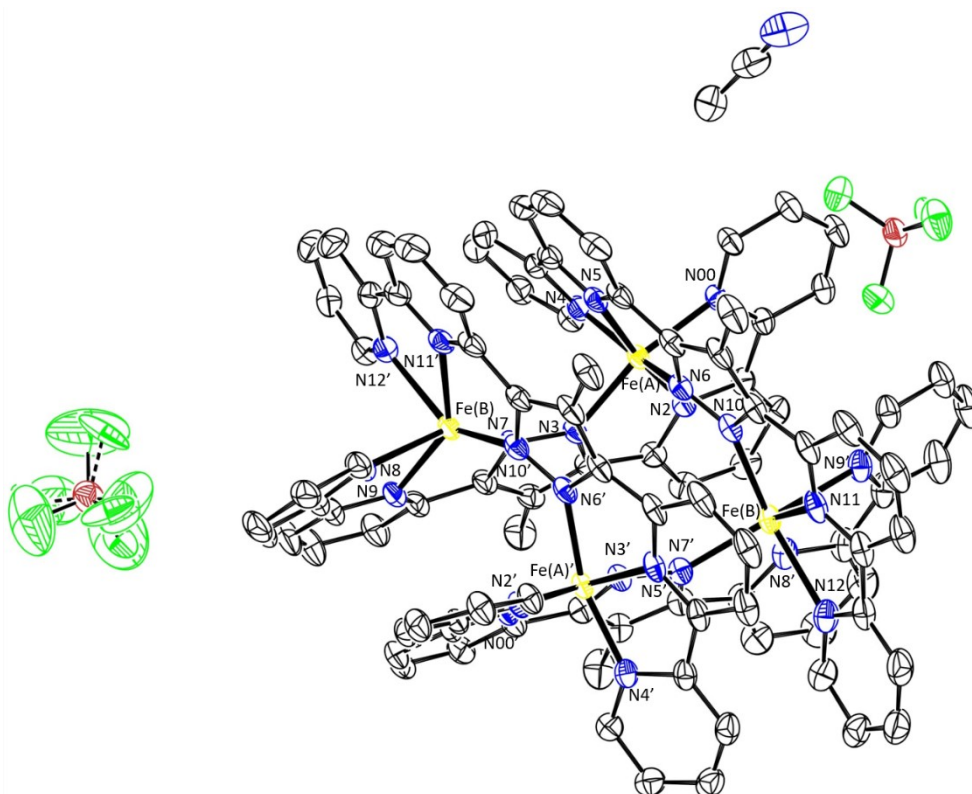


Figure S3. Thermal ellipsoid plot (50% of probability) for **FE4** at 100K.

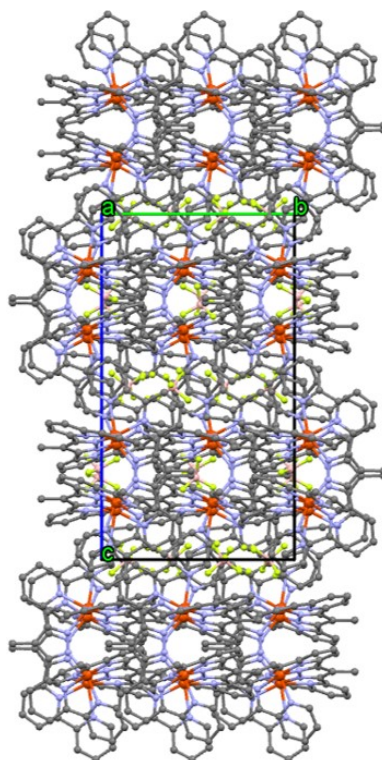


Figure S4. Packing of molecules down crystallographic '*a*' axis. Hydrogen atoms are omitted for clarity.

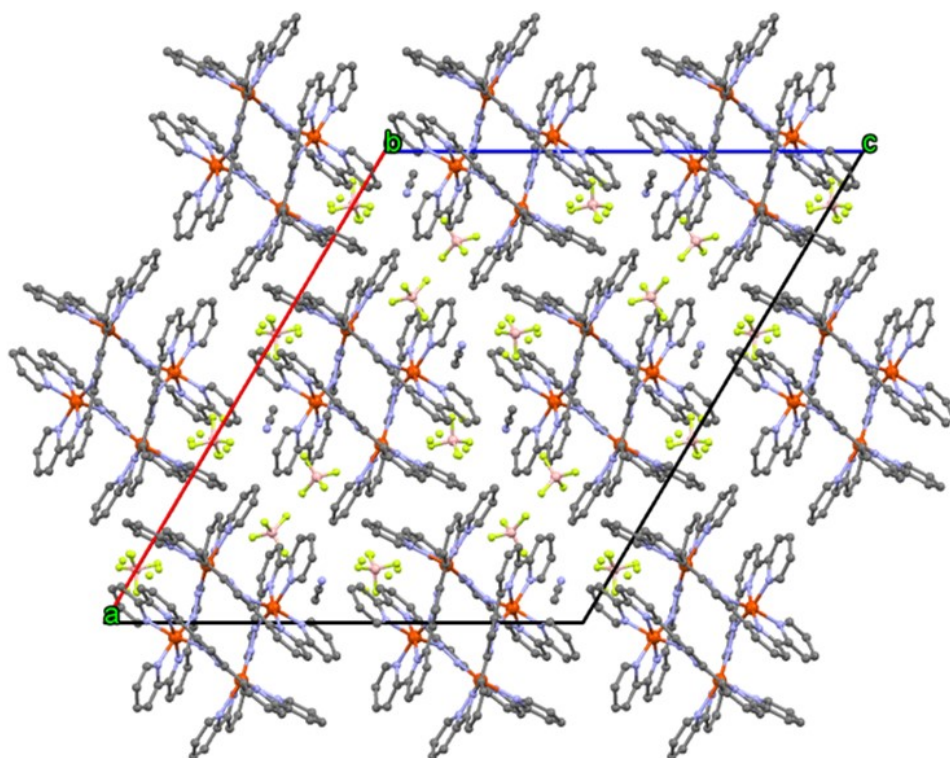


Figure S5. Packing of molecules down crystallographic '*b*' axis. Hydrogen atoms are omitted for clarity.

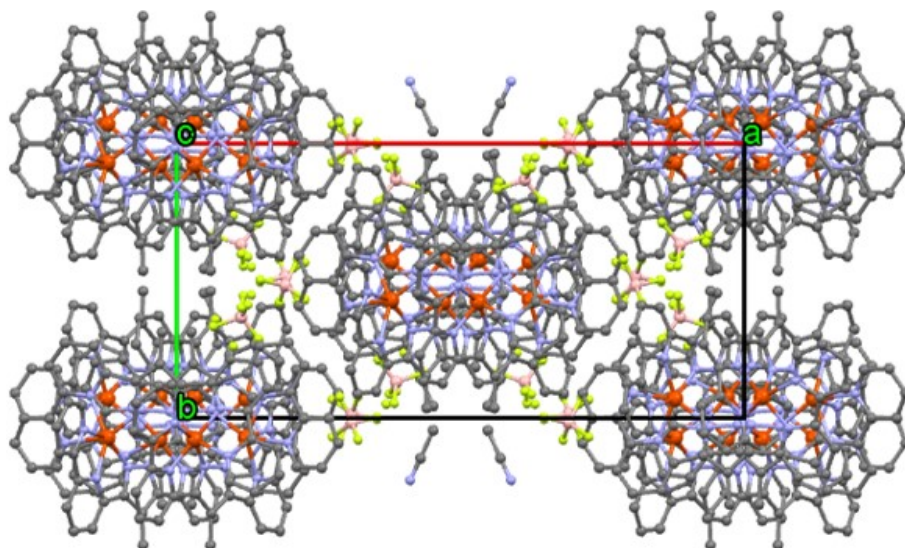


Figure S6. Packing of molecules down crystallographic 'c' axis. Hydrogen atoms are omitted for clarity.

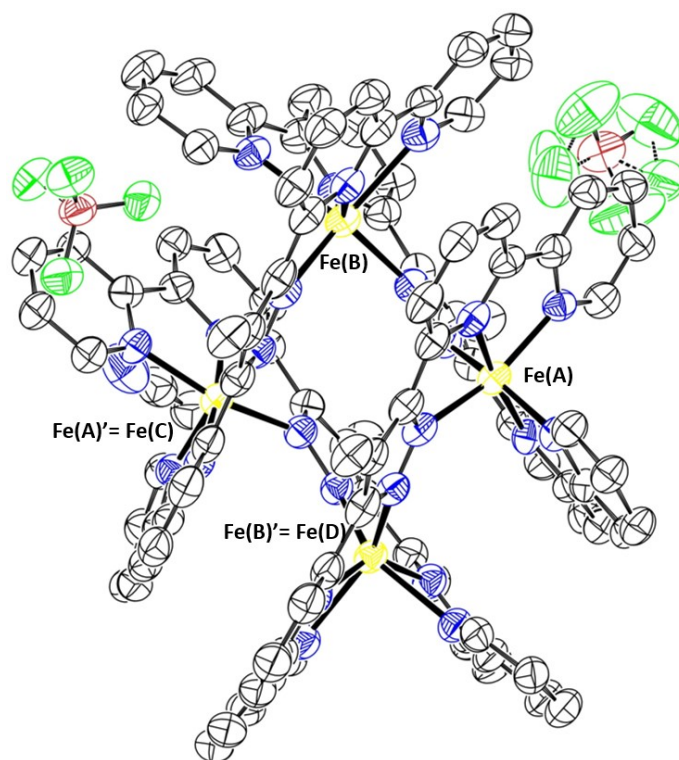


Figure S7. Thermal ellipsoid plot (50% of probability) for **FE4** for the -5ns data.

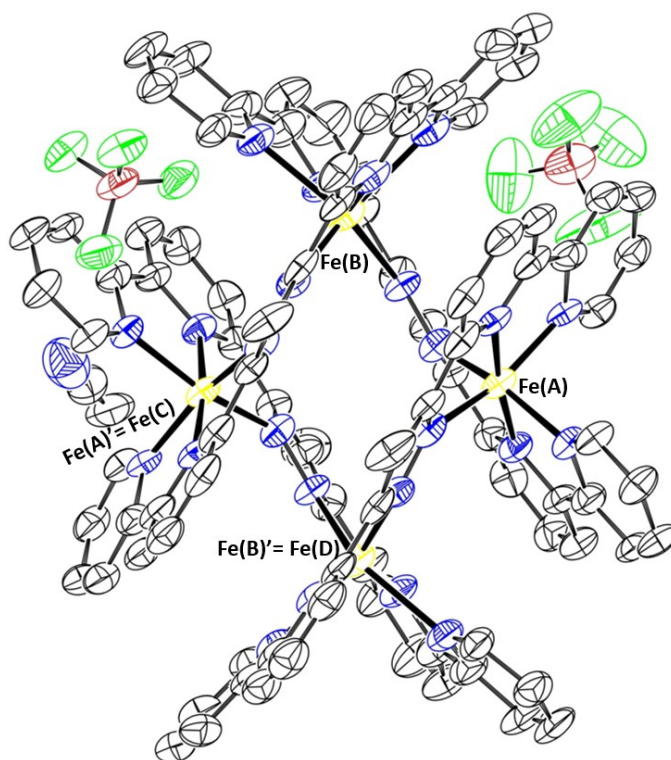


Figure S8. Thermal ellipsoid plot (50% of probability) for **FE4** for the -2ns data.

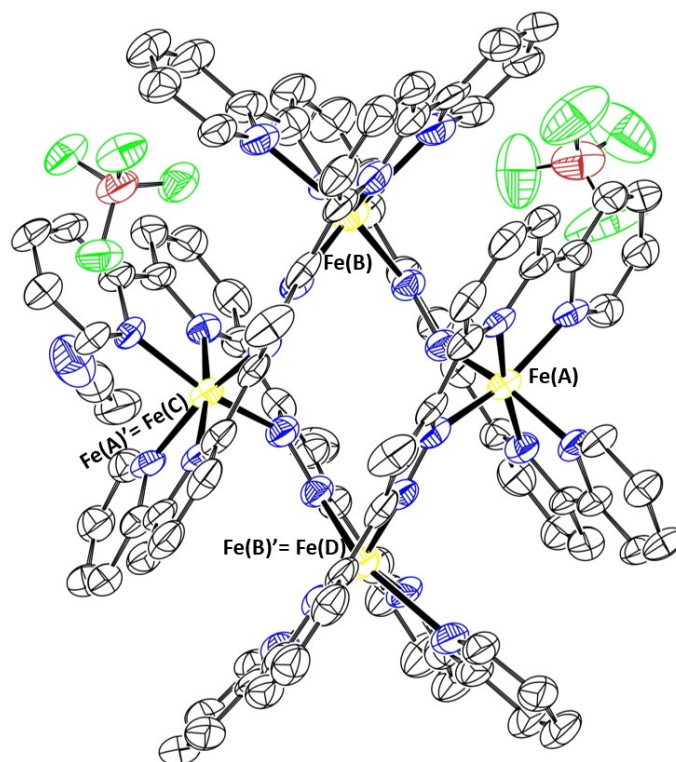


Figure S9. Thermal ellipsoid plot (50% of probability) for **FE4** for the -200ps data.

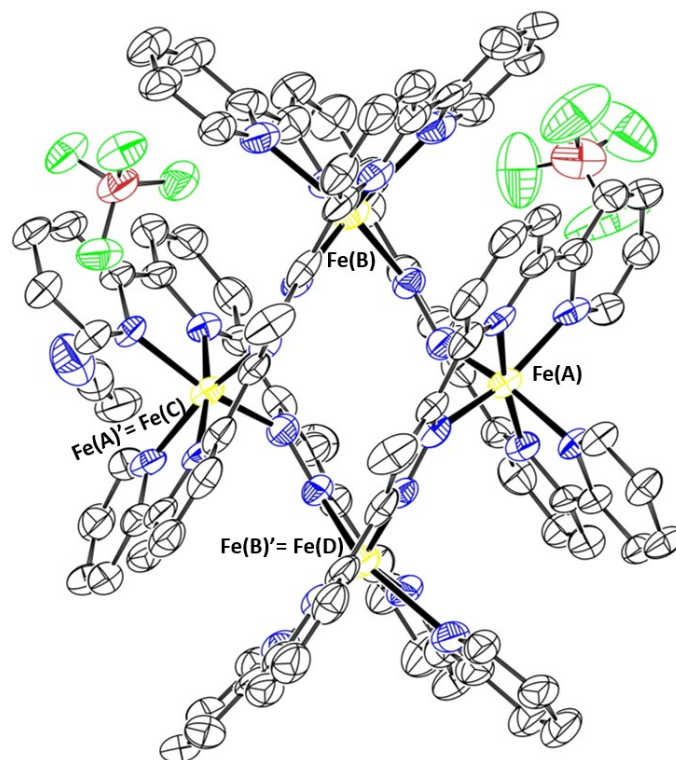


Figure S10. Thermal ellipsoid plot (50% of probability) for **FE4** for the 100ps data.

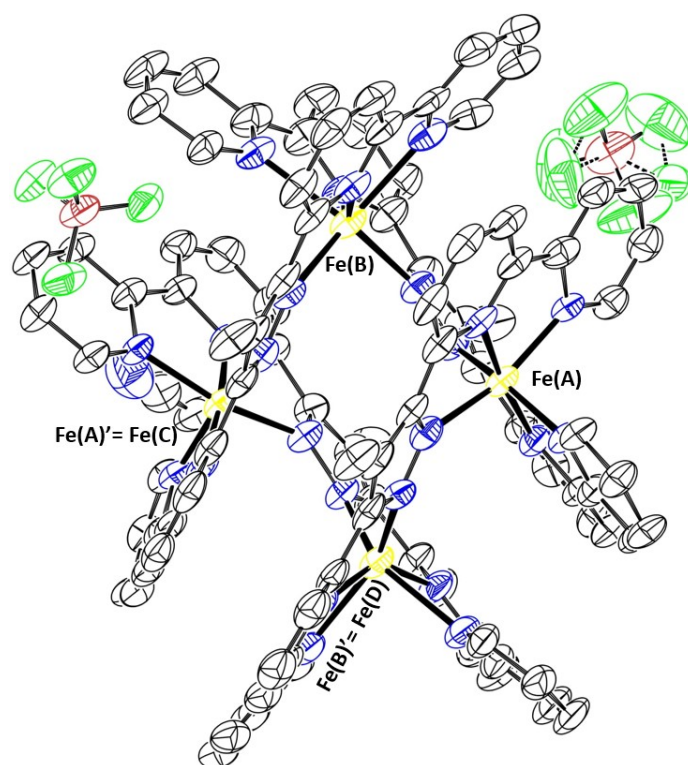


Figure S11. Thermal ellipsoid plot (50% of probability) for **FE4** for the 200ps data.

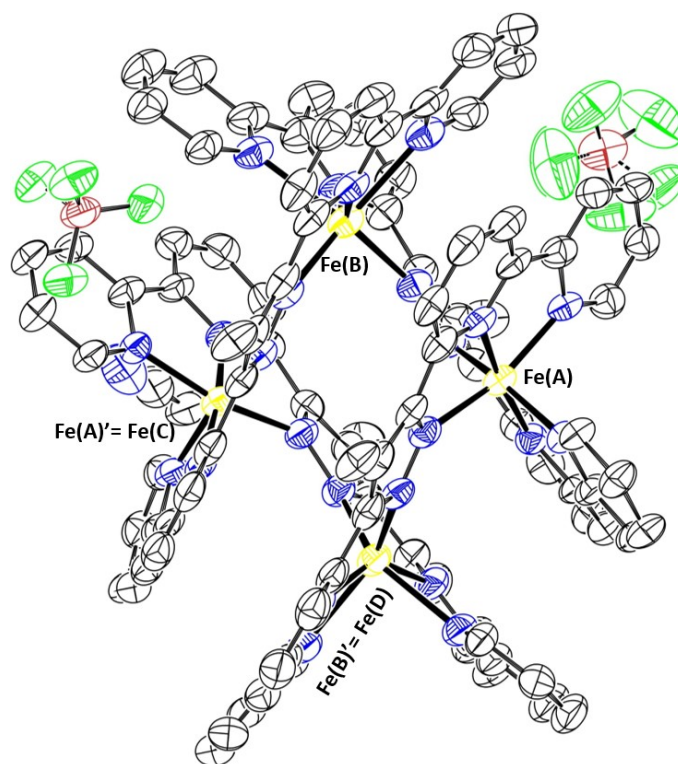


Figure S12. Thermal ellipsoid plot (50% of probability) for **FE4** for the 500ps data.

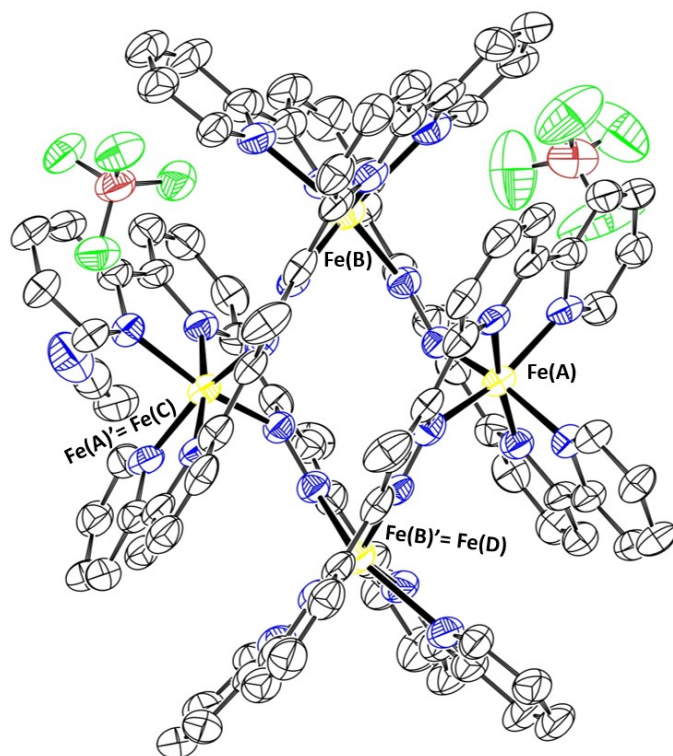


Figure S13. Thermal ellipsoid plot (50% of probability) for **FE4** for the 1ns data.

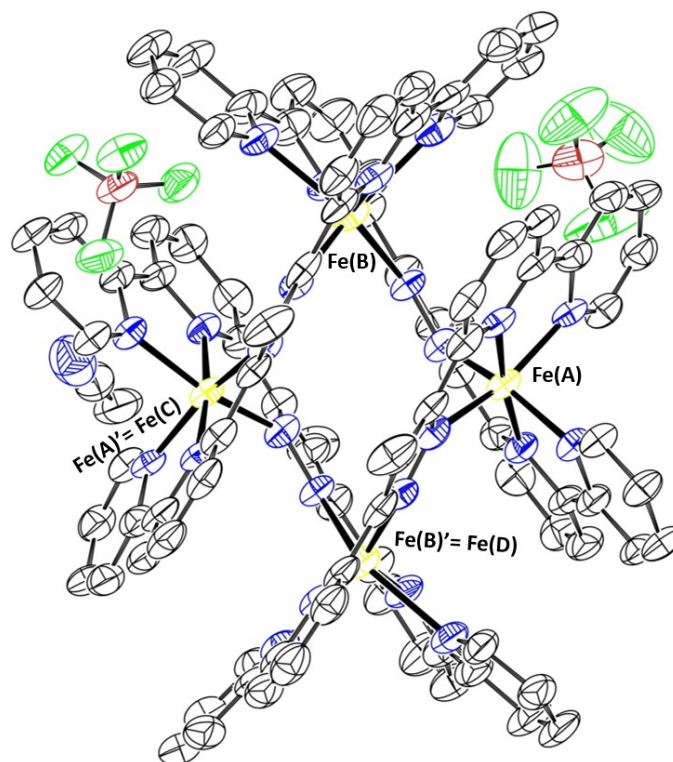


Figure S14. Thermal ellipsoid plot (50% of probability) for **FE4** for the 2ns data.

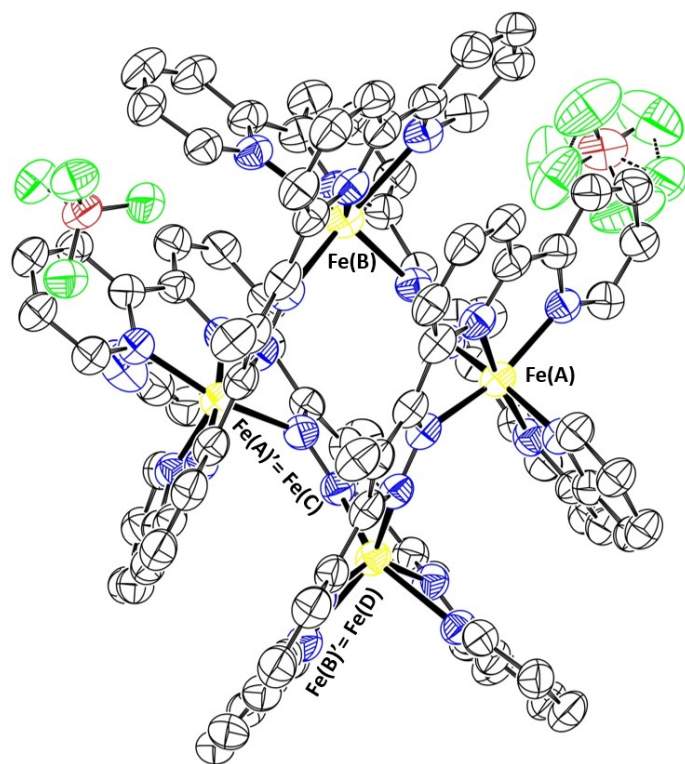
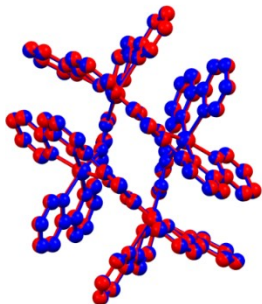
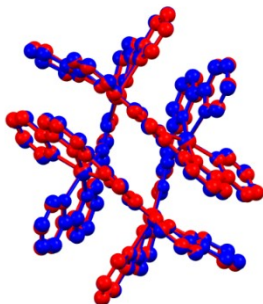
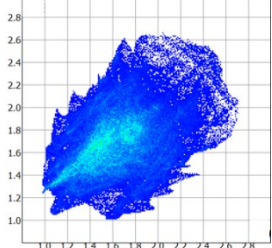
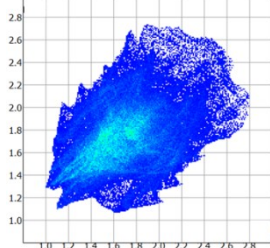
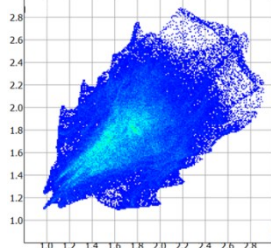


Figure S15. Thermal ellipsoid plot (50% of probability) for **FE4** for the 5ns data.

Structural details

Table S3. Structural data that provides a basic description of the SCO in **FE4**

Structural parameter	100 K	290 K	390 K
<i>Fe(A)-N6 polyhedron</i>			
<Fe1-N> (Å)	1.96 (2)	1.97 (2)	2.02 (2)
S(Oh)	2.315	2.390	3.098
S(itp)	10.529	10.386	9.421
Σ (°)	103.01 (8)	102.66 (13)	113.40 (13)
Θ (°)	306.7425	311.7653	368.8379
ζ (Å)	0.24 (5)	0.25 (5)	0.25 (6)
Vp (Å ³)	9.68	9.834	10.426
<i>Fe(B)-N6 polyhedron</i>			
<Fe2-N> (Å)	2.19 (4)	2.20 (4)	2.20 (4)
S(Oh)	8.401	8.444	8.902
S(itp)	4.417	4.408	4.290
Σ (°)	172.95 (8)	172.88	177.64 (12)
Θ (°)	708.9869	709.6041	734.0074
ζ (Å)	0.46 (9)	0.48 (9)	0.47 (9)
Vp (Å ³)	11.835	11.931	11.919
<i>Molecular Scale</i>			
Superposition of structures	100K (blue) & 290 K (red)	100K (blue) & 390 K (red)	
			
Maximum RMSD	0.1124	0.2356	
Average RMSD	0.0465	0.1206	
<i>Unit cell Changes</i>			
<i>a</i> (Å)	31.330 (6)	31.100 (6)	31.330 (6)
<i>b</i> (Å)	12.780 (3)	12.870 (3)	12.960 (3)
<i>c</i> (Å)	26.810 (6)	27.360 (6)	27.500 (6)
V (Å ³)	9033 (4)	9377 (4)	9551 (4)
<i>Crystal packing</i>			
Intermolecular interactions			
Separation between π - π planes (Å)	3.444, 4.503	3.509, 4.665	3.565, 4.769
Crystal density	1.571	1.513	1.486

$\Sigma = \sum_{i=1}^{12} |90 - \phi_i|$, the sum of the angular deviations from 90° for the 12 cis angles (ϕ_i)^{6,7}, $\Theta = \sum_{i=1}^{24} |60 - \theta_i|$ ⁸, $\zeta = (\text{Fe-N}_i) - \langle \text{Fe-N} \rangle$ ⁹. Information about S(Oh) and S(itp) is provided in the structural analysis section.

Structural Analysis

The Octadist program¹⁰ was used to determine the <Fe-N> bond length and the angular distortion parameter that describe the octahedral coordination environment of the metal centres in the **FE4** grid. The angular distortion parameter, Θ , is the sum of the deviations from 60° of the twenty-four N-Fe-N angles, six per pseudo three-fold axis, measured on a projection of opposite triangular faces of the {FeN₆} octahedron, orientated by superimposing the face centroids (Figure S16).^{8,11}

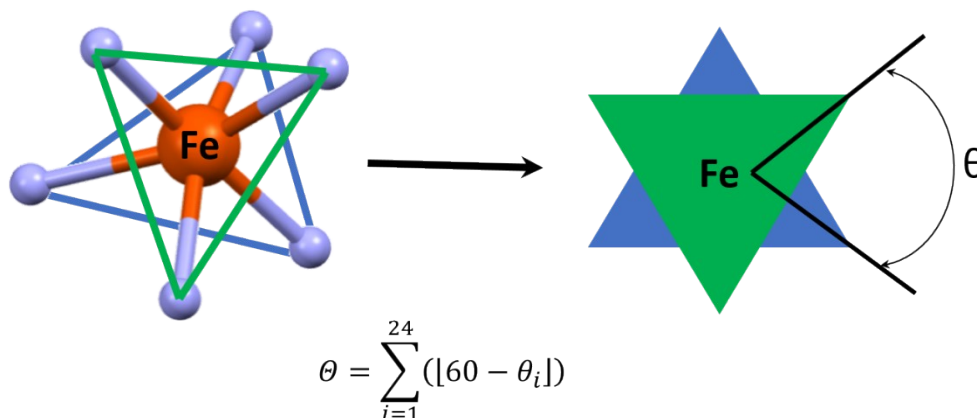


Figure S16. Environment of Fe^{II} ions and definition of the θ angle and the angular distortion parameter (Θ).^{8,11}

For comparison, continuous shape measurements (CShM) were also used to characterise the relative deviation of the metal coordination spheres in **FE4** from ideal polyhedra described by a particular point symmetry group (Table S2).¹² Mathematically, CShM of the coordination polyhedron Q with the geometric centre \vec{q}_0 relative to an ideal polyhedron P is expressed as:

$$S_Q = \min \left[\frac{\sum_{i=1}^N |\vec{q}_i - \vec{p}_i|^2}{\sum_{i=1}^N |\vec{q}_i - \vec{q}_0|^2} \right] \times 100 \quad (\text{S1})$$

where \vec{q}_i and \vec{p}_i are the position vectors for atoms of two polyhedral. CShM relative to an ideal octahedron (S(Oh)) and an ideal trigonal prism (S(itp)) were calculated using the SHAPE program¹³. The calculation of S(Oh) and S(itp) were performed for all crystallographic-symmetry independent metal atoms.

It is well-known that the {FeN₆} coordination sphere of LS Fe^{II} ions is more regular, i.e., closer to an ideal octahedron. Therefore, the S(Oh) parameter is small and closer to 0, while the parameter S(itp) >> 0. Contrary, Fe^{II} ions in the HS state are characterised by a more irregular structure with structural parameters S(Oh) >> 0 and S(itp) closer to zero.

Temperature difference

The well-known Wilson plot¹⁴ is frequently used to estimate the scale factor, k_s , and the overall isotropic temperature factor (B) of a data set. This plot can be obtained by statistical comparison of the observed

intensities (I_{obs}) with the average squared structure factor equals $\sum_{i=1}^M f_i^2$ for each $\sin \theta/\lambda$ range according to:

$$\ln \left(\frac{I_{obs}}{\sum_{i=1}^M f_i^2} \right) = \ln(k_s) - 2B(\sin \theta/\lambda)^2 \quad (S2)$$

Where M is the number of atoms and f_i is the scattering factor of the i th atom.

The change in the overall isotropic temperature factor (ΔB) between two data sets at different temperature can be estimated from modified Wilson plots. The plots are obtained by a scale-factor refinement of the low temperature data (e.g. 100K) with the high-temperature data (e.g. 290K) structural model and plotting the $\ln(I^{100K}/I^{290K})$. The slope of the dependence of $\ln(I^{100K}/I^{290K})$ with $(\sin \theta/\lambda)^2$ gives the overall increase of isotropic atomic motion, ΔB (equation S3), which is associated with temperature difference between the data sets.¹⁵

$$\ln \left(\frac{I^{100K}}{I^{290K}} \right) = -2\Delta B^{100K-290K}(\sin \theta/\lambda)^2 \quad (S3)$$

The greater the temperature difference between data sets the greater the value of ΔB , that means a more negative slope of the plot. This feature is used to analyse the temperature increase during the photo-crystallographic experiments as explain below.

During the photo-crystallographic experiments, the energy deposited by the laser pulse largely exceed the energy necessary for the LS to HS transition, which results in some heat diffusion and global warming. A modified Wilson plot, known as photo-Wilson plot (Fig. S17), is then used to estimate the lase-induced temperature increase due to heat dissipation, in a similar way as described above for the temperature-Wilson plots. From the photo-Wilson plot is possible to calculate the variation of the isotropic temperature factor between the data sets at time “t” and the reference data at time $t < 0$ ($\Delta B^{t-t < 0}$)¹⁵:

$$\ln \left(\frac{I^{dt}}{I^{dt < 0}} \right) = -2\Delta B^{dt-dt < 0}(\sin \theta/\lambda)^2 \quad (S4)$$

where, I^{dt} and $I^{dt < 0}$ are the observed intensities of data sets at delay time “dt” and the reference data at delay time $dt < 0$. Note that both the thermal-Wilson plot and the photo-Wilson plot were brought to the same scale before calculating the value of ΔB . For more information about this topic, the reader is referred to the literature¹⁵.

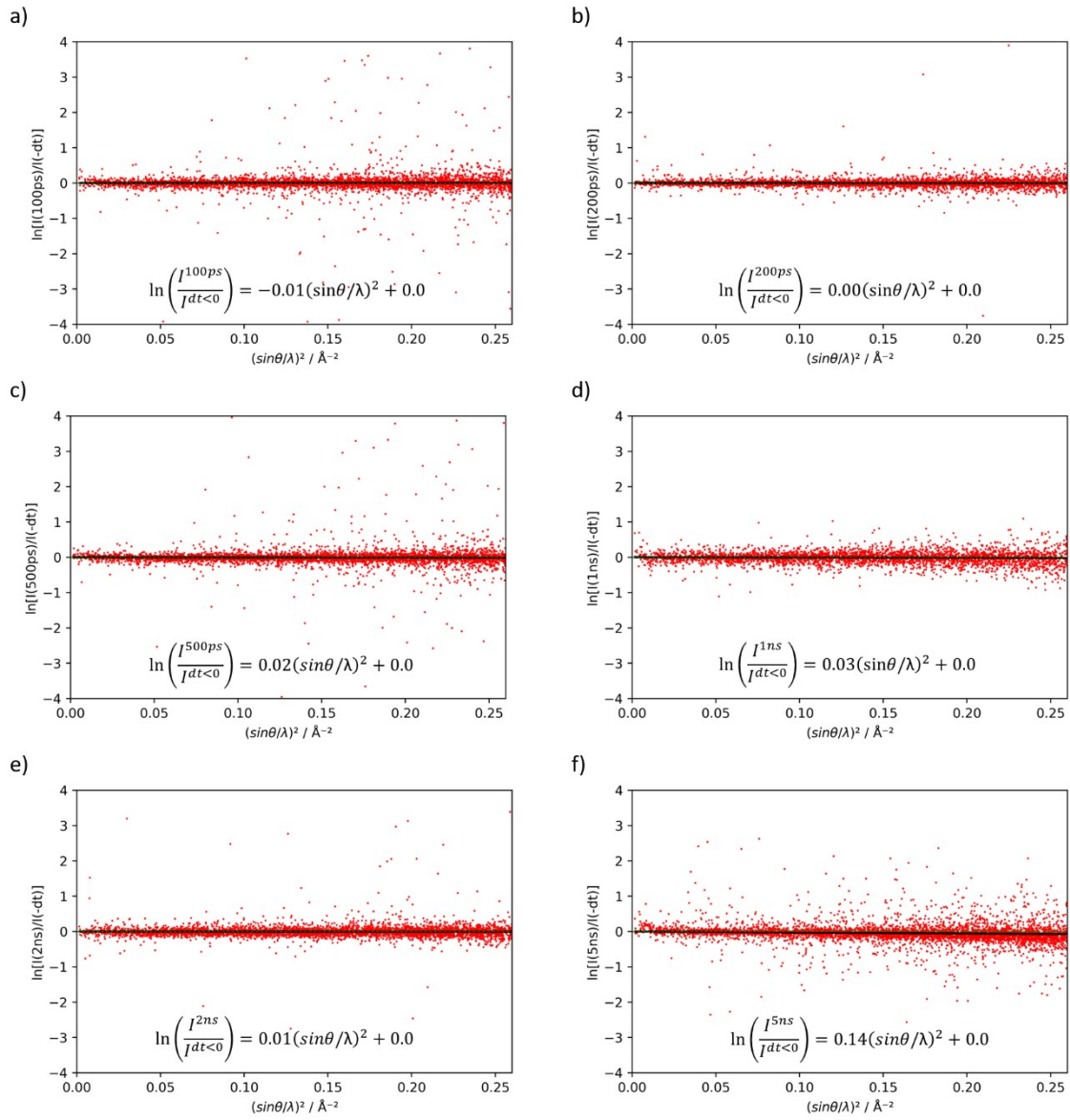


Figure S17. PhotoWilson plots of **FE4**

References

- 1 B. Schneider, S. Demeshko, S. Neudeck, S. Dechert and F. Meyer, *Inorg. Chem.*, 2013, **52**, 13230–13237.
- 2 G. Busca, T. Montanari, M. Bevilacqua and E. Finocchio, *Colloids Surf. Physicochem. Eng. Asp.*, 2008, **320**, 205–212.
- 3 M. P. Marzocchi and S. Dobos, *Spectrochim. Acta Part Mol. Spectrosc.*, 1974, **30**, 1437–1444.
- 4 N. S. Marinković, M. Hecht, J. S. Loring and W. R. Fawcett, *Electrochimica Acta*, 1996, **41**, 641–651.
- 5 P. Schäringer, T. E. Müller, A. Jentys and J. A. Lercher, *J. Catal.*, 2009, **263**, 34–41.
- 6 P. Guionneau, M. Marchivie, G. Bravic, J.-F. Létard and D. Chasseau, in *Spin Crossover in Transition Metal Compounds II*, eds. P. Gütllich and H. A. Goodwin, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004, pp. 97–128.
- 7 M. A. Halcrow, *Chem. Soc. Rev.*, 2011, **40**, 4119.
- 8 M. Marchivie, P. Guionneau, J.-F. Létard and D. Chasseau, *Acta Crystallogr. B*, 2005, **61**, 25–28.
- 9 M. Buron-Le Cointe, J. Hébert, C. Baldé, N. Moisan, L. Toupet, P. Guionneau, J. F. Létard, E. Freysz, H. Cailleau and E. Collet, *Phys. Rev. B*, , DOI:10.1103/PhysRevB.85.064114.
- 10 R. Ketkaew, Y. Tantirungrotechai, P. Harding, G. Chastanet, P. Guionneau, M. Marchivie and D. J. Harding, *Dalton Trans*, 2021, **50**, 1086–1096.
- 11 M. Marchivie, P. Guionneau, J.-F. Létard and D. Chasseau, *Acta Crystallogr. B*, 2003, **59**, 479–486.
- 12 H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1992, **114**, 7843–7851.
- 13 M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, *SHAPE program, version 2.1*, Barcelona, 2003.
- 14 A. J. C. WILSON, *Nature*, 1942, **150**, 152–152.
- 15 M. S. Schmökel, R. Kamiński, J. B. Benedict and P. Coppens, *Acta Crystallogr. A*, 2010, **66**, 632–636.