Electronic Supplementary Material (ESI) for Dalton Transactions.


# Single crystal-to-single crystal transformation – from two distinct to three distinct spin crossover centers in 2D coordination polymer $[Fe(bbtr)_3](CF_3SO_3)_2$

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**Table S1**. Crystallographic data for crystal structures of **1** (before conversion) determined at 300 and 100 K.

| T/K | | 300 | 100 |
|---|---|---|---|
| CCDC number | | 2116786 | 2116787 |
| Chemical formula | | $C_{26}H_{36}F_6FeN_{18}O_6S_2$ | |
| Formula Mass | | 930.70 | |
| Crystal system | | Trigonal | |
| Space group | | R -3 | |
| *Z* | | 9 | |
| Unit cell dimensions<br>*a*/Å<br>*c*/Å | | <br>19.5718(3)<br>28.7483(7) | <br>19.0003(2)<br>28.6098(5) |
| Unit cell volume/Å$^3$ | | 9536.8(4) | 8944.7(3) |
| F(000) | | 4302 | 4302 |
| $D_x$ (Mg m$^{-3}$) | | 1.458 | 1.555 |
| μ (mm$^{-1}$) | | 0.541 | 0.577 |
| Theta range for data collection/$^o$ | | 2.975 to 26.364 | 3.027 to 26.367 |
| Completeness | | theta = 25.242°<br>99.8 % | theta = 25.242°<br>99.8 % |
| Range of *h*, *k*, *l* | | -24 ≤ *h* ≤ 24<br>-15 ≤ *k* ≤ 24<br>-35 ≤ *l* ≤ 35 | -23 ≤ *h* ≤ 23<br>-14 ≤ *k* ≤ 23<br>-35 ≤ *l* ≤ 35 |
| No. of measured reflections | | 23729 | 21853 |
| No. of independent reflections | | 4339 | 4060 |
| $R_{int}$ | | 0.0367 | 0.0255 |
| Data / restraints / parameters | | 4339 / 26 / 351 | 4060 / 26 / 333 |
| Goodness-of-fit on F$^2$ | | 1.042 | 1.047 |
| Final $R_1$ values ($I > 2\sigma(I)$) | | 0.0490 | 0.0231 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | | 0.1213 | 0.0552 |
| Final $R_1$ values (all data) | | 0.0638 | 0.0242 |
| Final $wR(F^2)$ values (all data) | | 0.1309 | 0.0557 |
| Largest diff. peak and hole/eÅ$^3$ | | 0.480 and -0.290 | 0.190 and -0.184 |
| disorder - ligand | | 0.48(3):0.52(3) | 0.373(4):0.627(4) |
| disorder - triflate | | 0.591(6):0.409(6) | 0.886(2):0.114(2) |
| BASF | | 0.524(2) | 0.523(1) |
| d (Fe – N) / Å | Fe2 – N3<br>Fe2 – N13<br>Fe1 – N23 | 2.192(3)<br>2.178(3)<br>2.195(3) | 1.9871(13)<br>1.9828(14)<br>1.9933(13) |

**Table S2**. Crystallographic data for crystal structures of **1c** (after conversion) determined at 100 and 280K.

| | | | |
|---|---|---|---|
| T/K | | 100 | 280 |
| CCDC number | | 2116788 | 2116789 |
| Chemical formula | | $C_{26}H_{36}F_6FeN_{18}O_6S_2$ | |
| Formula Mass | | 930.70 | |
| Crystal system | | Hexagonal | |
| Space group | | P $6_3$ | |
| *Z* | | 6 | |
| Unit cell dimensions<br>*a*/Å<br>*c*/Å | | <br>19.04230(10)<br>19.1734(2) | <br>19.5869(3)<br>19.0349(6) |
| Unit cell volume/Å$^3$ | | 6021.00(9) | 6324.3(3) |
| F(000) | | 2868 | 2868 |
| $D_x$ (Mg m$^{-3}$) | | 1.540 | 1.466 |
| μ (mm$^{-1}$) | | 4.806 | 4.575 |
| Theta range for data collection/$^o$ | | 4.806 to 73.555 | 4.515 to 73.843 |
| Completeness | | theta = 67.684°<br>99.5 % | theta = 67.684°<br>99.5 % |
| Range of *h*, *k*, *l* | | $-19 \leq h \leq 23$<br>$-22 \leq k \leq 23$<br>$-23 \leq l \leq 23$ | -19 ≤ *h* ≤ 24<br>-23 ≤ *k* ≤ 24<br>-23 ≤ *l* ≤ 23 |
| No. of measured reflections | | 42832 | 45063 |
| No. of independent reflections | | 7986 | 8386 |
| $R_{int}$ | | 0.0397 | 0.0599 |
| Data / restraints / parameters | | 7986 / 39 / 535 | 8386 / 268 / 536 |
| Goodness-of-fit on $F^2$ | | 1.047 | 1.262 |
| Final $R_1$ values ($I > 2\sigma(I)$) | | 0.0787 | 0.1022 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | | 0.2153 | 0.2455 |
| Final $R_1$ values (all data) | | 0.0878 | 0.1691 |
| Final $wR(F^2)$ values (all data) | | 0.2327 | 0.2975 |
| Largest diff. peak and hole/eÅ$^3$ | | 3.089 and -0.479 | 2.373 and -0.524 |
| disorder - triflate | | 0.409(8):0.591(8)<br>0.480(9):0.520(9) | 0.523(5):0.245(4):0.232(4)<br>0.463(4):0.537(4) |
| BASF | | 0.499(4) | 0.479(5) |
| d (Fe – N) / Å | Fe1 – N3A<br>Fe1 – N3B<br>Fe2 – N3C<br>Fe2 – N3D<br>Fe3 – N3E<br>Fe3 – N3F | 1.995(7)<br>2.001(6)<br>1.967(7)<br>1.999(7)<br>2.016(7)<br>1.958(2) | 2.213(9)<br>2.174(9)<br>2.207(11)<br>2.167(12)<br>2.174(11)<br>2.184(13) |

**Table S3**. Crystallographic data for crystal structures of **1** (before conversion) determined at 14 K and as result of light irradiation (520 nm) at 14 K.

| | | | |
|---|---|---|---|
| T/K | | 14 | 14 |
| CCDC number | | 2116790 | 2116791 |
| Chemical formula | | $C_{26}H_{36}F_6FeN_{18}O_6S_2$ | |
| Formula Mass | | 930.70 | |
| Crystal system | | Trigonal | |
| Space group | | R -3 | |
| *Z* | | 9 | |
| Unit cell dimensions<br>*a*/Å<br>*c*/Å | | <br>18.9537(3)<br>28.4241(6) | <br>19.3002(4)<br>28.2386(9) |
| Unit cell volume/Å$^3$ | | 8843.1(3) | 9109.6(5) |
| F(000) | | 4302 | 4302 |
| $D_x$ (Mg m$^{-3}$) | | 1.573 | 1.527 |
| μ (mm$^{-1}$) | | 0.583 | 0.566 |
| Theta range for data collection/° | | 2.583 to 26.356 | 2.832 to 26.367 |
| Completeness | | theta = 25.242°<br>99.6 % | theta = 25.242°<br>99.8 % |
| Range of *h*, *k*, *l* | | -22 ≤ *h* ≤ 22<br>-23 ≤ *k* ≤ 23<br>-35 ≤ *l* ≤ 35 | -24 ≤ *h* ≤ 23<br>-24 ≤ *k* ≤ 24<br>-35 ≤ *l* ≤ 35 |
| No. of measured reflections | | 20192 | 20171 |
| No. of independent reflections | | 4017 | 4135 |
| $R_{int}$ | | 0.0260 | 0.0366 |
| Data / restraints / parameters | | 4017 / 38 / 339 | 4135 / 38 / 333 |
| Goodness-of-fit on F$^2$ | | 1.043 | 1.055 |
| Final $R_1$ values ($I > 2\sigma(I)$) | | 0.0414 | 0.0486 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | | 0.1078 | 0.1267 |
| Final $R_1$ values (all data) | | 0.0428 | 0.0505 |
| Final $wR(F^2)$ values (all data) | | 0.1093 | 0.1289 |
| Largest diff. peak and hole/eÅ$^3$ | | 2.154 and -0.946 | 1.977 and -1.087 |
| disorder - ligand | | 0.477(7):0.523(7) | 0.470(9):0.530(9) |
| disorder - triflate | | 0.749(3):0.251(3) | 0.796(3):0.204(3) |
| BASF | | 0.529(2) | 0.535(2) |
| d (Fe – N) / Å | Fe2 – N3<br>Fe2 – N13<br>Fe1 – N23 | 1.987(2)<br>1.978(3)<br>1.992(2) | 2.193(3)<br>2.165(3)<br>2.187(2) |

**Table S4**. Crystallographic data for crystal structures of **1c** (after conversion) determined at 14 K and as result of light irradiation (520 nm) at 14 K.

| T/K | | 14 | 14 |
|---|---|---|---|
| CCDC number | | 2116792 | 2116793 |
| Chemical formula | | $C_{26}H_{36}F_6FeN_{18}O_6S_2$ | |
| Formula Mass | | 930.70 | |
| Crystal system | | Hexagonal | |
| Space group | | P $6_3$ | |
| *Z* | | 6 | |
| Unit cell dimensions<br>*a*/Å<br>*c*/Å | | <br>19.0500(2)<br>19.0504(4) | <br>19.4504(3)<br>18.7290(4) |
| Unit cell volume/Å$^3$ | | 5987.18(19) | 6136.3(2) |
| F(000) | | 2868 | 2868 |
| $D_x$ (Mg m$^{-3}$) | | 1.549 | 1.511 |
| μ (mm$^{-1}$) | | 0.574 | 0.560 |
| Theta range for data collection/$^o$ | | 2.391 to 38.104 | 2.360 to 38.154 |
| Completeness | | theta = 25.242°<br>95.6 % | theta = 25.242°<br>96.0 % |
| Range of *h*, *k*, *l* | | -32 ≤ *h* ≤ 31<br>-32 ≤ *k* ≤ 32<br>-20 ≤ *l* ≤ 20 | -32 ≤ *h* ≤ 31<br>-32 ≤ *k* ≤ 32<br>-20 ≤ *l* ≤ 20 |
| No. of measured reflections | | 72967 | 88268 |
| No. of independent reflections | | 17049 | 17647 |
| $R_{int}$ | | 0.0411 | 0.1207 |
| Data / restraints / parameters | | 17049 / 58 / 493 | 17647 / 257 / 543 |
| Goodness-of-fit on $F^2$ | | 1.028 | 1.019 |
| Final $R_1$ values ($I > 2\sigma(I)$) | | 0.1025 | 0.1048 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | | 0.2738 | 0.2741 |
| Final $R_1$ values (all data) | | 0.1351 | 0.1677 |
| Final $wR(F^2)$ values (all data) | | 0.3124 | 0.3437 |
| Largest diff. peak and hole/eÅ$^3$ | | 3.317 and -1.478 | 3.039 and -0.725 |
| disorder - triflate | | 0.398(8):0.602(8)<br>0.521(9):0.479(9) | 0.282(7):0.559(7):0.158(5)<br>0.528(6):0.472(5) |
| BASF | | 0.510(3) | 0.514(4) |
| d (Fe – N) / Å | Fe1 – N3A | 1.983(6) | 2.183(7) |
| | Fe1 – N3B | 2.005(6) | 2.179(7) |
| | Fe2 – N3C | 1.996(6) | 2.190(7) |
| | Fe2 – N3D | 1.992(6) | 2.169(8) |
| | Fe3 – N3E | 2.019(7) | 2.208(8) |
| | Fe3 – N3F | 1.980(6) | 2.167(7) |

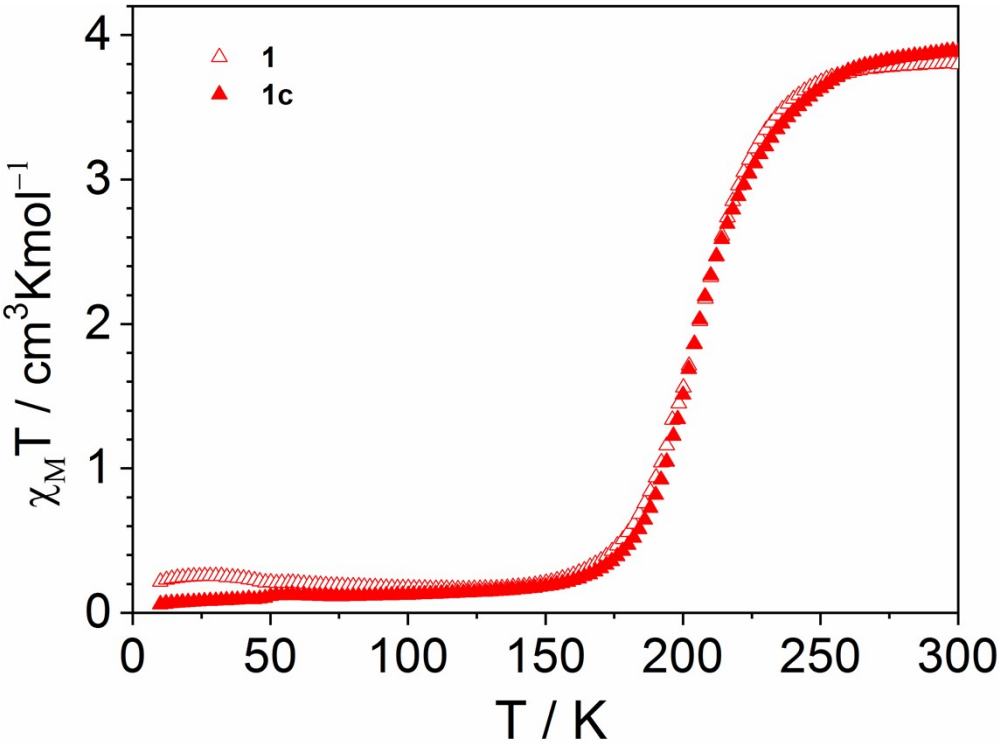



**Figure S1**. $\chi_M T(T)$ dependences recorded in heating mode for **1** (filled triangles) and **1c** (open triangles) after putting on insert in magnetometer chamber cooled to 10 K.

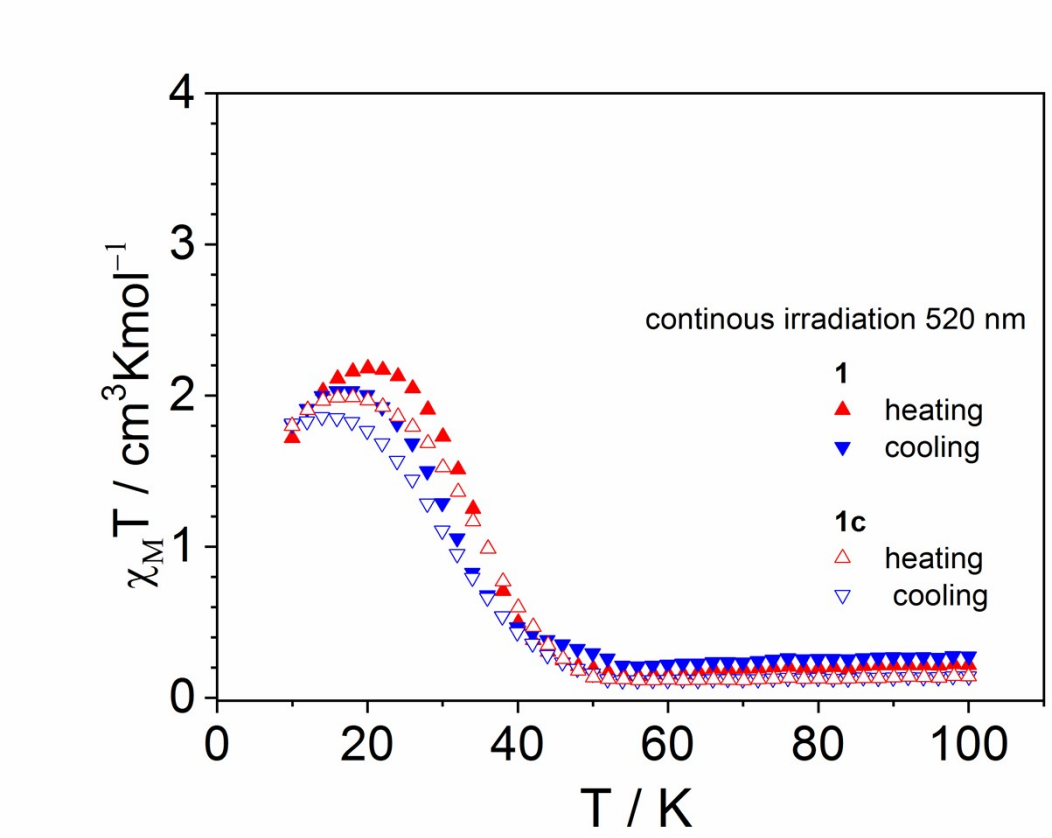
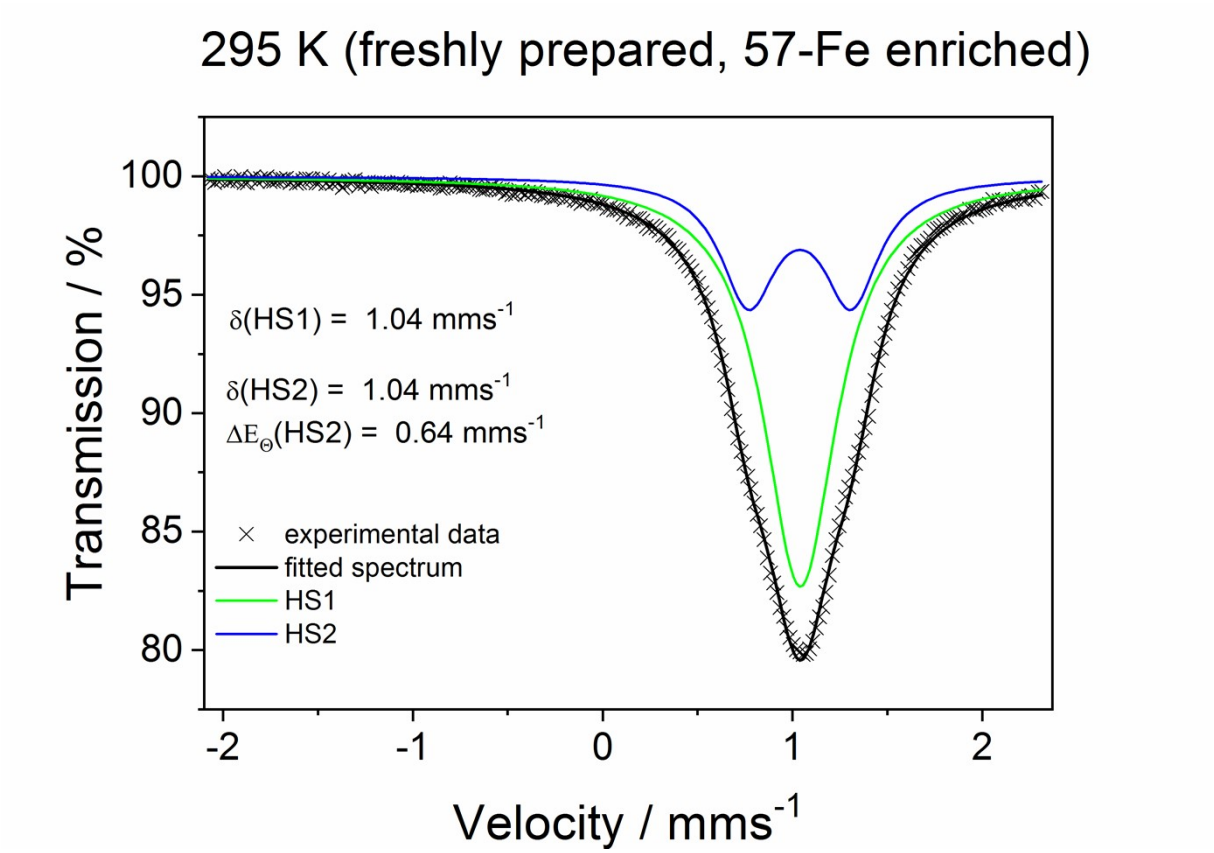
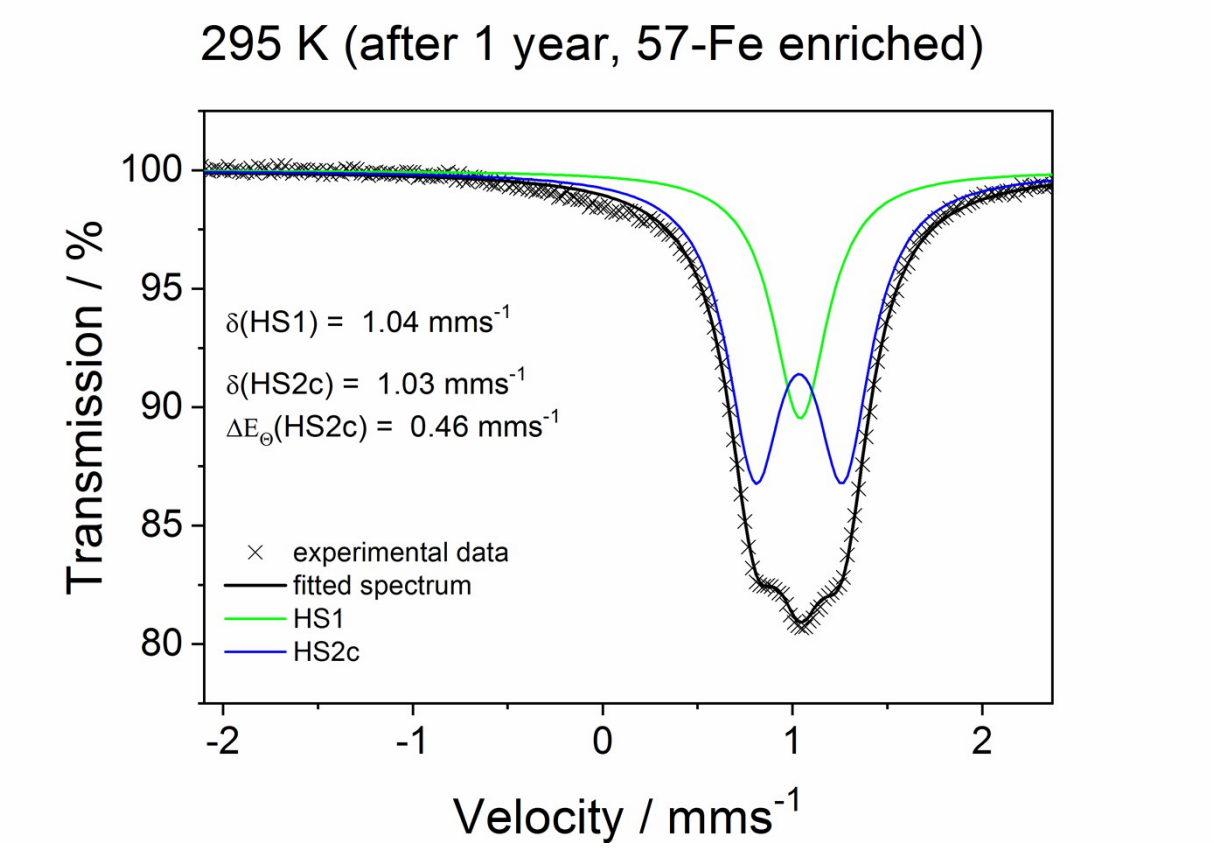



**Figure S2**. $\chi_M T(T)$ dependences recorded under continuous light irradiation $\lambda$ = 520 nm (LITH experiments) for **1** (filled triangles) and **1c** (open triangles). Red – heating; blue – cooling.

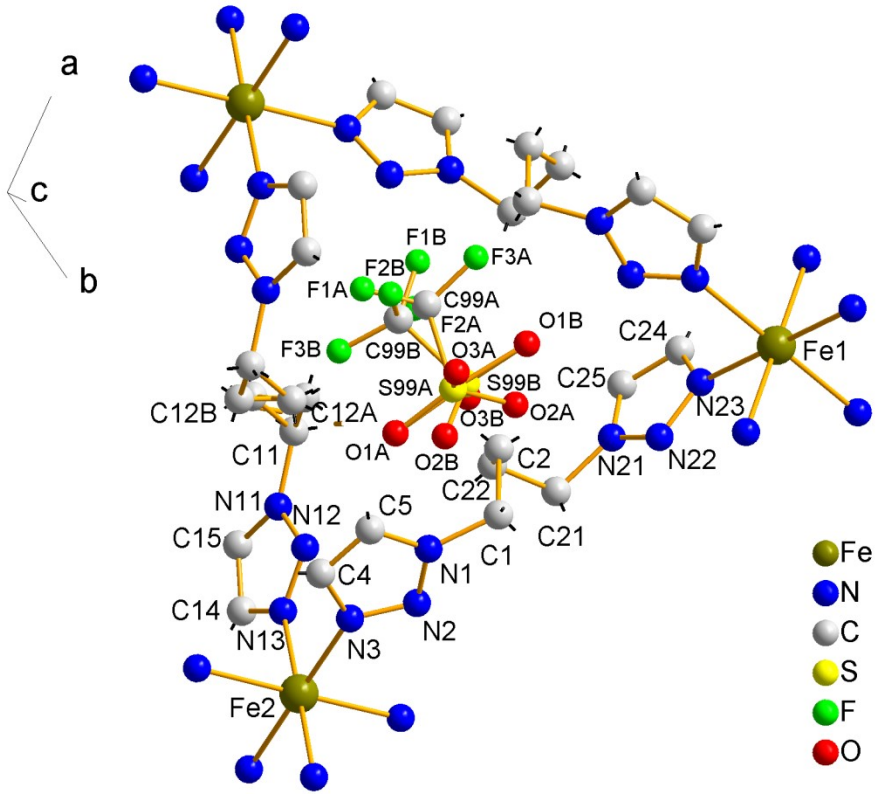



a)

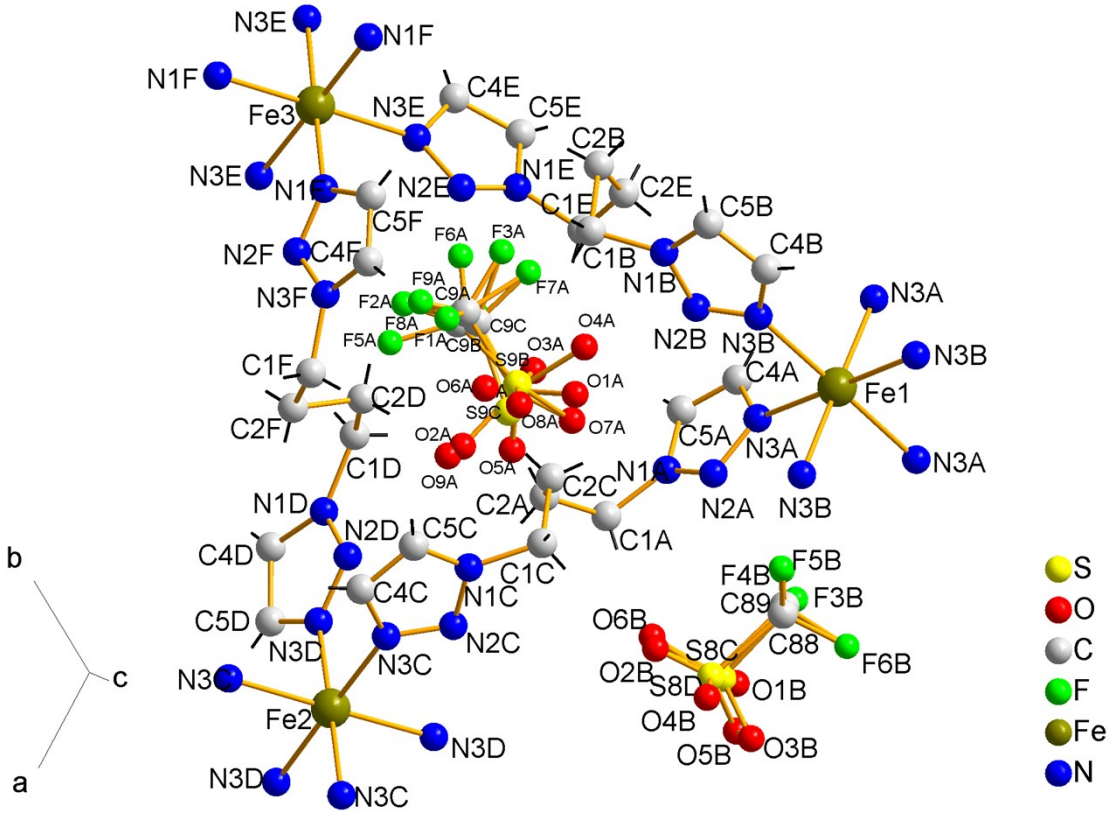



b)

**Figure S3**. Mössbauer spectra (295 K) for $^{57}$Fe enriched **1** (a) and **1c** (b).




a)




b)

**Figure S4**. Fragments of the polymeric layers in **1** (a) and **1c** (b) together with labelled atoms forming asymmetric units.

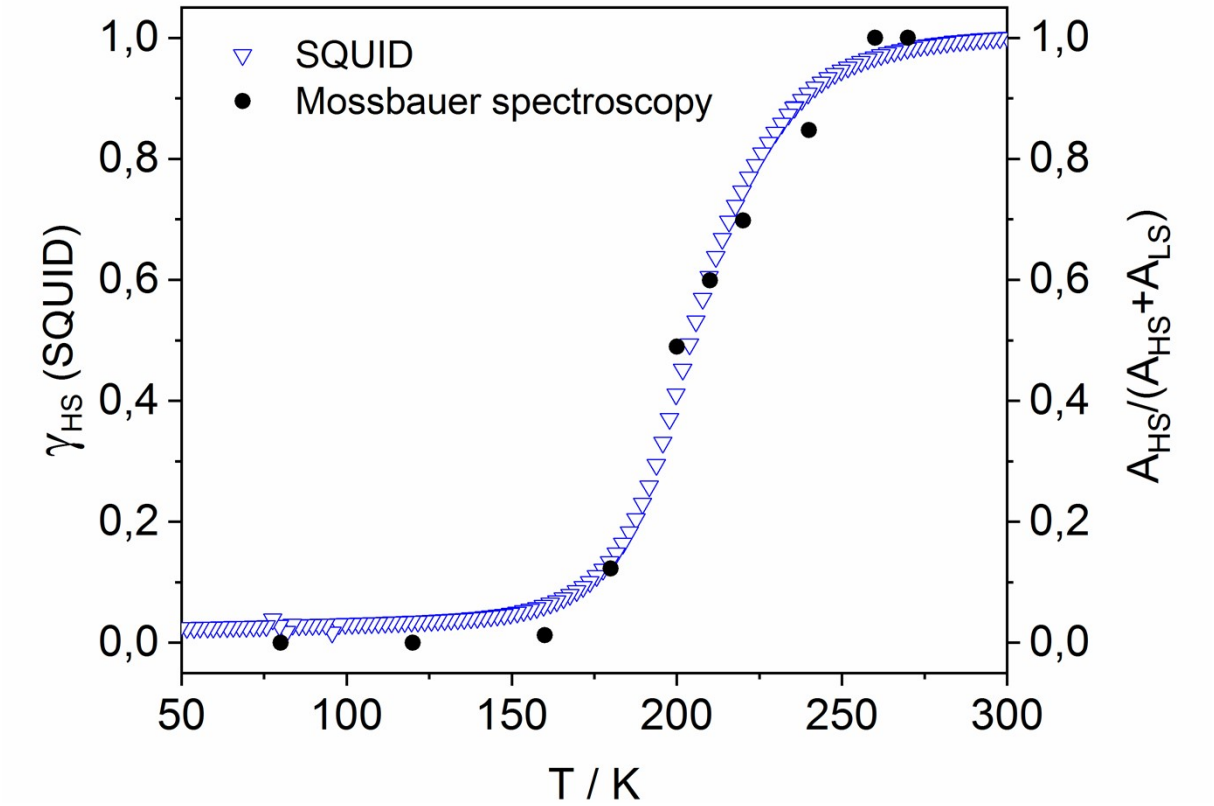



**Figure S5**. $\gamma_{HS}$(T) derived from magnetic studies (SQUID, cooling mode, blue open triangles) and relative area $A_{HS}/(A_{HS}+A_{LS})$ *vs.* T dependence (Mössbauer spectroscopy, cooling mode, black circles) for **1c**. $A_{HS}$ (right axis label) denotes a sum of $A_{HS1}$ and $A_{HS2c}$ areas.

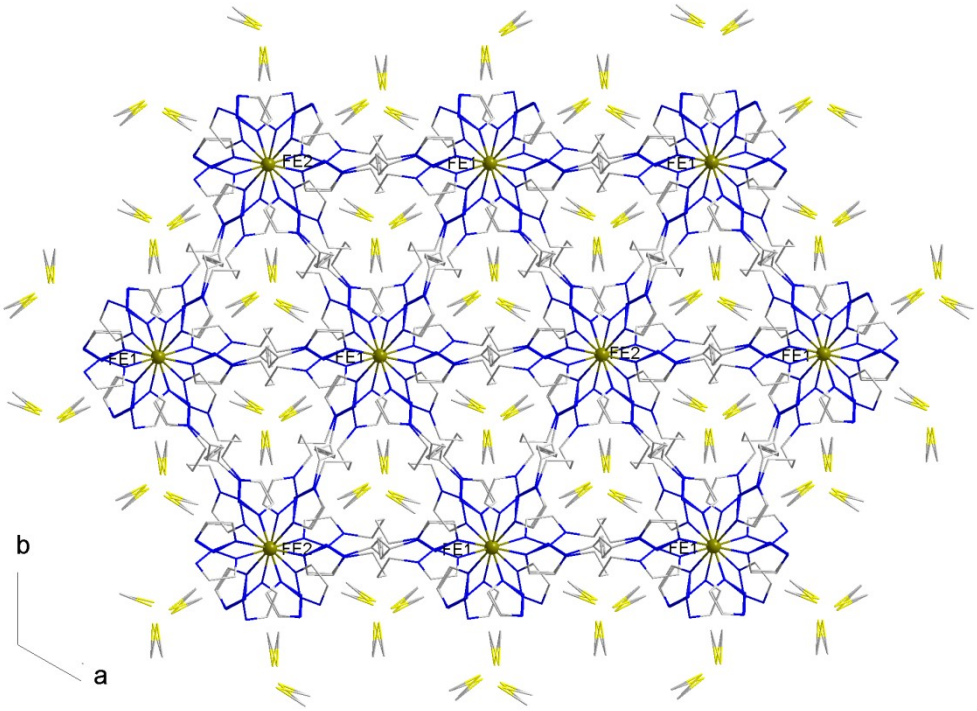



**Figure S6**. View along *c* axis of three adjusted layers in **1** (300 K).

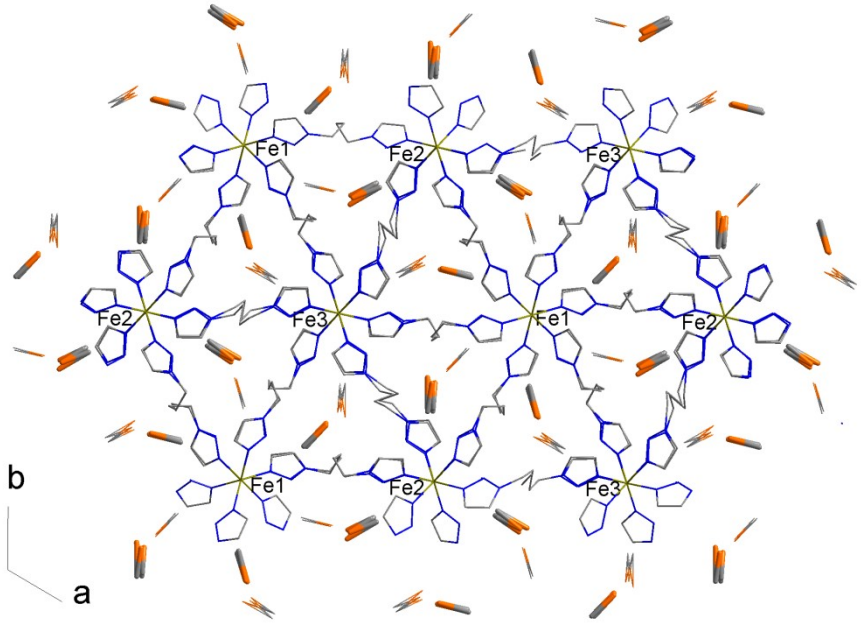
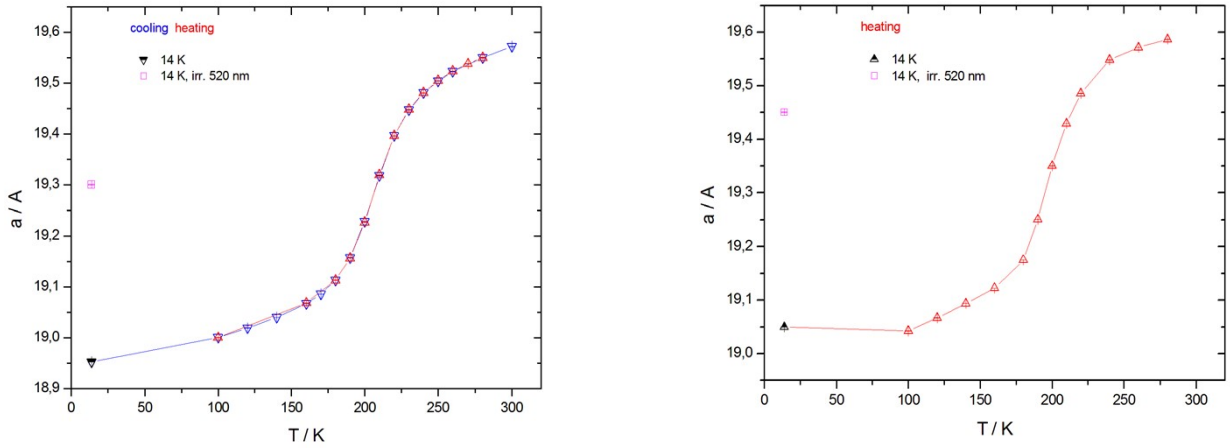


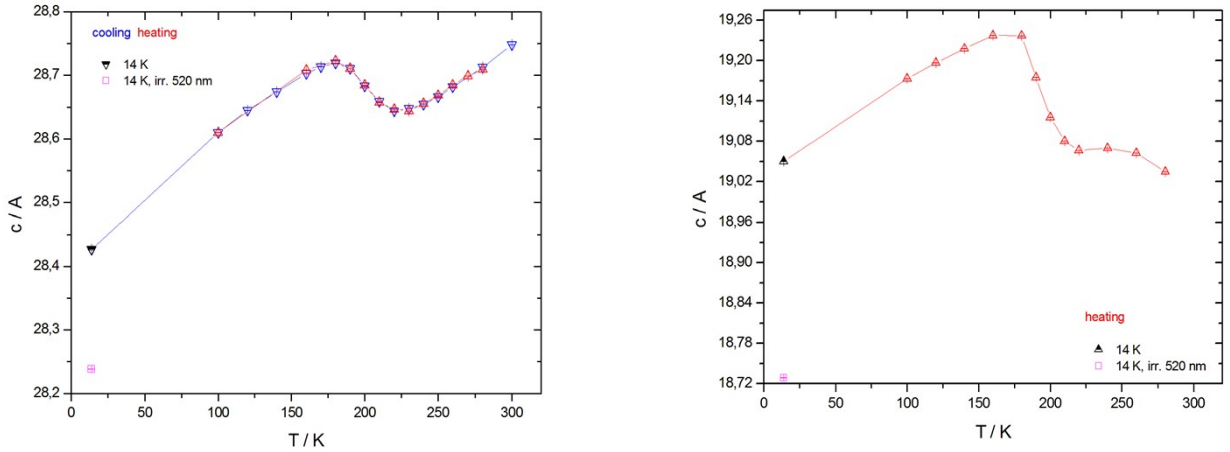

**Figure S7**. View along *c* axis of three adjusted layers in **1c** (view along *c* direction) at 280 K.

**1** **1c**

a) d)




b) e)




c) f)

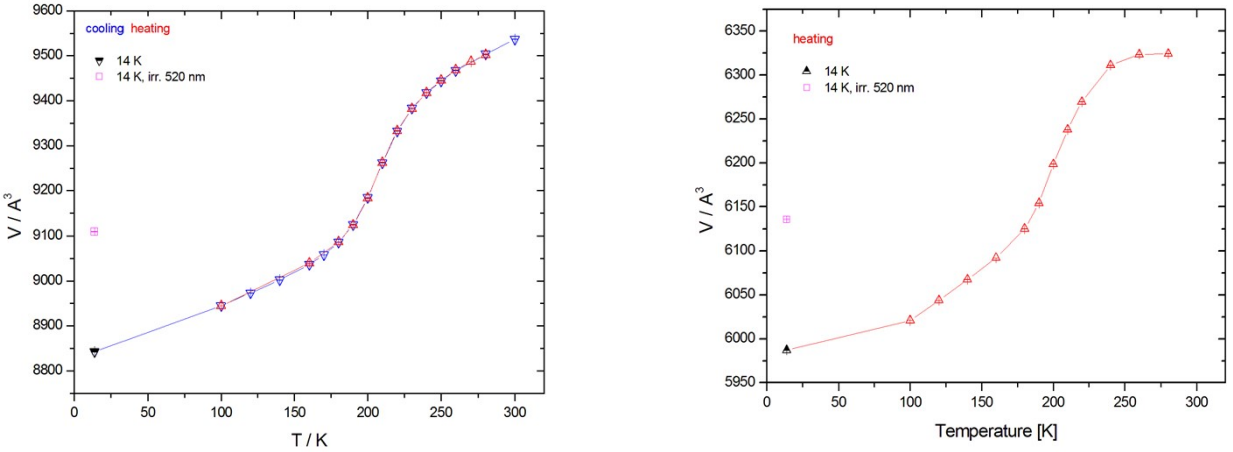
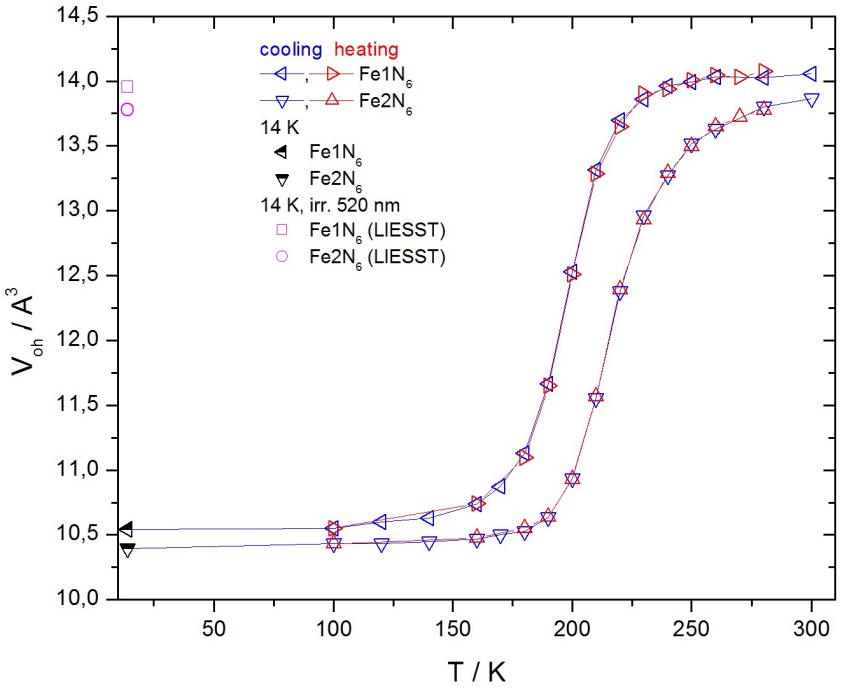
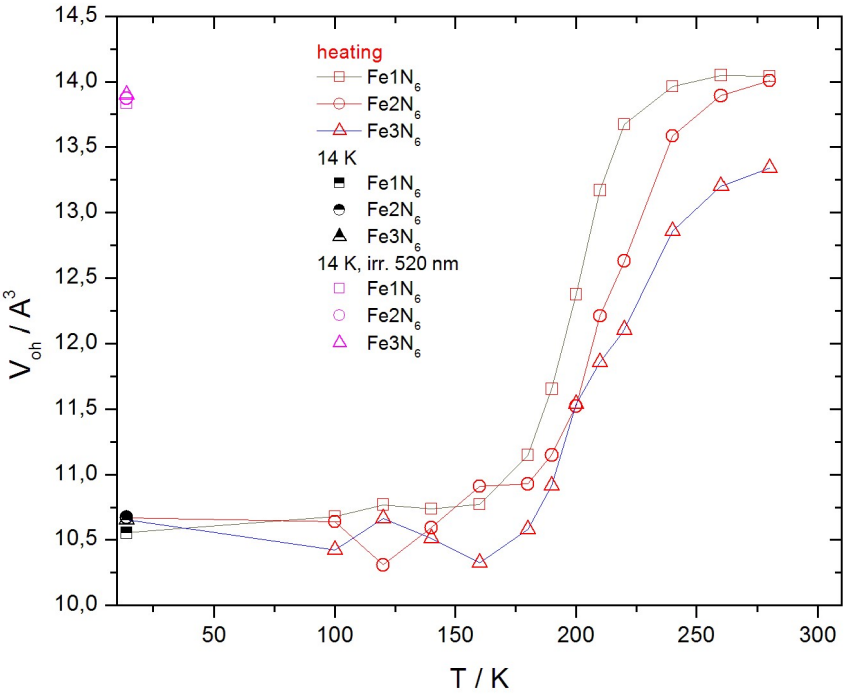



**Figure S8**. Temperature dependence of unit cell parameters for **1** (left column) and **1c** (right column).

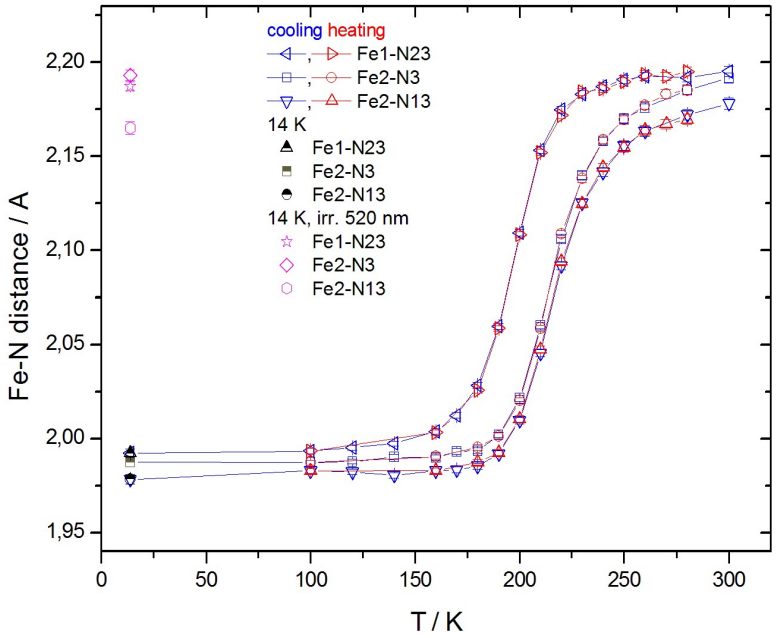



a)

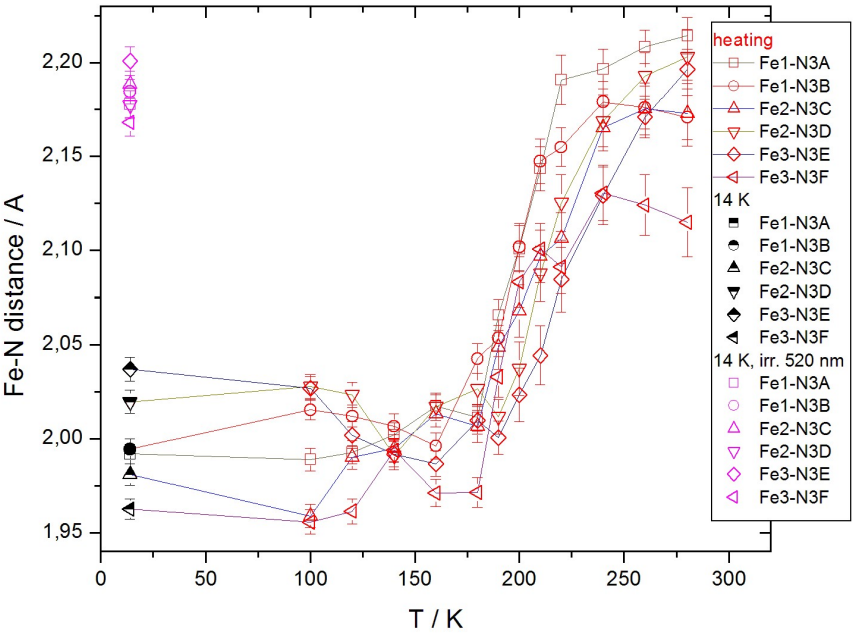



b)

**Figure S9**. Temperature dependence of [$FeN_6$] octahedral volumes $V_{oh}$ for **1** (a) and **1c** (b).




a)




b)

**Figure S10**. Temperature dependence of the Fe-N distances for **1** (a) and **1c** (b).