# Electronic Supplementary Information

## Thermal and Light induced Spin Crossover Behavior of a Dinuclear Fe(II) Compound

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**Physical measurements**

The C, H, N elemental analysis was performed on an Elementar Vario MICRO CUBE analyzer.

**Magnetic measurements**

Samples were fixed by parafilm to avoid moving during measurement and sealed capsule. Direct current susceptibility measurements were performed on Quantum Design MPMS XL-5 SQUID magnetometer on polycrystalline sample. All dc susceptibilities were corrected for diamagnetic contribution from the sample holder, parafilm and diamagnetic contributions from the molecule using the pascal's constants.

**X-ray Data Collection and Structure Determinations**

X-ray single-crystal diffraction data for complexes LS **1**, HS **1** were collected on a Agilent SuperNova Dual Atlas CCD diffractometer at 100 K and 180 K with Mo Kα radiation (λ = 0.71073 Å). All the structures were determined by direct methods using the OLEX-2 program and refined with OLEX-2. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on $F^2$. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

**$^{57}$Fe Mössbauer spectroscopy**

Mössbauer experiments were carried out using a $^{57}$Co/Rh (925 MBq) source in a constant-acceleration transmission spectrometer (made by Tpologic Systems) equipped with an Iwatani HE05/CW404 cryostat. The spectrometer was calibrated using standard -Fe foil. The driving speed of radiation source was carried out during ± 4.0 mm/sec.

**General Methods**

All materials were purchased from company and used directly. L was synthesized according to literature procedures.

**Synthesis**

$[Fe_2(L)_5(SCN)_4]\cdot H_2O$ (**1**). A solution of 20 mmol L and 20 mmol ammonium thiocyanate in 10 ml of methnol is added to the solution of 10 mmol $Fe(BF_4)_2\cdot 6(H_2O)$ in 10 mL of methanol. The mixture was refluxed under nitrogen atmosphere for 3 hours. Then the reaction was gradually cooled down and filtered. The filtrate was collected. After several days evaporation, columnar yellow crystals suitable for X-ray measurement were obtained. Yields (20 mg, about 32% yield). Anal. Calcd (%) for $C_{59}H_{60}Fe_2N_{24}S_4O_{10}$ : C, 37.55; H, 2.06; N, 21.44 Found: C, 37.96; H, 1.96; N,. 21.89.

**Table S1.** Crystallographic data for low-spin (LS) **1**, high-spin (HS) **1**

| Compound | $[Fe_2(L\text{-}Cl\text{-}2,5)_5(SCN)_4]$ $(H_2O)$ | $[Fe_2(L\text{-}Cl\text{-}2,5)_5(SCN)_4]$ $(H_2O)$ |
|---|---|---|
| formula | $C_{49}H_{32}Fe_2N_{24}S_4O_1Cl_{10}$ | $C_{49}H_{32}Fe_2N_{24}S_4O_1Cl_{10}$ |
| fwt | 1567.42 | 1567.42 |
| temperature (K) | 100 | 180 |
| crystal system | triclinic | triclinic |
| space group | *P-1* | *P-1* |
| a/Å | 12.2288(3) | 12.3828(4) |
| b/Å | 13.7545(4) | 13.9794(5) |
| c/Å | 21.2048(6) | 21.2486(8) |
| α/° | 105.680(3) | 105.370(3) |
| β/° | 94.481(2) | 93.751(3) |
| γ/° | 105.261(2) | 105.820(3) |
| $V$/m$^3$ | 3269.78(16) | 3374.5(2) |
| Z | 2 | 2 |
| Dc/Mg m$^{-3}$ | 1.592 | 1.543 |
| crystal size,mm$^{-3}$ | 0.2×0.2×0.2 | 0.2×0.2×0.2 |
| no.total reflns. | 12566 | 13027 |
| no.uniq.reflns($R_{int}$) | 10192( 0.0289) | 10254(0.0274) |
| no.params | 817 | 907 |
| *GOF* | 1.023 | 1.027 |
| $R_1$,$wR_2$[I>2σ(I)] | 0.0514, 0.1306 | 0.0508, 0.1318 |
| $R_1$,$wR_2$(all data) | 0.0664, 0.1421 | 0.0679, 0.1439 |

**Table S2**. Selected bond lengths (Å) and angles (°) for LS **1**, HS **1**

| Bond lengths (Å) | **1** (100 K, LS) | | |
|---|---|---|---|
| Fe(1)-N(7) | 1.951(3) | Fe(2)-N(1) | 2.018(4) |
| Fe(1)-N(9) | 1.957(3) | Fe(2)-N(2) | 2.023(4) |
| Fe(1)-N(11) | 1.961(3) | Fe(2)-N(5) | 2.055(3) |
| Fe(1)-N(8) | 1.964(3) | Fe(2)-N(3) | 2.066(4) |
| Fe(1)-N(12) | 1.969(3) | Fe(2)-N(6) | 2.076(3) |
| Fe(1)-N(10) | 1.972(3) | Fe(2)-N(4) | 2.080(3) |

| Bond lengths (Å) | **1** (180 K, HS) | | |
|---|---|---|---|
| Fe(1)-N(12) | 2.022(5) | Fe(2)-N(1) | 2.089(5) |
| Fe(1)-N(9) | 2.056(5) | Fe(2)-N(6) | 2.110(5) |
| Fe(1)-N(8) | 2.091(4) | Fe(2)-N(3) | 2.173(4) |
| Fe(1)-N(11) | 2.104(5) | Fe(2)-N(2) | 2.174(5) |
| Fe(1)-N(7) | 2.118(4) | Fe(2)-N(5) | 2.195(5) |
| Fe(1)-N(10) | 2.124(4) | Fe(2)-N(4) | 2.200(4) |

| Angles (°) | **1** (100 K, LS) | | |
|---|---|---|---|
| N(7)-Fe(1)-N(9) | 91.20(11) | N(1)-Fe(2)-N(2) | 91.34(13) |
| N(7)-Fe(1)-N(11) | 89.84(12) | N(1)-Fe(2)-N(5) | 90.37(12) |
| N(9)-Fe(1)-N(11) | 89.38(12) | N(2)-Fe(2)-N(5) | 177.80(12) |
| N(7)-Fe(1)-N(8) | 179.00(12) | N(1)-Fe(2)-N(3) | 90.42(13) |
| N(9)-Fe(1)-N(8) | 89.37(12) | N(2)-Fe(2)-N(3) | 90.85(13) |
| N(11)-Fe(1)-N(8) | 89.35(11) | N(5)-Fe(2)-N(3) | 90.51(12) |
| N(7)-Fe(1)-N(12) | 88.54(11) | N(1)-Fe(2)-N(6) | 90.86(13) |
| N(9)-Fe(1)-N(12) | 177.40(11) | N(2)-Fe(2)-N(6) | 88.64(13) |
| N(11)-Fe(1)-N(12) | 93.20(11) | N(5)-Fe(2)-N(6) | 89.96(11) |
| N(8)-Fe(1)-N(12) | 90.92(11) | N(3)-Fe(2)-N(6) | 178.63(12) |
| N(7)-Fe(1)-N(10) | 91.36(11) | N(1)-Fe(2)-N(4) | 177.11(12) |
| N(9)-Fe(1)-N(10) | 87.60(12) | N(2)-Fe(2)-N(4) | 91.23(12) |
| N(11)-Fe(1)-N(10) | 176.78(11) | N(5)-Fe(2)-N(4) | 87.02(11) |
| N(8)-Fe(1)-N(10) | 89.48(11) | N(3)-Fe(2)-N(4) | 90.85(12) |
| N(12)-Fe(1)-N(10) | 89.82(11) | N(6)-Fe(2)-N(4) | 87.89(11) |

| Angles (°) | **1** (180 K, HS) | | |
|---|---|---|---|
| N(12)-Fe(1)-N(9) | 94.72(18) | N(1)-Fe(2)-N(6) | 93.82(19) |
| N(12)-Fe(1)-N(8) | 94.46(18) | N(1)-Fe(2)-N(3) | 89.93(17) |
| N(9)-Fe(1)-N(8) | 87.01(18) | N(6)-Fe(2)-N(3) | 176.15(17) |
| N(12)-Fe(1)-N(11) | 91.04(18) | N(1)-Fe(2)-N(2) | 91.13(19) |
| N(9)-Fe(1)-N(11) | 89.86(18) | N(6)-Fe(2)-N(2) | 90.35(19) |
| N(8)-Fe(1)-N(11) | 173.88(16) | N(3)-Fe(2)-N(2) | 90.44(16) |
| N(12)-Fe(1)-N(7) | 88.77(16) | N(1)-Fe(2)-N(5) | 92.21(19) |

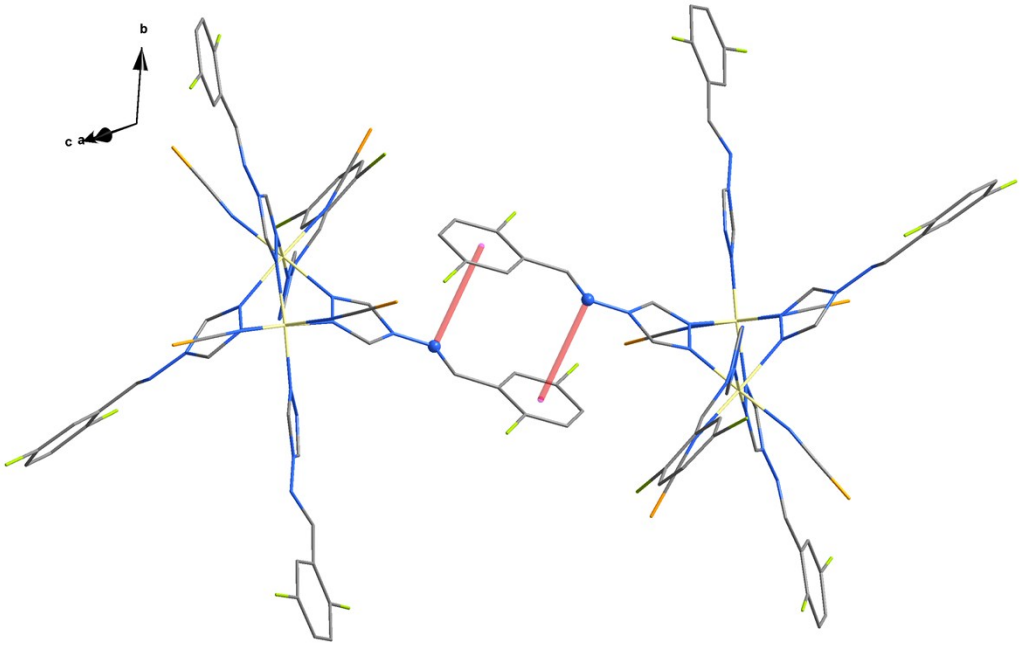
| | | | |
|---|---|---|---|
| N(9)-Fe(1)-N(7) | 175.28(18) | N(6)-Fe(2)-N(5) | 88.43(19) |
| N(8)-Fe(1)-N(7) | 89.54(15) | N(3)-Fe(2)-N(5) | 90.56(16) |
| N(11)-Fe(1)-N(7) | 93.27(15) | N(2)-Fe(2)-N(5) | 176.51(17) |
| N(12)-Fe(1)-N(10) | 176.46(16) | N(1)-Fe(2)-N(4) | 175.85(17) |
| N(9)-Fe(1)-N(10) | 88.21(18) | N(6)-Fe(2)-N(4) | 90.30(17) |
| N(8)-Fe(1)-N(10) | 87.68(17) | N(3)-Fe(2)-N(4) | 85.95(15) |
| N(11)-Fe(1)-N(10) | 86.97(17) | N(2)-Fe(2)-N(4) | 89.41(16) |
| N(7)-Fe(1)-N(10) | 88.42(15) | N(5)-Fe(2)-N(4) | 87.33(16) |

**Table S3.** Mössbauer parameters for **1**

| Compound **1** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Temp. (K) | **Fe(II)_HS (Blue)** | | | | **Fe(II)_LS (Red)** | | | |
| | δ(mm·s$^{-1}$) | ΔEQ (mm·s$^{-1}$) | Are Fraction (%) | Γ/2 | δ(mm·s$^{-1}$) | ΔEQ (mm·s$^{-1}$) | Are Fraction (%) | Γ/2 |
| r.t. | 1.07 | 2.18 | 96.9 | 0.41 | 0.50 | 0.14 | 3.1 | 0.25 |
| 200 | 1.11 | 2.55 | 96.8 | 0.39 | 0.50 | 0.14 | 3.2 | 0.25 |
| 150 | 1.16 | 2.70 | 91.7 | 0.38 | 0.48 | 0.16 | 8.3 | 0.19 |
| 100 | 1.17 | 2.70 | 55.0 | 0.44 | 0.50 | 0.11 | 45.0 | 0.25 |
| 20 | 1.19 | 2.72 | 34.1 | 0.45 | 0.51 | 0.15 | 65.9 | 0.30 |

**Table S4.** HOMO, LUMO energy and electron affinity of the two ligands

| | HOMO(au) | LUMO(au) | Affinity |
|---|---|---|---|
| 4-phenylimino-1,2,4-triazole | -0.2595 | -0.09135 | 2.4858 |
| 2,5-dichloride-4-phenylimino-1,2,4-triazole | -0.2670 | -0.1037 | 2.8210 |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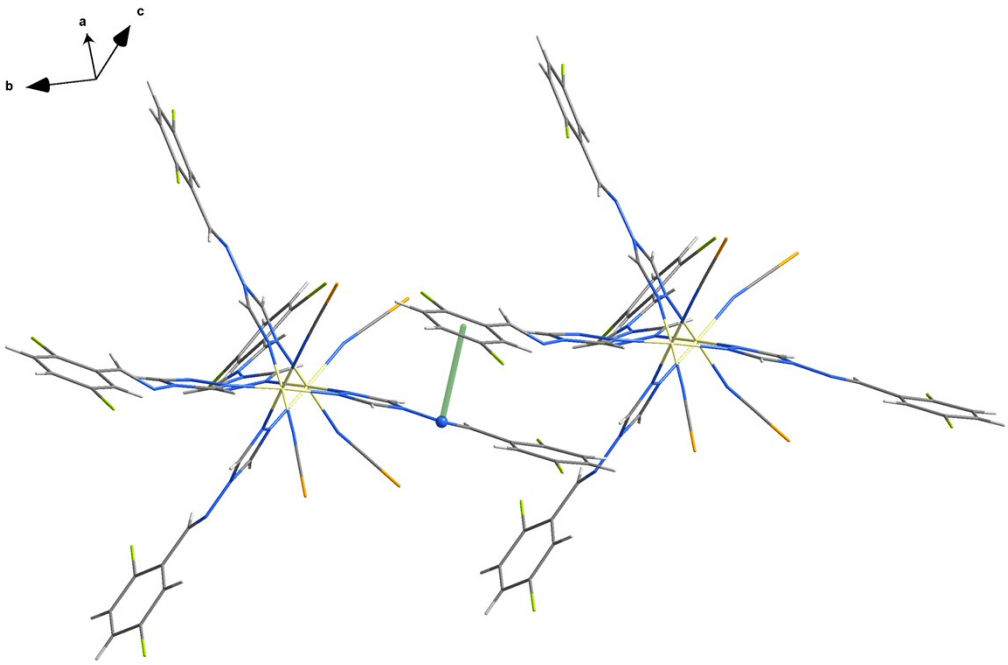
c a


a
c
b

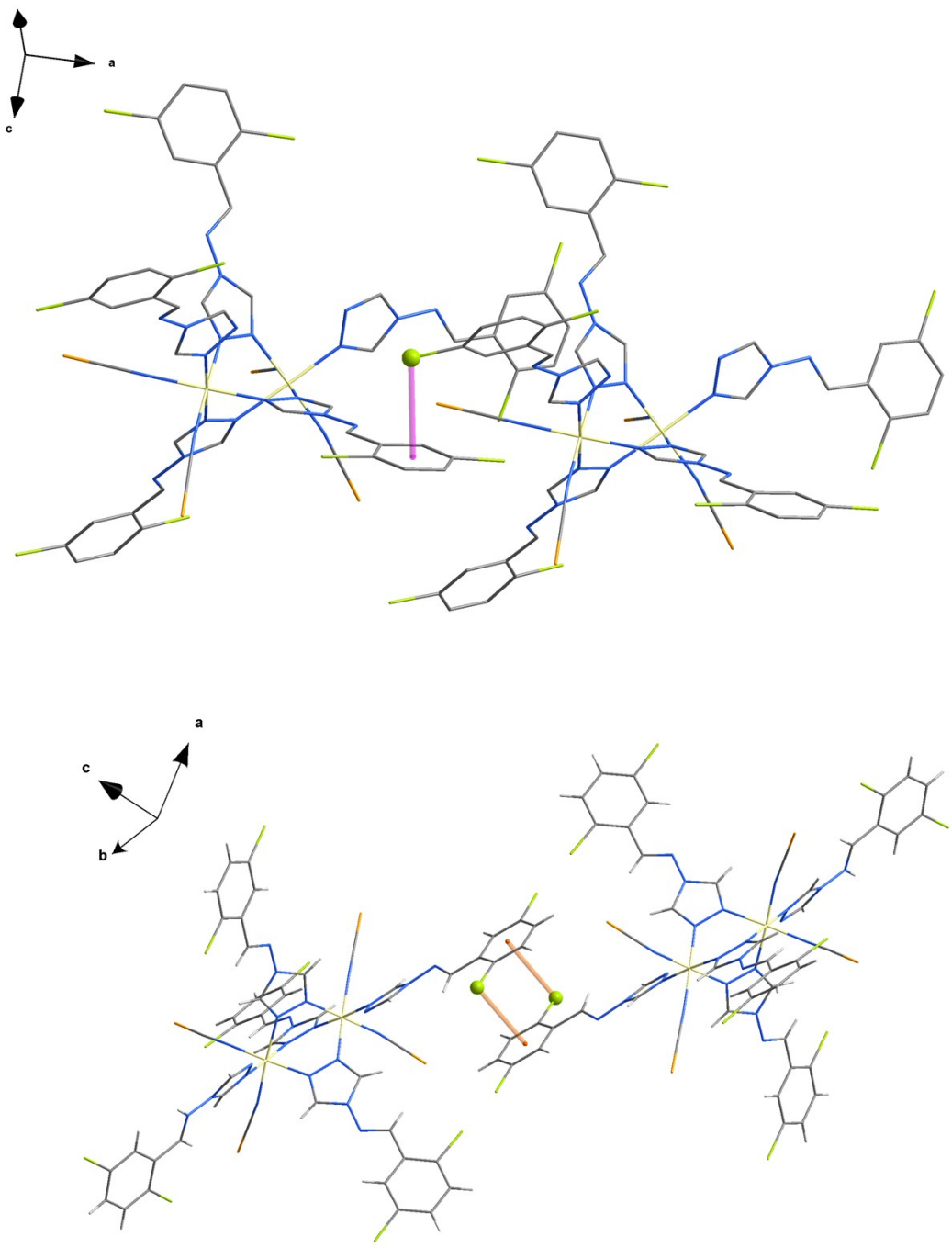



Fig. S1 View of the crystal packing of **1** (H atom and solvent molecule has been omitted)
red lines: N10–Ph (symmetry operations : 1-x,1-y,1-z, d=3.396Å) , parallel stacking of the phenylimino with two interactions;
green line: N12–Ph(symmetry operations :2-x, 1-y, 1-z, d=3.295Å ), rotated stacking groups with one sole interaction;
pink line: Cl9-ph(symmetry operations :2-x, 1-y, 1-z, d=3.682Å ),
orange line: Cl6-ph(symmetry operations :2-x, -y, 1-z, d=3.525Å ).

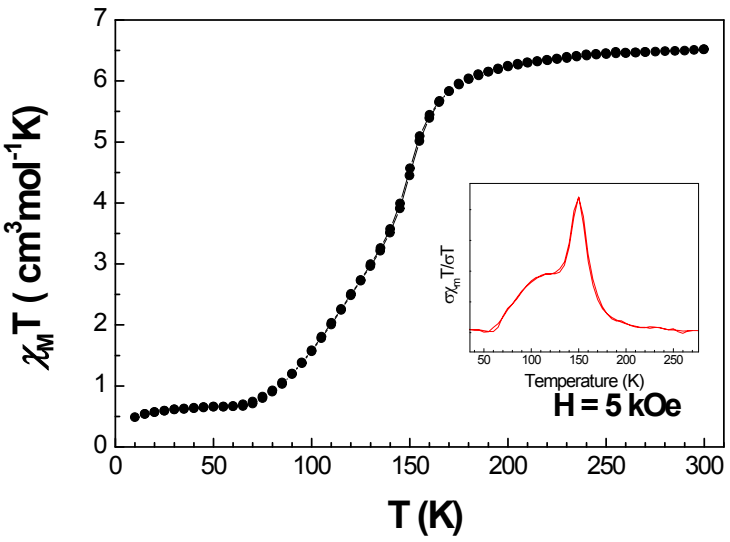



Fig. S2 $\chi_m T$ vs. $T$ plots for compound **1**. Inset: first derivative of the $\chi_m T$ vs. $T$

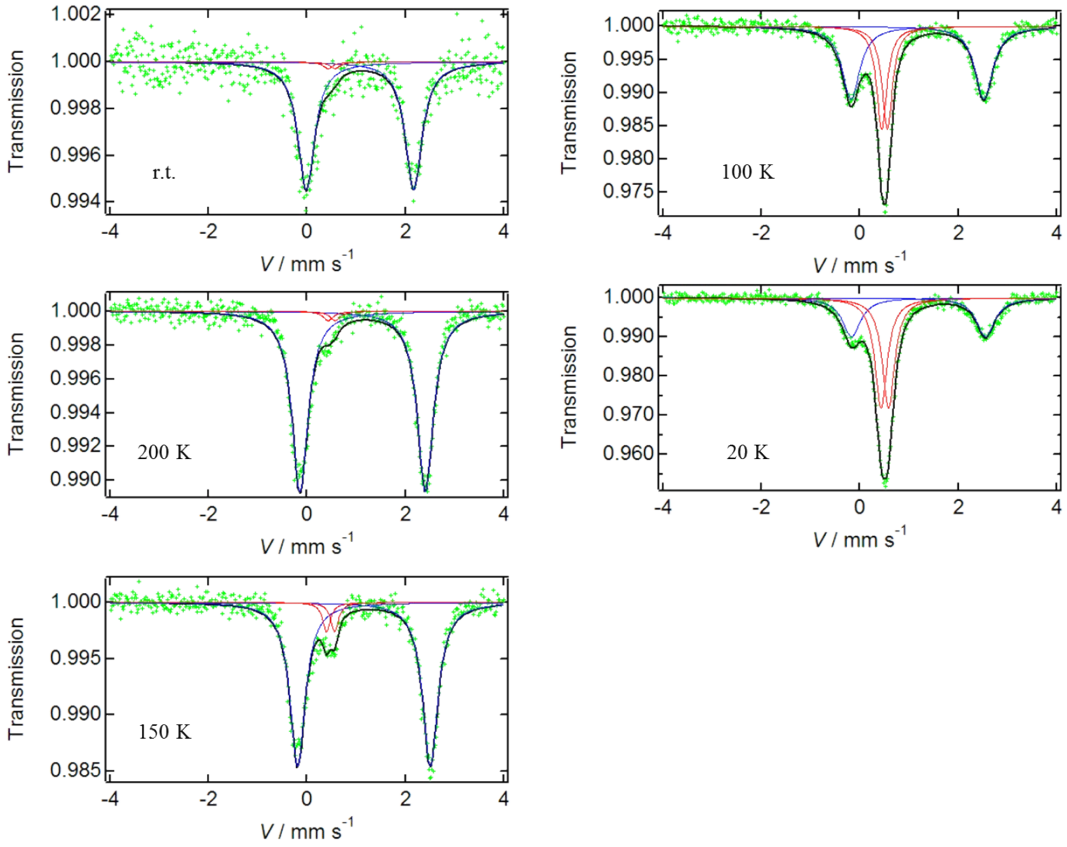



Fig.S3 Mössbauer Spectroscopy of compound **1** of separate temperature (Green dots: observed, black line: calculated, blue line: HS phase, red line: LS phase)