

Supporting Information

Polymorphism-dependent $T_{1/2}$ shift of 100 K in a hysteretic spin crossover complex related to differences in intermolecular weak CH \cdots X hydrogen bonds (X = S vs S and N)

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Experimental

Syntheses

All reagents and solvents were purchased from commercial sources and used for the syntheses without further purification. Phenyl azide (**a**),¹ (1-Phenyl-1,2,3-triazol-4-yl)methanol (**b**),² 1-phenyl-1,2,3-triazole-4-carbaldehyde (**c**),³ and 1-methyl-1,2,3-triazole-4-carbaldehyde (**f**)^{3,4} were prepared by modifying the reported procedures. Complexiation and crystallization processes of $[\text{Fe}^{\text{II}}\text{L}^{\text{Me}}(\text{NCS})_2]$ were performed under nitrogen atmosphere using Schlenk techniques.

Preparation of (1-Phenyl-1,2,3-triazol-4-yl)methanol (**b**)

NaNO_2 (6.902 g, 100 mmol) and hydrazine hydrate (12.516 g, 250 mmol) were added to a solution of aniline (4.661 g, 50 mmol) in CH_2Cl_2 (20 mL) at room temperature. To the mixture was added AcOH (24.020 g, 400 mmol) dropwise and the mixture was stirred at room temperature for 20 hr. The reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL); the extracts were washed with H_2O (30 mL) and concentrated under reduced pressure to give an oily product of phenyl azide (**a**). To a solution of **a** in MeOH (30 mL), a solution of 2-propyn-1-ol (2.803 g, 50 mmol) in MeOH (5 mL) and powdered $\text{Cu}^{\text{II}}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (1.250 g, 5 mmol) were added. Hydrazine hydrate (2.503 g, 50 mmol) in MeOH (15 mL) was then added dropwise to the above mixture, and the mixture was stirred at room temperature for 23 hr. The reaction mixture was filtered, and the filtrate was stand in a freezer, during which time the white crystals were precipitated. White blocks were collected by suction filtration. Yield: 5.284 g (60%). mp 114–115 °C (from MeOH) (lit.,² 120–121 °C from CHCl_3), ^1H NMR (600 MHz; CDCl_3 ; Me_4Si): δ 7.99 (s, 1H), 7.73 (d, $J = 7.6$ Hz, 2H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.45 (t, $J = 7.6$ Hz, 1H), 4.90 (d, $J = 4.8$ Hz, 2H). Anal. Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{O}$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.65; H, 5.16; N, 24.03.

Preparation of 1-phenyl-1,2,3-triazole-4-carbaldehyde (**c**)

MnO_2 (90%) (28.984 g, 300 mmol) was added to a solution of **b** (5.258 g, 30 mmol) in acetone (50 mL), and the mixture was stirred at room temperature for 48 h. The reaction mixture was passed through a celite pad and the filtrate was evaporated under reduced

pressure to obtain the white solids. They were collected by suction filtration, washed with H₂O, and dried in vacuo. Yield: 3.931 g (76%). mp 98–99 °C (from acetone) (lit.,³ 96 °C from CHCl₃-Et₂O), ¹H NMR (600 MHz; CDCl₃; Me₄Si): δ 10.24 (s, 1H), 8.53 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.60–7.52 (m, 3H). Anal. Calcd for C₉H₇N₃O: C, 62.42; H, 4.07; N, 24.27. Found: C, 62.25; H, 4.02; N, 24.38.

Preparation of 1-methyl-1,2,3-triazole-4-carbaldehyde (f)

To a solution of **c** (3.471 g, 20 mmol) in MeOH (80 mL) was added an aqueous solution (40%) of methylamine (3.109 g, 40 mmol), and the resulting solution was stirred for 48 hr at room temperature. The resulting solution was evaporated under reduced pressure to obtain the crude yellow solid. Recrystallization was performed from Et₂O. The products were collected by suction filtration, washed with H₂O (50 mL) and then hexane (10 mL), and dried in vacuo. Pale yellow solid of 1-phenyl-1,2,3-triazol-4-yl-methylideneaminomethyl (**d**). Yield: 2.490 g (67%). mp 70–71 °C (from Et₂O) (lit.,^{3,4} 87 °C from Et₂O-petroleum ether), ¹H NMR (600 MHz; CDCl₃; Me₄Si): δ 8.53 (d, *J* = 2.1 Hz, 1H), 8.41 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 3.56 (d, *J* = 2.0 Hz, 3H).

A solution of **d** (2.421 g, 13 mmol) in 1-PrOH (5 mL) was heated at 80 °C for 16 hr. The resulting solution was stand in a freezer, during which time the off-white solids were precipitated. They were collected by suction filtration, washed with 1-PrOH (5 mL), and dried in vacuo. White solid of 1-methyl-1,2,3-triazol-4-yl-methylideneaminophenyl (**e**). Yield: 1.744 g (72%). mp 141–142 °C (from 1-PrOH) (lit.,^{3,4} 154 °C from Et₂O-petroleum ether), ¹H NMR (600 MHz; CDCl₃; Me₄Si): δ 8.67 (s, 1H), 8.13 (s, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.27–7.21 (m, 3H), 4.18 (s, 3H).

Hydrochloric acid (36%) (1.821 g, 18 mmol) was added to a solution of **e** (1.681 g, 9 mmol) in CH₂Cl₂ (20 mL), and the mixture was stirred for 1 h at room temperature. Then, the resulting mixture was filtered to remove the orange-yellow precipitates. The filtrate was further added hydrochloric acid (36%) (0.930 g, 9 mmol), and was stirred for 2 hr at room temperature. The resulting mixture was added H₂O (10 mL), extracted with CH₂Cl₂ (9 × 10 mL), dried (MgSO₄), filtered, and concentrated in vacuo to give a pale yellow solid. The crude product was dissolved in hot water, the solution was filtered, and then, the filtrate was

concentrated. The pure product was collected by suction filtration and dried in vacuo. Yield: 0.873 g (87%). mp 112–113 °C (from H₂O) (lit.,^{3,4} 113 °C from CHCl₃-Et₂O), ¹H NMR (600 MHz; CDCl₃; Me₄Si): δ 10.15 (s, 1H), 8.10 (s, 1H), 4.20 (s, 3H).

Preparation of *N,N'*-bis[(1-methyl-1,2,3-triazol-4-yl)methylene]-propane-1,3-diamine (L^{Me})

The ligand L^{Me} was prepared by mixing 1-methyl-1,2,3-triazole-4-carbaldehyde (0.222 g, 2 mmol) and 1,3-diaminopropane (0.074 g, 1 mmol) in MeOH (20 mL) or CHCl₃ (20 mL) and stirring at ambient temperature for 1.5 h. The ligand solution thus prepared was used for the synthesis of Fe^{II} complex without further purification and isolation.

Preparation of [Fe^{II}L^{Me}(NCS)₂] (Mixture of Polymorphs **1A and **1B**)**

KNCS (0.194 g, 2 mmol) in methanol (7 mL) was added to a solution of Fe^{II}SO₄·7H₂O (0.278 g, 1 mmol) in methanol (7 mL) and the resulting mixture was immediately filtered. The filtrate and the methanolic solution of the ligand L^{Me} (20 mL) were mixed under nitrogen atmosphere, and the resulting mixture was stand for several days at ambient temperature, during which time the precipitated mixture of orange crystals **1A** and dark red-purple block crystals **1B** were collected by suction filtration. Crystals of polymorph **1A** were manually separated from **1B** under the microscope. Yield: 0.150 g as **1A**, 0.288 g as a total of **1A** and **1B** (35% as **1A**, 67% as a total of **1A** and **1B**). Anal. Calcd for [Fe^{II}L^{Me}(NCS)₂] (**1A**) = C₁₃H₁₆N₁₀S₂Fe: C, 36.12; H, 3.73; N, 32.40. Found: C, 36.30; H, 3.73; N, 31.95. IR (KBr): ν_{C=N} 1644 cm⁻¹, ν_{NCS} 2080 (shoulder at 2115) cm⁻¹.

Selective Crystallization of Polymorph **1B**

L-ascorbic acid (0.016 g, 0.09 mmol) in methanol (3 mL) was added to a solution of Fe^{II}SO₄·7H₂O (0.278 g, 1 mmol) in methanol (3 mL) followed by the addition of KNCS (0.194 g, 2 mmol) in methanol (3 mL), and the resulting mixture was stirred at ambient temperature for 6 min. The reaction mixture was filtered, and the filtrate and the CHCl₃ solution of the ligand L^{Me} (20 mL) were mixed under nitrogen atmosphere. The resulting mixture was stand for several days at ambient temperature, during which the precipitated dark red-purple block crystals **1B** were collected by suction filtration. Yield: 0.166 g (38%). Anal. Calcd for

[Fe^{II}L^{Me}(NCS)₂] (**1B**) = C₁₃H₁₆N₁₀S₂Fe: C, 36.12; H, 3.73; N, 32.40. Found: C, 35.96; H, 3.73; N, 32.19. IR (KBr): $\nu_{\text{C=N}}$ 1614 cm⁻¹, ν_{NCS} 2070, 2112 cm⁻¹.

Physical Measurements

Elemental C, H, and N analyses were performed on a J-Science Lab MICRO CORDER JM-10. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on polycrystalline powders deposited on a glass plate, using a Mac Science MXP3V powder diffractometer at Cu K α radiation. IR spectra were recorded at room temperature using a PerkinElmer Spectrum100 FT-IR spectrometer with the samples prepared as KBr disks. ¹H NMR spectra were recorded on a JEOL ECA-600 spectrometer. The melting point was measured through a Yanaco MP-S3 micro melting point meter and was uncorrected. Thermogravimetric data were collected on a TG/DTA6300 (SII Nano Technology Inc.) instrument at a rate of 10 K min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed with a DSC6200 (SII Nano Technology Inc.) over the temperature range of 173–423 K, at a sweep rate of 5 K min⁻¹ under a nitrogen atmosphere using aluminum hermetic pans with an empty pan as reference. Magnetic susceptibility data were collected at Institute for Molecular Science (IMS), Okazaki, Japan. Data in the settle mode were recorded over the temperature range of 200–300 K for **1A** and 300–400 K for **1B** using a Quantum Design MPMS-XL7 SQUID magnetometer under an applied magnetic field of 0.5 T. In the sweep mode magnetic data were collected using a Quantum Design MPMS-7 SQUID magnetometer with the same field at a rate of 1 K min⁻¹. Quartz glass tubes with a small amount of glass wool filler were used as sample containers. Only **1B** was wrapped in an aluminum foil and was then inserted into the quartz glass tube, since **1B** is diamagnetic at room temperature. The calibration was done with palladium metal. Corrections for diamagnetism of the sample were made using Pascal's constants⁵ and a background correction for the sample holder was applied.

Crystallographic Data Collection and Structure Analyses

X-ray diffraction data of polymorphs **1A** and **1B** were collected by a Rigaku AFC7R Mercury CCD diffractometer at IMS using graphite monochromated Mo K α radiation ($\lambda = 0.71075 \text{ \AA}$)

operated at 5 kW power (50 kV, 100 mA). The temperature of the crystal was maintained at the selected value by means of a Rigaku cooling device to within an accuracy of ± 2 K. In polymorph **1A**, first, the diffraction data were collected at 280 K. Following the measurement at 280 K, the crystal was then cooled to 250 K and the subsequent measurements were performed. In polymorph **2B**, the diffraction data were collected at 296 K. Following the measurement at 296 K, the crystal was then warmed to 380 K and the subsequent measurements were performed. The data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by the direct method⁶ and refined on F^2 full-matrix least-squares using SHELXL-2014⁷ with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were fixed in calculated positions and refined by using a riding model. At 380 K, the central six-membered chelate ring of polymorph **1B** was disordered over two possible conformations and the occupancy factors for the possible two positions of C(6) (C6A:C6B = 0.51:0.49) were refined using the tools available from the SHELXL-2014 program package. All calculations were performed by using the Yadokari-XG software package.⁸

Crystallographic data reported in this manuscript have been deposited to Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1428204-1428207. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

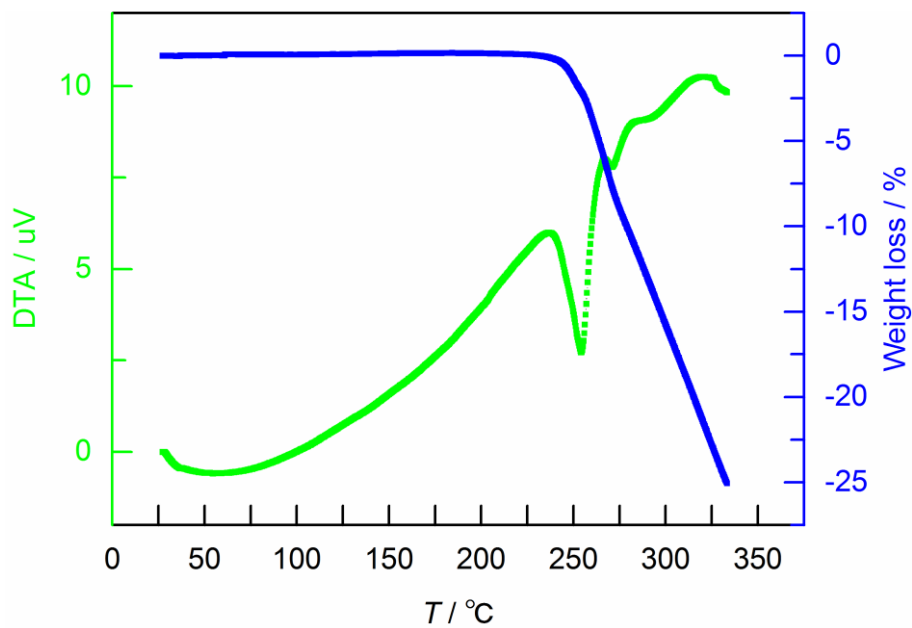


Figure S1. TG/DTA curves of polymorph **1A**.

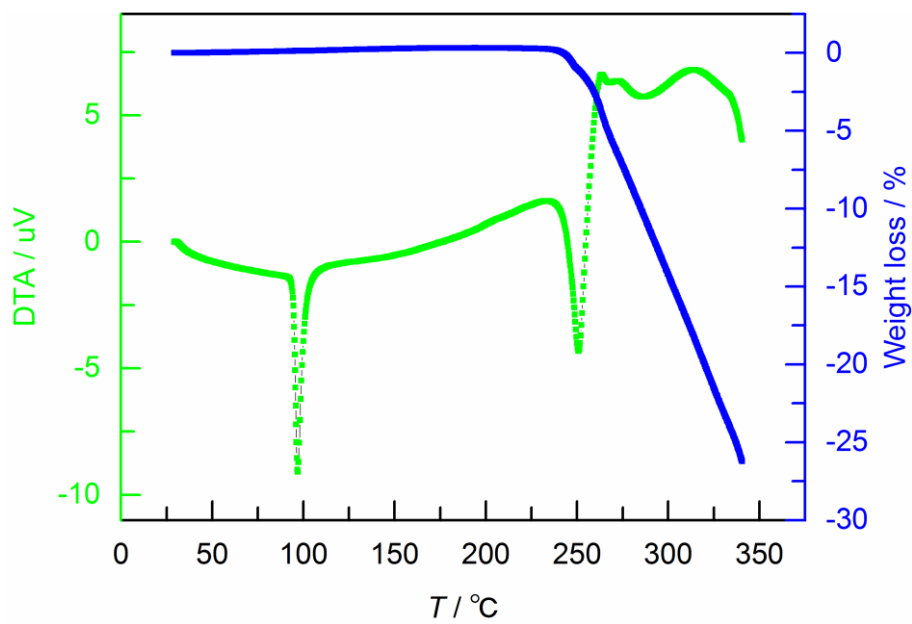


Figure S2. TG/DTA curves of polymorph **1B**.

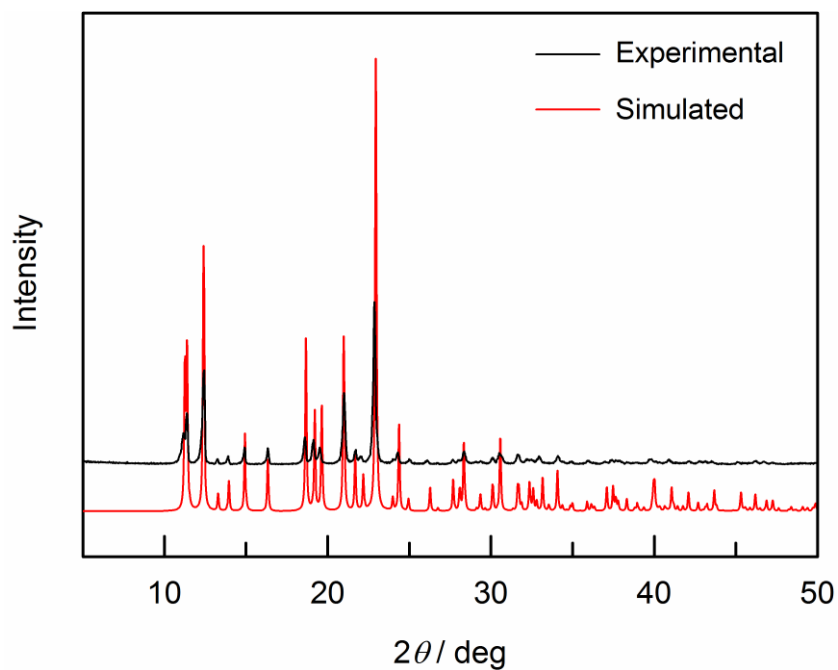


Figure S3. Experimental PXRD pattern of polymorph **1A** at room temperature (black) with the one calculated from the single crystal X-ray data at 280 K (red).

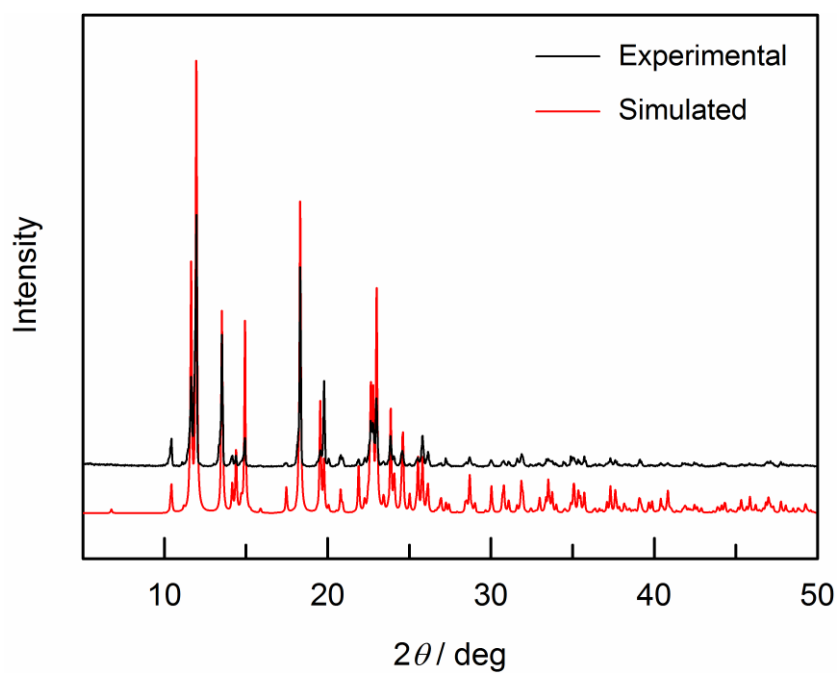


Figure S4. Experimental PXRD pattern of polymorph **1B** at room temperature (black) with the one calculated from the single crystal X-ray data at 296 K (red).

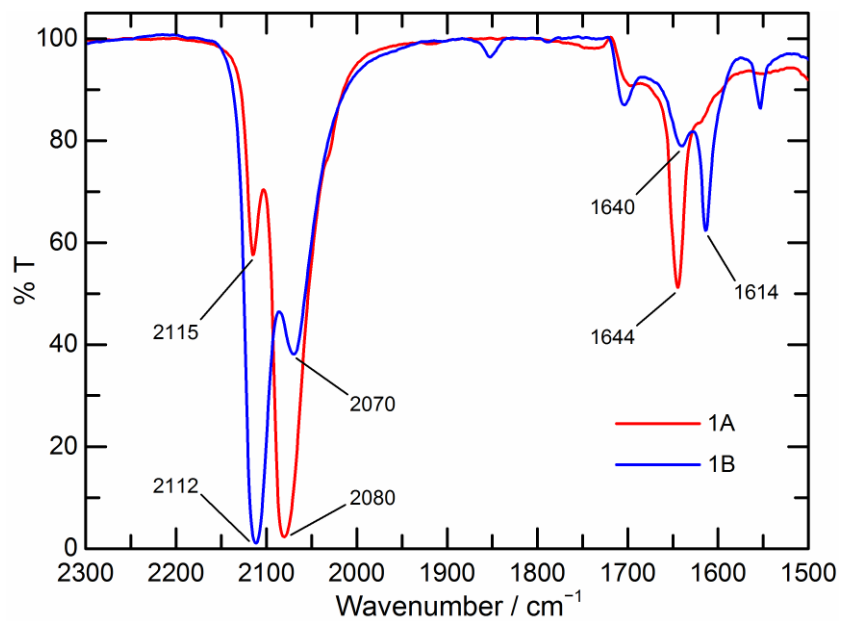


Figure S5. IR spectra (KBr) for polymorphs **1A** (HS, red) and **1B** (LS, blue) at room temperature.

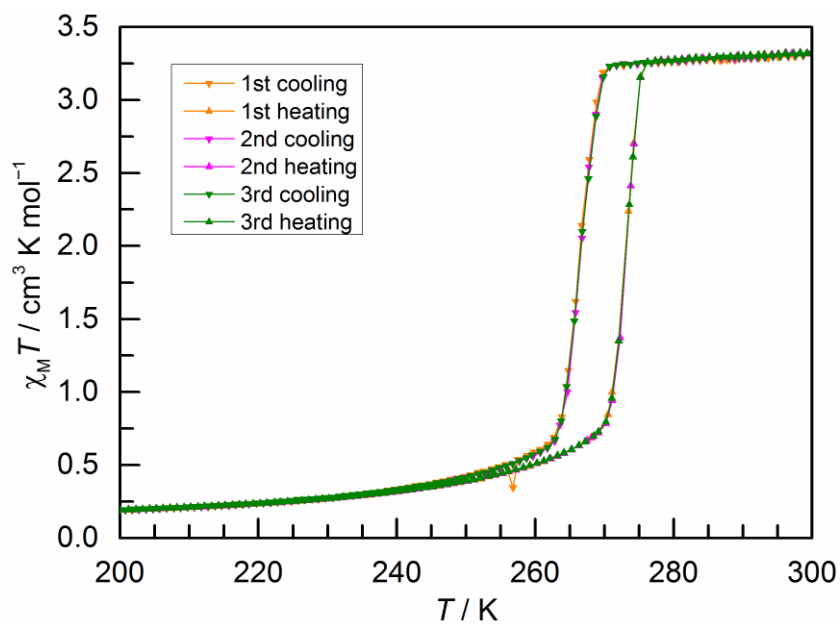


Figure S6. Temperature dependence of the $\chi_M T$ product of polymorph **1A** in the heating (\blacktriangle) and cooling (\blacktriangledown) modes over three successive thermal cycles at a sweep rate of 1 K min^{-1} .

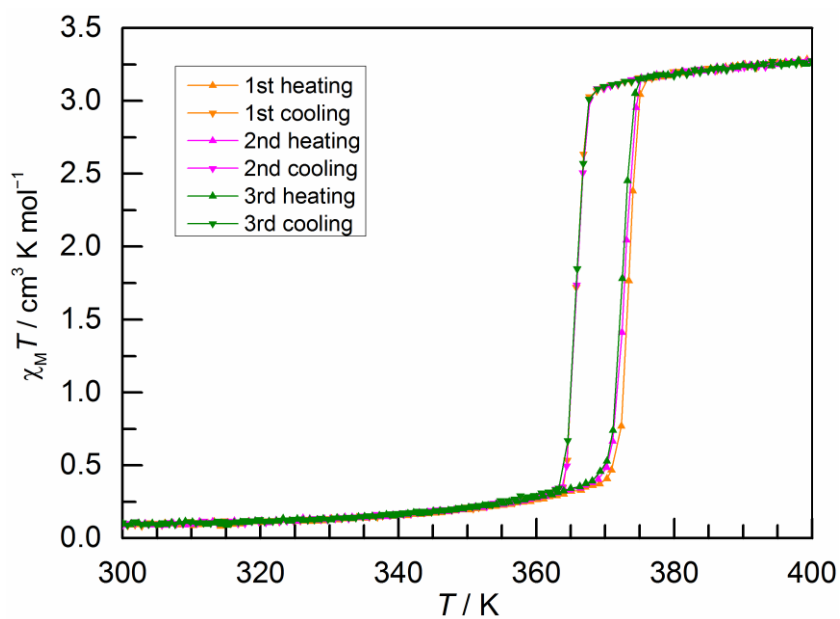


Figure S7. Temperature dependence of the $\chi_M T$ product of polymorph **1B** in the heating (\blacktriangle) and cooling (\blacktriangledown) modes over three successive thermal cycles at a sweep rate of 1 K min^{-1} .

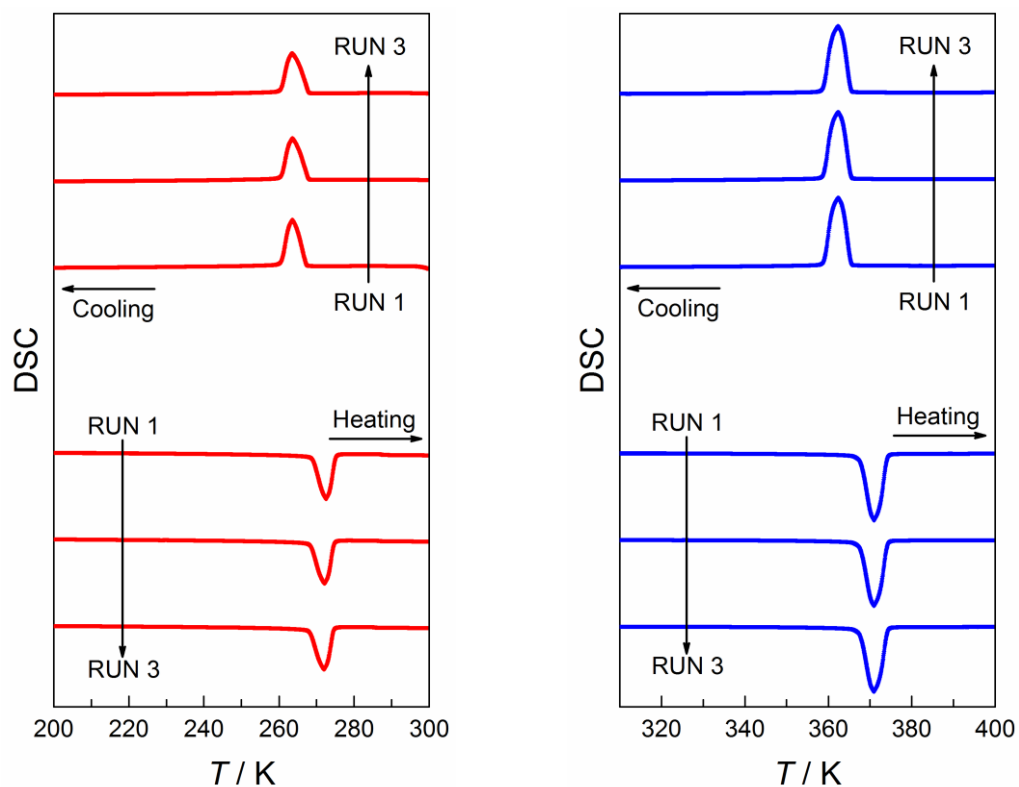


Figure S8. DSC curves of polymorphs **1A** (left, red) and **1B** (right, blue) over three successive thermal cycles at a sweep rate of 5 K min^{-1} , where in the temperature region of the SCO transition.

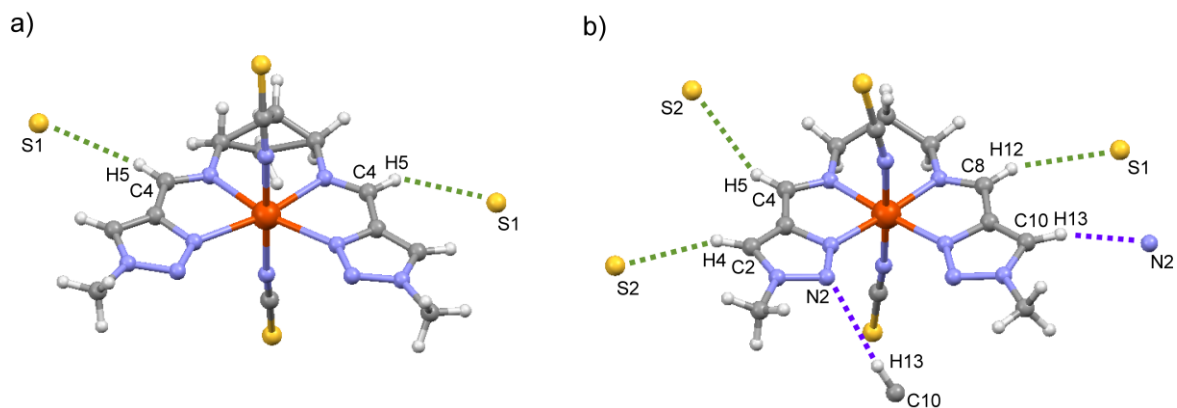


Figure S9. Selected intermolecular interactions related to the triazole and imine CH proton donor of the equatorial ligand L^{Me} of polymorphs **1A** and **1B** at around RT. **1A** at 280 K (a) and **1B** at 296 K (b). Intermolecular CH \cdots S and CH \cdots N hydrogen bonds are indicated as green and purple dotted lines, respectively.

Table S1. X-ray crystallographic data of polymorphs **1A** and **1B**

Complex	Polymorph 1A		Polymorph 1B	
	250 K	280 K	296 K	380 K
Formula	C ₁₃ H ₁₆ N ₁₀ S ₂ Fe			
Formula weight	432.33			
Crystal system	Monoclinic		Monoclinic	
Space group	C2/c (No. 15)		P2 ₁ /n (No. 14)	
<i>a</i> , Å	15.27(3)	16.324(8)	8.1325(5)	8.496(8)
<i>b</i> , Å	9.786(18)	8.928(4)	8.9739(6)	9.275(8)
<i>c</i> , Å	13.27(3)	13.831(7)	26.230(2)	25.99(2)
β , deg	110.53(2)	105.685(6)	93.858(2)	97.228(14)
<i>V</i> , Å ³	1857(6)	1940.6(16)	1909.9(2)	2032(3)
<i>Z</i>	4	4	4	4
<i>T</i> , K	250(2)	280(2)	296(2)	380(2)
<i>d</i> _{calcd} , g cm ⁻³	1.546	1.480	1.504	1.414
μ , mm ⁻¹	1.058	1.012	1.028	0.967
<i>R</i> ₁ ^a (all data)	0.0949	0.0707	0.0562	0.1237
<i>wR</i> ₂ ^b (all data)	0.2260	0.1842	0.1314	0.2474
<i>S</i>	1.092	0.982	1.033	1.072
CCDC number	1428207	1428206	1428205	1428204

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}$.

Table S2. Relevant coordination bond lengths (Å) and angles (°) of polymorphs **1A** and **1B** at different temperatures

Complex Temperature	Polymorph 1A		Polymorph 1B	
	250 K	280 K	296 K	380 K
	Bond Lengths (Å)			
Fe(1)-N(3)	1.979(4)	2.236(3)	1.976(2)	2.207(4)
Fe(1)-N(4)	1.945(5)	2.185(3)	1.960(3)	2.159(5)
Fe(1)-N(5)	1.929(5)	2.087(3)	1.956(3)	2.156(5)
Fe(1)-N(6)			1.968(2)	2.204(5)
Fe(1)-N(9)			1.956(2)	2.098(5)
Fe(1)-N(10)			1.937(2)	2.097(5)
Average Fe-N	1.951	2.169	1.959	2.154
	Bond Angles (°)			
N(3)-Fe-N(4)	80.7(2)	76.56(11)	81.18(11)	76.46(18)
N(3)-Fe-N(5)	91.03(17)	89.01(10)	176.25(10)	166.85(18)
N(3)-Fe-N(6)			101.37(9)	116.04(17)
N(3)-Fe-N(9)			86.89(9)	85.77(18)
N(3)-Fe-N(10)			92.15(9)	90.87(17)
N(4)-Fe-N(5)	88.39(19)	89.43(11)	96.52(13)	90.8(2)
N(4)-Fe-N(6)			176.64(11)	167.44(18)
N(4)-Fe-N(9)			88.14(10)	88.30(19)
N(4)-Fe-N(10)			88.91(10)	91.06(19)
N(5)-Fe-N(6)			80.82(11)	76.69(19)
N(5)-Fe-N(9)			90.09(10)	90.8(2)
N(5)-Fe-N(10)			90.75(10)	92.48(19)
N(6)-Fe-N(9)			89.79(9)	91.40(18)
N(6)-Fe-N(10)			93.18(9)	89.94(17)
N(9)-Fe-N(10)			177.00(10)	176.63(19)
N(3)-Fe-N(3) ⁱ	102.6(2)	117.47(13)		
N(3)-Fe-N(4) ⁱ	176.48(17)	165.97(10)		
N(3)-Fe-N(5) ⁱ	90.33(17)	90.67(11)		
N(4)-Fe-N(4) ⁱ	96.0(3)	89.41(16)		
N(4)-Fe-N(5) ⁱ	90.16(19)	91.00(10)		
N(5)-Fe-N(5) ⁱ	177.8(2)	179.39(15)		
Σ ^a	43.4	61.5	48.3	66.2
Θ ^b	85.2	168.7	82.8	165.3

^a Σ = the sum of |90 – φ| for the 12 *cis* N-Fe-N angles in the octahedral coordination sphere.⁹

^b Θ = the sum of |60 – θ| for the 24 N-Fe-N angles describing the trigonal twist angles.¹⁰

Symmetry operation for **1A**: (i), –x, y, –z + 1/2.

Table S3. Possible hydrogen bonding interactions (Å, °) for polymorphs **1A** and **1B** at different temperatures

Complex	Temp.	C-H...X	$d(\text{C-H})^a$	$d(\text{H}\cdots\text{X})$	$d(\text{C}\cdots\text{X})$	$\angle(\text{C-H}\cdots\text{X})$
Polymorph 1A	250 K	C(1)-H(2)···S(1) ^{vi}	1.08	3.01	3.983(11)	149
		C(1)-H(3)···S(1) ^{iv}	1.08	2.81	3.599(10)	130
		C(2)-H(4)···S(1) ^{vi}	1.08	2.69	3.627(10)	145
		C(4)-H(5)···S(1) ^v	1.08	2.61	3.658(10)	162
		C(5)-H(7)···S(1) ⁱⁱⁱ	1.08	3.00	3.905(13)	141
		C(6)-H(8)···S(1) ⁱⁱ	1.08	3.08	3.699(18)	117
	280 K	C(1)-H(2)···S(1) ^{vi}	1.08	2.68	3.685(5)	155
		C(1)-H(3)···S(1) ^{iv}	1.08	2.98	3.813(5)	134
		C(4)-H(5)···S(1) ^v	1.08	2.83	3.746(4)	142
		C(5)-H(7)···S(1) ⁱⁱⁱ	1.08	2.82	3.835(5)	156
C(6)-H(8)···S(1) ⁱⁱ		1.08	2.99	3.646(7)	119	
Polymorph 1B	296 K	C(1)-H(2)···S(1) ⁱⁱ	1.08	2.94	3.660(5)	124
		C(2)-H(4)···S(2) ⁱ	1.08	2.86	3.807(4)	146
		C(4)-H(5)···S(2) ^{vii}	1.08	2.85	3.858(4)	155
		C(7)-H(10)···S(2) ^{iv}	1.08	2.87	3.732(5)	137
		C(7)-H(11)···S(2) ^{viii}	1.08	2.70	3.579(5)	138
		C(8)-H(12)···S(1) ⁱⁱⁱ	1.08	2.81	3.760(4)	146
		C(11)-H(15)···S(1) ^v	1.08	2.76	3.823(5)	167
		C(10)-H(13)···N(2) ^{vi}	1.08	2.71	3.603(4)	139
	380 K	C(2)-H(4)···S(2) ⁱ	1.08	2.80	3.747(8)	146
		C(4)-H(5)···S(2) ^{vii}	1.08	2.99	4.005(9)	157
		C(5)-H(6A)···S(2) ^{vii}	1.08	3.04	4.070(10)	158
		C(6A)-H(9A)···S(1) ^{ix}	1.08	2.89	3.845(16)	147
		C(7)-H(10A)···S(2) ^{iv}	1.08	2.80	3.747(9)	146
		C(7)-H(11A)···S(2) ^{viii}	1.08	2.83	3.738(10)	141
		C(8)-H(12)···S(1) ⁱⁱⁱ	1.08	2.92	3.832(7)	142
		C(10)-H(13)···S(1) ⁱⁱⁱ	1.08	3.01	3.846(8)	135
		C(11)-H(15)···S(1) ^v	1.08	2.89	3.748(9)	136
		C(11)-H(14)···N(2) ^{vi}	1.08	2.70	3.525(11)	133

^a The C–H bond lengths are normalized to 1.08 Å by the program PLATON.¹¹

Symmetry operations for **1A**: (ii), $-1/2 + x, 1/2 + y, z$; (iii), $1/2 - x, 1/2 + y, 1/2 - z$. (iv), $1/2 - x, -1/2 + y, 1/2 - z$; (v), $x, -y, 1/2 + z$; (vi), $1/2 - x, 1/2 - y, -z$.

Symmetry operations for **1B**: (i), $1 + x, y, z$; (ii), $x, 1 + y, z$; (iii), $-1 + x, y, z$; (iv), $x, -1 + y, z$; (v), $1/2 - x, 1/2 + y, 1/2 - z$; (vi), $1/2 - x, -1/2 + y, 1/2 - z$; (vii), $-x, -y, -z - 1$; (viii), $-x - 1, -y, -z - 1$; (ix), $-x, -y - 1, -z - 1$.

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