Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Observation of Proton-Transfer-Coupled Spin Transition by Single-Crystal Neutron-Diffraction Measurement

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Materials and Methods

Materials

All reagents and solvents used in this study were purchased from TCI Co., Ltd., Wako Pure Chemical Industries Ltd., Alfa Aesar., and Sigma-Aldrich Chemical Co., and used without further purification. The ligand *N'*-(di(pyridin-2-yl)methylene)-3-methoxybenzohydrazide (HL-3OMe) was synthesized according to the previous report [S1].

Synthesis of $[Fe(HL\text{-}3OMe)_2](HFDF)_2$ (**[3OMe]**) (HFDF = 1,1,2,2,3,3-Hexafluoropropane-1,3-disulfonimide).

HL-3OMe (266 mg, 0.8 mmol) and $FeCl_2 \cdot 4H_2O$ (79 mg, 0.4 mmol) were dissolved in ethanol (15 ml) in a glass bottle under a N_2 atmosphere. LiHFDF (240 mg, 0.8 mmol) was added to the ethanol solution containing HL-3OMe and $FeCl_2 \cdot 4H_2O$ at about 45 ºC. The resultant solution was capped tightly under N_2 atmosphere and kept in oven at 45 ºC. Large black crystals of **[3OMe]** were obtained under a slow crystallization. (296 mg, 23%). $C_{44}H_{32}F_{12}FeN_{10}O_{12}S_4$ (1304.86); calcd. C 40.50, H 2.47, N 10.73; found C 40.68, H 2.50, N 10.78.

Magnetic property measurement

Magnetic susceptibility measurement for **[3OMe]** was conducted on a Quantum Design MPMS-5S superconducting quantum-interference device magnetometer under a 5-kOe field. The temperature sweeping rate in the measurement of single-crystal and polycrystalline sample was 3 K and 1 K min^{-1}, respectively. The measurement samples were prepared by encapsulating each crystalline compound into a gelatin capsule.

Differential scanning calorimetry (DSC)

DSC measurement was conducted on a SII Nanotechnology DSC6220 with a heating rate of 5 K min^{-1}. The measurement sample was prepared by putting into aluminum pan.

IR spectroscopy

The IR spectra of **[3OMe]** at 300 and 120 K were recorded using an FT-IR spectrophotometer (FT/IR-660 plus, Jasco) equipped with a helium-flow-type refrigerator (Helitran LT-3–110). Samples were prepared by depositing ground-powdered samples onto the CaF_2 plates.

Single-crystal X-ray structure measurement

All single crystals for the X-ray measurements were coated with oil base cryoprotectant and mounted on nylon loops. Diffraction data were collected at 363 and 123 K under a nitrogen gas stream, respectively, on a Rigaku CCD or an HPC X-ray diffractometer, using multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected using a 0.5° oscillation angle. Bragg spots were integrated using the CrysAlis^{Pro} program package, and the empirical absorption correction (multi-scan) was applied using the SCALE3 ABSPACK program. Structures were solved by direct methods (SHELX-S ver. 2013/1 and SHELXT Version 2014/4) and refined by full-matrix least-squares (SHELXL Version 2018/1). The hydrogen atoms that coordinated with carbon atoms in all crystal structures and those that coordinated with nitrogen atoms in the crystal structure at 363 K were placed at the calculated positions, and the riding models were refined and reapplied. The hydrogen atoms that coordinated with nitrogen atoms in the crystal structure at 123 K were placed on the basis of the Fourier map differences.

CCDC 2174214 (363 K) and 2174215 (123 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Single-crystal neutron diffraction

Single-crystal neutron diffraction data were collected using the single-crystal diffractometer SENJU at the beamline BL18 of the Materials and Life-Science Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC), using the wavelength-resolved timeof-flight Laue diffraction method for wavelength ranging from 0.4 to 4.4 Å[S2]. A single crystal of **[3OMe]** (4.5 x 3.5 x 3.5 mm^3) was mounted on an aluminum pin and attached to a closed-cycle helium cryostat. Then, diffraction data were acquired at 130 K under vacuum conditions. After the measurment at 130 K, the sample was re-mounted on a goniometer with a heater, and warmed up to 350 K. Since the original crystal broke during the transition from the LT to the HT phase, the diffraction measurement at 350 K was performed using a piece of the original crystal (2.5 x 2.0 x 1.5 mm^3). Intensities of Bragg peaks were collected using 37 two-dimensional scintillation detectors to cover a wide area of reciprocal lattice space, and with 20 crystal orientations at 130 K and 22 orientations at 350 K, respectively. The exposure time for one crystal orientation was 2 hours at 130 K and 5 hours at 350 K, respectively. The accelerator power was 500 kW. Data reduction was performed using the STARGazer to obtain hkl indexes and the corresponding integrated intensities of reflections corrected for the detector efficiency, Lorentz factor, and scaling factor for

each crystal orientation[S3]. A least-squares refinement was performed using SHELXL with all reflections. Atomic coordinates resulting from X-ray crystal structure analyses at 130K and 350 K were used as initial structural models. All hydrogen atoms were determined using the nuclear difference Fourier map of the neutron data and refined anisotropically.

CCDC 2174216 (350 K) and 2174217 (130 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculation

All energy calculations for the complexes (^{HS}**[3OMe]**$_{Hyd}$, ^{HS}**[3OMe]**$_{Py}$, ^{LS}**[3OMe]**$_{Hyd}$, and ^{LS}**[3OMe]**$_{Py}$) in the singlet and quintet spin states were carried out using restricted and unrestricted B3LYP* functionals combined with the 6-311+G** basis set implemented in the Gaussian 16 package [S4]. The B3LYP* functional, developed by Reiher and co-workers [S5], is a reparametrized version of the B3LYP functional with 15% Hartree–Fock exchange instead of 20% in the original B3LYP functional [S6]. The B3LYP* functional was specifically developed to provide the best performance for accurate spin-state splitting while the original B3LYP functional results in the overestimation of HS stability. For comparison with the experimental results, the calculated vibrational frequencies were rescaled by the factor of 0.98 and represented with a Gaussian IR peak half-width at half height of 4 cm^{-1}. The intensity of each vibration modes are given by calculating the corresponding oscillator strength.

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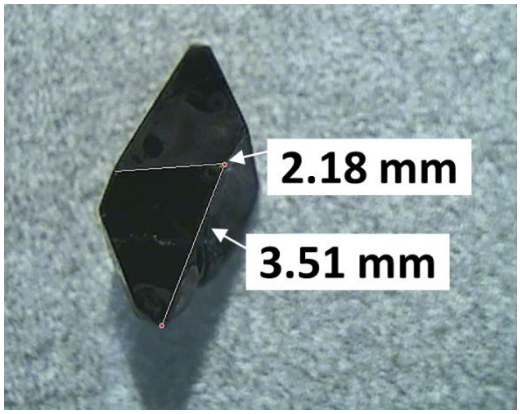

Figure S1. Size of the crystal viewed from the side.

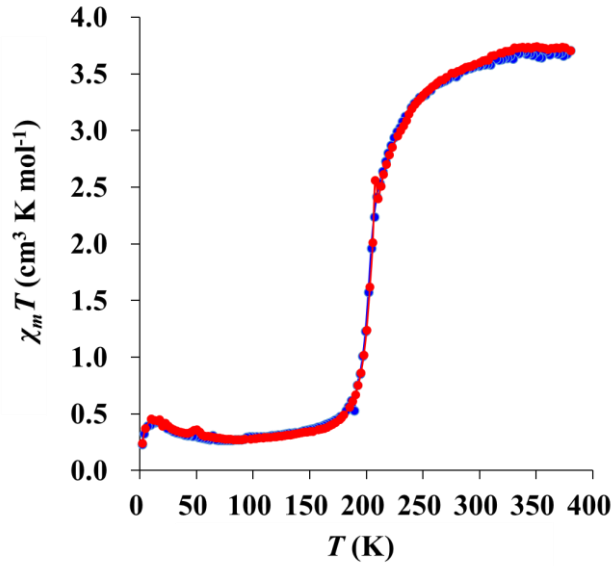

Figure S2. The $\chi_m T$-T plot of the **[3OMe]** single-crystal. The red and blue curves were obtained in the heating and cooling processes, respectively. The $\chi_m T$ values at 350 and 100 K were 3.73 and 0.28 cm^3 K mol^{-1}, respectively. The relatively larger $\chi_m T$ value in the entire temperature range compared with the measured value of the polycrystalline sample was likely due to magnetic anisotropy. The measured $\chi_m T$ values of LT phase divided by HT phase for the single-crystal was 7.5%, which is similar to the polycrystalline sample. Based on these results, it is considered that the ratio of residual HS state in the LT phase is almost the same in both single-crystal and polycrystalline samples.

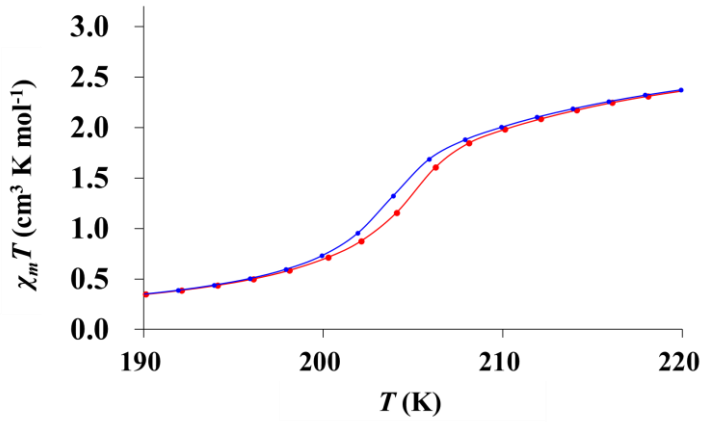

Figure S3. Enlarged view of the $\chi_m T$-T plot of the **[3OMe]** polycrystalline sample. The blue and red line represent the cooling and heating process, respectively.

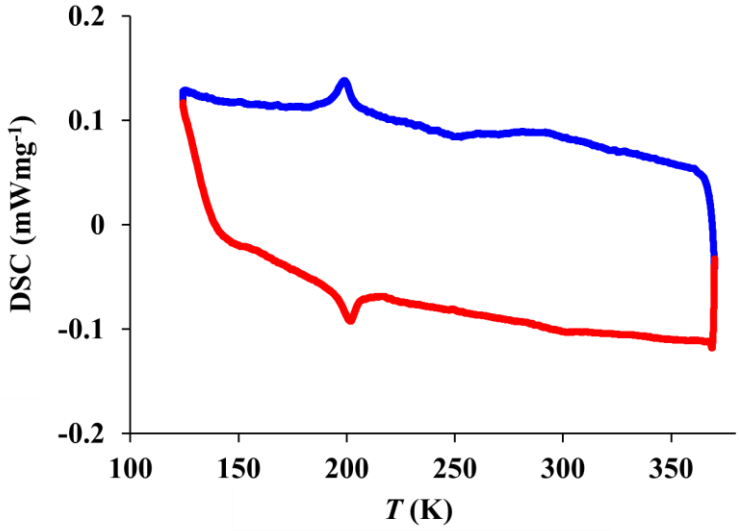

Figure S4. DSC curve of **[3OMe]**. The blue and red line represent the cooling and heating process.

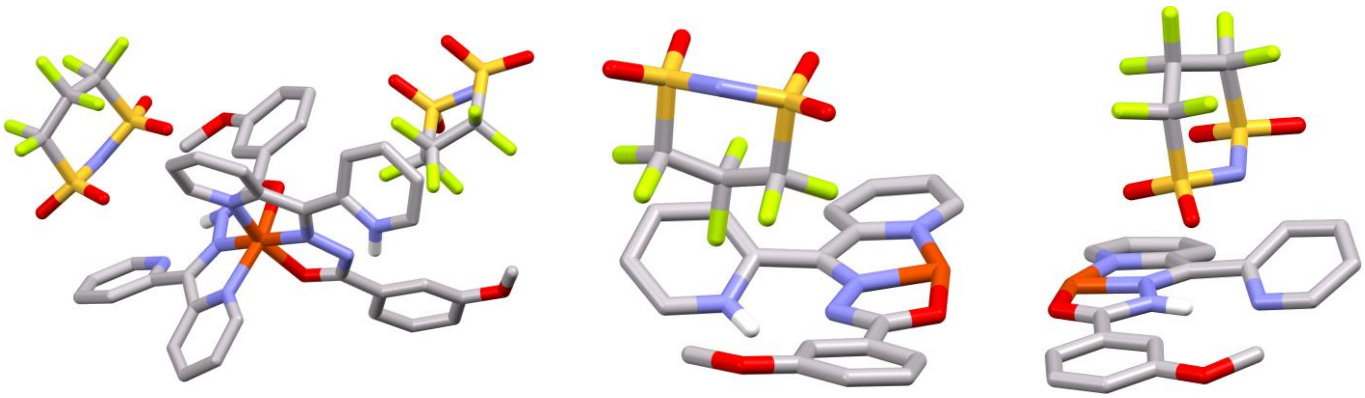

Figure S5. Overview of the orientation of HFDF anion around the Fe(II) complex in LT phase (left). The orientation of HFDF anion above the ligand that exhibits proton transfer (middle). The orientation of HFDF anion above the ligand that is unable to exhibit proton transfer (right).

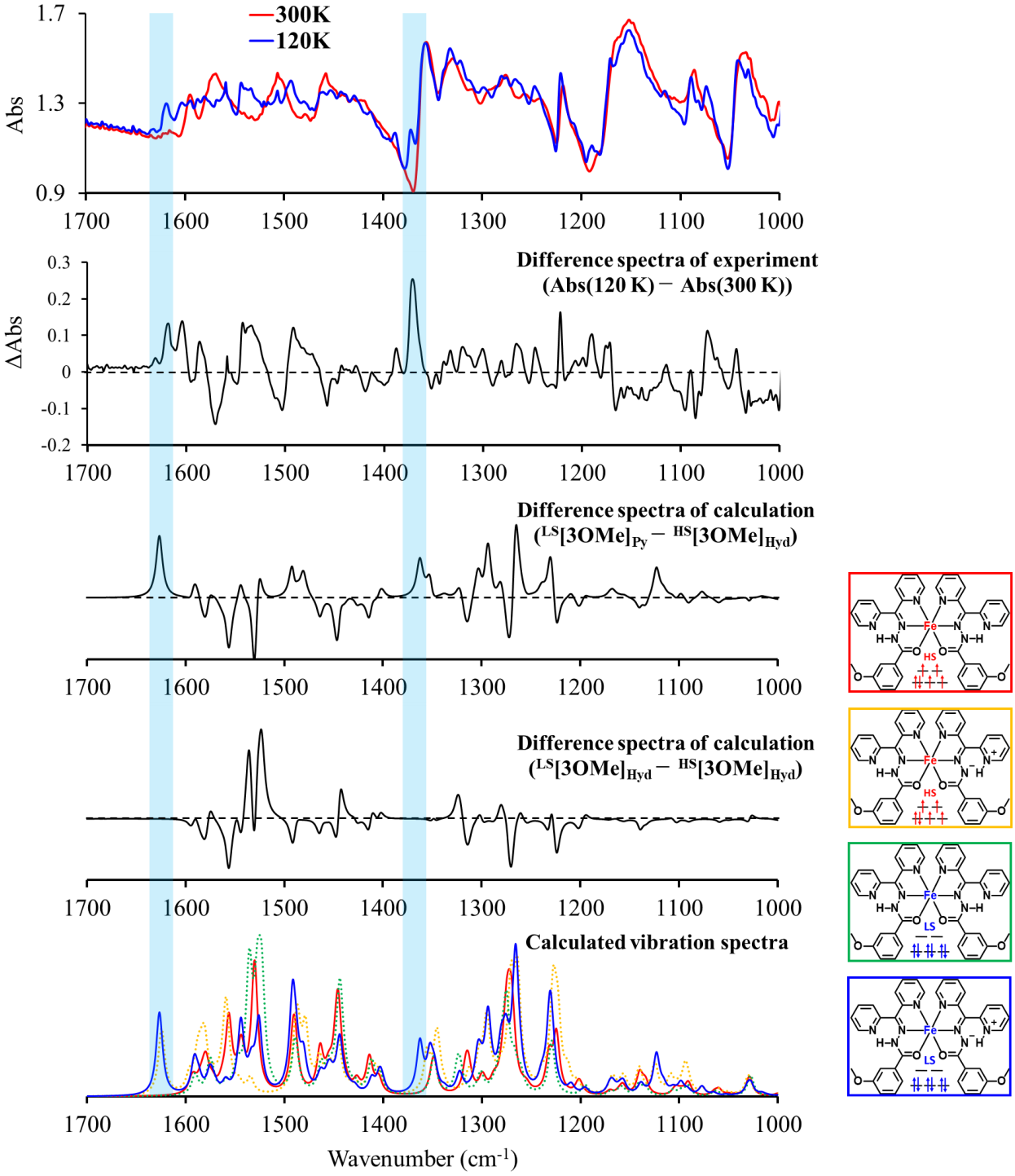

Figure S6. Variable temperature IR spectra, difference spectrum of 123 and 300 K ($Abs_{(123\ K)} - Abs_{(300\ K)}$), simulated vibration spectra of four states (^{HS}**[3OMe]**$_{Hyd}$, ^{HS}**[3OMe]**$_{Py}$, ^{LS}**[3OMe]**$_{Hyd}$, and ^{LS}**[3OMe]**$_{Py}$) by DFT calculations at a scaling factor of 0.98, and difference spectrum of calculated results. The peak around 1620 cm^{-1} is originated from the bending vibration of protonated pyridine ring (N_{Py}—H^+). The peak around 1370 cm^{-1} is originated from in-plane N_{Py}–H and C–H bending vibrations in the protonated pyridine ring coupled with the C–N_{Hyd} stretching and C–N_{Hyd} bending vibrations in the deprotonated hydrazone moiety.

In previous studies on PCST complexes, the peaks around 1620 and 1370 cm^{-1} appeared with proton transfer from N_{Hyd} to N_{Py}, and these peaks were not found only with spin transition.[S1] The difference spectra of calculated results for ^{LS}[3OMe]$_{Py}$ and ^{HS}[3OMe]$_{Hyd}$ (PCST process) showed the appearance of the same characteristic peaks, which were not found in the difference spectra of calculated results for ^{LS}[3OMe]$_{Hyd}$ and ^{HS}[3OMe]$_{Hyd}$ (spin transition process). The experimental spectrum of **[3OMe]** showed peaks at around these frequency regions with cooling. These results suggest clearly the occurrence of proton transfer from N_{Hyd} to N_{Py} with spin transition from HS to LS states.

Figure S7. Size of the crystal used for the single-crystal neutron diffraction measurement at 350 K.

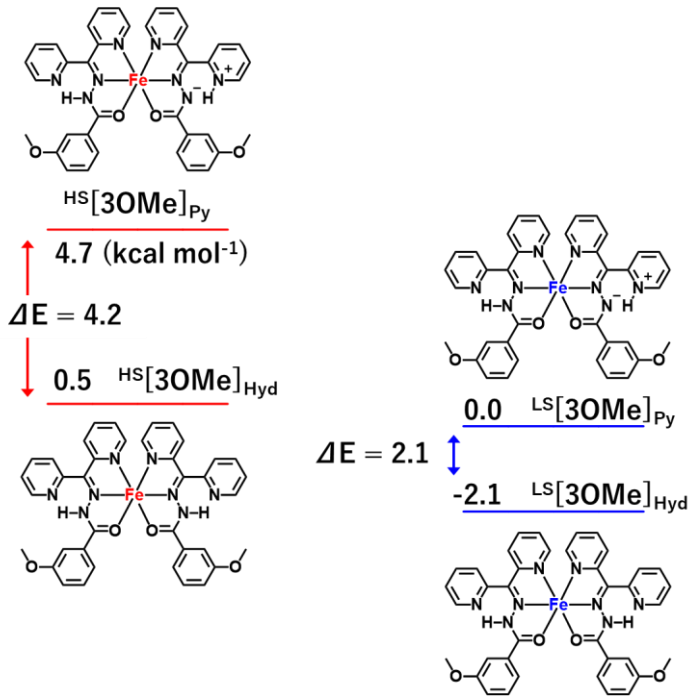

Figure S8. Computed energy diagram of four states (^{HS}**[3OMe]**$_{Hyd}$, ^{HS}**[3OMe]**$_{Py}$, ^{LS}**[3OMe]**$_{Hyd}$ and ^{LS}**[3OMe]**$_{Py}$) by the DFT calculation. The units are in kcal mol^{-1}.

The DFT calculations showed that ^{HS}**[3OMe]**$_{Hyd}$ was more stable than ^{HS}**[3OMe]**$_{Py}$ by 4.2 kcal mol^{-1}, and in good agreement with the experimental observations. The calculated energy difference between ^{LS}**[3OMe]**$_{Hyd}$ and ^{LS}**[3OMe]**$_{Py}$ was decreased compared with the case in HS states, but the magnitude correlation was not consistent with the experimental results. ^{LS}**[3OMe]**$_{Hyd}$ was more energetically favorable than ^{LS}**[3OMe]**$_{Py}$ in the present calculation models and this tendency has also been confirmed in the reported PCST complexes.[S1] This inconsistency between the experimental and DFT calculation results occurred because the isolated molecule was calculated without considering the intermolecular interactions.

Table S1. Crystallographic parameters for the X-ray and neutron crystal structures of **[3OMe]**.

	Neutron		X-ray	
Data	LT phase	HT phase	LT phase	HT phase
Temperature (K)	130	350	123	363
Empirical formula	$C_{44}H_{32}F_{12}Fe$ $N_{10}O_{12}S_4$	$C_{44}H_{32}F_{12}Fe$ $N_{10}O_{12}S_4$	$C_{44}H_{32}F_{12}Fe$ $N_{10}O_{12}S_4$	$C_{44}H_{32}F_{12}Fe$ $N_{10}O_{12}S_4$
Formula weight	1304.88	1304.88	1304.88	1304.88
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	17.090(3)	17.84431(5)	17.0591(6)	17.9201(10)
b/Å	17.886(2)	18.07445(13)	17.8559(4)	18.1588(7)
c/Å	18.179(3)	18.68645(7)	18.1668(7)	18.7085(11)
α/°	90	90	90	90
β/°	117.147(10)	119.1357(2)	117.356(5)	119.419(8)
γ/°	90	90	90	90
Volume/Å^3	4944.7(14)	5264.28(5)	4914.9(3)	5302.9(6)
Z	4	4	4	4
ρ_{calc}g/cm^3	1.753	1.646	1.763	1.634
μ/mm^{-1}	1.594	1.497	0.598	0.554
F(000)	2640	2640	2640.0	2640.0
Radiation	Neutrons (λ = 1.000)	Neutrons (λ = 1.000)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.946 to 101.61	6.964 to 64.322	5.004 to 50.7	4.358 to 50.75
Index ranges	-25 ≤ h ≤ 26, -26 ≤ k ≤ 27, -27 ≤ l ≤ 27	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19	-20 ≤ h ≤ 20, -20 ≤ k ≤ 21, -20 ≤ l ≤ 21	-21 ≤ h ≤ 20 -17 ≤ k ≤ 21, -20 ≤ l ≤ 22
Reflections collected	64073	26221	23307	43985
Independent reflections	17488 [R_{int} = 0.1917, R_{sigma} = 0.1602]	6210 [R_{int} = 0.3045, R_{sigma} = 0.2193]	8807 [R_{int} = 0.0161, R_{sigma} = 0.0187]	9705 [R_{int} = 0.0212, R_{sigma} = 0.0193]
Data/restraints /parameters	17488/0/1036	6210/0/1238	8807/0/750	9705/1081/1040
Goodness-of-fit on F^2	1.053	1.151	1.032	1.745
Final R indexes [I>=2σ (I)]	R_1 = 0.0654 wR_2 = 0.1259	R_1 = 0.1206 wR_2 = 0.2902	R_1 = 0.0429 wR_2 = 0.1141	R_1 = 0.1478, wR_2 = 0.4104
Final R indexes [all data]	R_1 = 0.1400, wR_2 = 0.1466	R_1 = 0.2435, wR_2 = 0.3493	R_1 = 0.0462, wR_2 = 0.1166	R_1 = 0.1753, wR_2 = 0.4351

Table S2. Coordination distances, angles, and intramolecular hydrogen bond distances of **[3OMe]** obtained from single-crystal X-ray at 363 and 123 K and neutron diffraction measurement at 350 K and 130 K, and ^{LS}**[3OMe]**$_{Py}$ and ^{HS}**[3OMe]**$_{Hy}$ obtained from DFT calculations.

	Calculation		Neutron		X-ray	
Phase	—	—	LT phase	HT phase	LT phase	HT phase
Temperature (K)	—	—	130	350	123	363
Abbreviation	^{LS}[3OMe]$_{Py}$	^{HS}[3OMe]$_{Hy}$	^{LS}[LT]$_{Py}$	^{HS}[HT]$_{Hy}$	^{LS}[LT]$_{Py}$	^{HS}[HT]$_{Hy}$
Spin State	LS	HS	LS	HS	LS	HS
Fe1–N1	1.983	2.199	1.965(1)	2.146(8)	1.965(2)	2.153(6)
Fe1–N2	1.879	2.157	1.864(1)	2.113(5)	1.865(2)	2.113(4)
Fe1–O1	1.969	2.091	1.950(2)	2.09(1)	1.951(2)	2.082(4)
Fe1–N5	1.981	2.218	1.978(2)	2.165(7)	1.980(3)	2.167(6)
Fe1–N6	1.894	2.161	1.876(1)	2.094(5)	1.868(2)	2.086(4)
Fe1–O2	2.000	2.158	2.044(3)	2.13(1)	2.007(2)	2.126(7)
(Fe—N)$_{avg}$	1.934	2.183	1.921	2.129	1.920	2.130
(Fe—O)$_{avg}$	1.985	2.124	1.997	2.11	1.979	2.104
C7–N4–C11	124.0	118.7	123.9(1)	118.8(8)	123.6(3)	116.5(9)
C25–N8–C29	118.9	118.7	119.1(2)	124.3(9)	119.1(3)	116(1)
N2–N3–C12	109.7	115.0	108.0(1)	114.5(5)	107.5(2)	114.0(5)
N6–N7–C30	114.0	115.8	113.8(1)	115.1(5)	113.5(2)	113.6(6)
N3・・N4	2.582	2.681	2.690(2)	2.735(8)	2.681(3)	2.714(8)
N3・・H1	1.696	1.029	1.978(5)	1.01(2)	2.03(5)	—
N4・・H1	1.052	1.902	1.032(4)	1.99(2)	0.89(5)	—
N7・・N8	2.668	2.682	2.609(2)	2.665(7)	2.601(3)	2.655(9)
N7・・H2	1.033	1.029	1.042(3)	1.08(2)	0.82(5)	—
N8・・H2	1.876	1.906	1.785(5)	1.88(2)	1.86(5)	—

Table S3. Optimized coordinates for ^{HS}**[3OMe]**$_{Hyd}$, ^{HS}**[3OMe]**$_{Py}$, ^{LS}**[3OMe]**$_{Hyd}$, and ^{LS}**[3OMe]**$_{Py}$.

^{HS}**[3OMe]**$_{Hyd}$

Fe	-0.02299400	-0.73796500	0.27503500
O	0.96220700	-0.28978500	-1.51433300
O	-0.70442900	1.25702800	0.73680400
N	-2.10324800	-0.63371600	-0.30213100
N	-0.64559400	-2.79306600	-0.28039900
N	2.06961200	-0.52245800	0.75063100
O	6.16457200	1.74614300	-3.85849400
N	0.22210100	-1.24774300	2.40029100
N	-2.68076300	0.57647300	-0.12945800
H	-3.58484600	0.71912100	-0.59872900
N	4.81307900	-0.12818800	1.52699700
O	-5.54904200	4.87145900	0.57780700
N	2.83167000	-0.08055200	-0.27866400
H	3.84440200	-0.02399700	-0.10613800
C	-2.74563600	-1.68740000	-0.71876600
C	-1.85474400	-2.87307200	-0.89482500
N	-4.76324000	-0.55695100	-1.38318200
C	-1.86586400	1.56194300	0.39633500
C	4.25170800	0.88970600	-2.61509900
H	4.74266400	1.03998700	-1.66132300
C	0.21468500	-3.81039000	-0.40593100
H	1.16050200	-3.70668600	0.11837500
C	-0.74147400	-1.76955600	3.17048000
H	-1.73187100	-1.82810800	2.72768200
C	1.78818200	-1.62753600	4.17977100
H	2.80759600	-1.60605400	4.54310700
C	2.18647300	-0.00822000	-1.48853200
C	1.47947400	-1.13926300	2.90636900
C	2.48892700	-0.55626300	1.98461100
C	3.81263800	-0.05519600	2.43366500
C	-4.97147100	-2.88256000	-0.80496900
H	-4.52167400	-3.79474900	-0.43174300
C	-0.05738200	-4.94751000	-1.16588600
H	0.67456200	-5.74452700	-1.23469300
C	2.93517800	0.38359200	-2.68427100
C	-4.20438800	-1.72516800	-0.99539300
C	-2.18268800	-3.96483200	-1.70024800
H	-3.12024500	-3.98899300	-2.24075700
C	-1.27157800	-5.01334700	-1.83727400
H	-1.51250700	-5.86440000	-2.46624400
C	2.96869300	0.58597900	-5.08869800
H	2.48159200	0.47183700	-6.05151100
C	-2.41114800	2.91790500	0.53139500
C	4.91334500	1.24088400	-3.79278900
C	-0.51698500	-2.22983800	4.46505100
H	-1.33572600	-2.63709900	5.04769500
C	6.02834700	0.30092600	1.87805200
H	6.80718800	0.20460800	1.12603800
C	4.26322100	1.08025800	-5.03145100
H	4.80147600	1.36056600	-5.93120200
C	2.29196600	0.23924700	-3.92041800
H	1.27969500	-0.14455100	-3.95340600
C	-3.79655500	3.18063300	0.46850400
H	-4.51109700	2.37316400	0.36347300
C	4.00133600	0.52527500	3.69501800
H	3.17334700	0.64255700	4.38361100
C	0.77865300	-2.17496100	4.96826500
H	1.00669700	-2.55851100	5.95751600
C	6.90313700	1.95416800	-2.65520800

H	7.86304200	2.36405400	-2.96690900
H	7.06743600	1.00709700	-2.12591100
H	6.39643900	2.67325700	-1.99984300
C	-1.49672400	3.95975500	0.72831300
H	-0.43768900	3.73752400	0.77723600
C	6.31088900	0.85291000	3.12846900
H	7.31621700	1.18452300	3.36466100
C	-4.25119700	4.49430700	0.60017600
C	-6.89713200	-1.64897500	-1.53395000
H	-7.95271400	-1.57619500	-1.77262800
C	-6.33814500	-2.83694100	-1.07504300
H	-6.95347700	-3.71892200	-0.92834000
C	-1.96470700	5.26796100	0.84323700
H	-1.26363600	6.08411600	0.98393200
C	5.26981600	0.98755200	4.04092700
H	5.43762900	1.44741000	5.00964800
C	-6.06931700	-0.53171000	-1.65964100
H	-6.47173500	0.42253300	-1.98958100
C	-3.32380800	5.53755200	0.78060400
H	-3.70438100	6.54937700	0.87620700
C	-6.56493700	3.88376900	0.41172500
H	-6.54750900	3.15594200	1.23228200
H	-6.46100200	3.37054400	-0.55267100
H	-7.50907200	4.42682100	0.43094600

^{HS}[3OMe]$_{Py}$

Fe	0.03844100	-0.36837800	0.61874100
O	1.06398800	-1.06857700	-0.99814800
O	-0.76447900	1.44147000	-0.29704600
N	-2.01879400	-0.78077100	0.12199000
N	-0.42988800	-2.38228300	1.45355600
N	2.07188200	0.25100200	0.86513100
O	6.58019400	-1.88794100	-3.30435100
N	0.13882100	0.61182100	2.56982500
N	-2.67613900	0.23573800	-0.48001600
H	-3.57327800	-0.00401100	-0.92274800
N	4.44285900	1.81055300	0.81856800
O	-5.87027700	3.85678800	-2.43739300
N	2.91088900	-0.00238200	-0.14519900
C	-2.57904400	-1.90994100	0.44970400
C	-1.61110500	-2.89529000	1.02133200
N	-4.64533900	-1.56624900	-0.73612100
C	-1.93824800	1.38337800	-0.71183500
C	4.50776900	-1.29746000	-2.16146700
H	5.01351100	-0.96284000	-1.26531500
C	0.49330900	-3.21070400	1.95490000
H	1.41534900	-2.74927300	2.29641400
C	-0.83247000	0.56152800	3.49412300
H	-1.78104300	0.14370500	3.16870500
C	1.60515800	1.54018400	4.22171600
H	2.59698500	1.85904100	4.51654200
C	2.29845900	-0.78762700	-1.08859700
C	1.34890200	1.13298800	2.90584500
C	2.35490100	1.12853100	1.81937600
C	3.48141500	2.05682600	1.75836400
C	-4.71931300	-3.06029900	1.14734300
H	-4.22196400	-3.52079700	1.99253200
C	0.31283900	-4.59090000	2.03690500
H	1.09270300	-5.21873800	2.45318800
C	3.09768200	-1.28202900	-2.21391800
C	-4.02354200	-2.21064500	0.27644200
C	-1.84778900	-4.27102400	1.03812900

H	-2.76316100	-4.67792900	0.62794000
C	-0.87304900	-5.12742100	1.55207000
H	-1.04263600	-6.19938800	1.56328200
C	3.15930500	-2.22994500	-4.43338500
H	2.64756900	-2.58692800	-5.32123900
C	-2.58675900	2.48135700	-1.44217000
C	5.22971400	-1.79497900	-3.24646000
C	-0.66305500	1.00236600	4.80050500
H	-1.48373300	0.94914200	5.50680800
C	5.51034200	2.60520500	0.60862300
H	6.18753600	2.29880300	-0.18033700
C	4.54632000	-2.25192500	-4.38869300
H	5.13272900	-2.62549700	-5.22202200
C	2.42435000	-1.75717300	-3.34744200
H	1.34142900	-1.74018000	-3.37077200
C	-3.98947500	2.57640800	-1.56186700
H	-4.63716800	1.86006100	-1.07091200
C	3.61895000	3.23722700	2.51046700
H	2.84943900	3.52168300	3.21394400
C	0.59165200	1.47928400	5.17269400
H	0.78540500	1.78811900	6.19500700
C	7.35607200	-1.49225500	-2.17687700
H	8.39352500	-1.68152100	-2.45052000
H	7.09918500	-2.08430000	-1.28984200
H	7.22818900	-0.42252900	-1.96447400
C	-1.75468500	3.44451800	-2.02437100
H	-0.68025200	3.35459300	-1.91935700
C	5.69309200	3.74291600	1.36629900
H	6.55782200	4.37437700	1.20170900
C	-4.54545300	3.64271800	-2.27209100
C	-6.69825300	-2.66800400	-0.15321600
H	-7.74859000	-2.83050000	-0.36977900
C	-6.07720200	-3.28495100	0.92763000
H	-6.63793400	-3.93390700	1.59283500
C	-2.32391100	4.49351700	-2.74540100
H	-1.68767400	5.23770700	-3.21325200
C	4.71632900	4.06447800	2.31772900
H	4.80768000	4.97589700	2.90021100
C	-5.94139500	-1.80646200	-0.94942700
H	-6.39449000	-1.28418500	-1.78809500
C	-3.70142500	4.59633000	-2.87068800
H	-4.15972000	5.41152100	-3.42128500
C	-6.80575800	2.95162700	-1.85396300
H	-6.70676600	2.92895500	-0.76171200
H	-6.68603600	1.94150700	-2.26571800
H	-7.79047700	3.33449000	-2.11940500
H	4.20319800	0.99070000	0.19181500

^{LS}[3OMe]$_{Hyd}$

Fe	-0.04035300	-0.71382000	0.19008600
O	0.70536700	0.10263300	-1.47570900
O	-0.50960700	1.11342300	0.85331700
N	-1.84909400	-0.65174900	-0.34945300
N	-0.17283400	-2.47122000	-0.71813300
N	1.78030700	-0.60110300	0.69290700
O	5.91337200	2.56870000	-3.31996600
N	-0.15141000	-1.49195700	2.01467600
N	-2.49273300	0.50608400	-0.03166400
H	-3.36493400	0.67996200	-0.55670300
N	4.50820200	-0.54409500	1.54645600
O	-5.43975400	4.56302400	1.40327200
N	2.58342200	-0.02412000	-0.24289700

H	3.59422100	-0.05662300	-0.04764800
C	-2.39757800	-1.64042500	-1.01829900
C	-1.39115300	-2.68560600	-1.31014900
N	-4.39771500	-0.46252900	-1.63115500
C	-1.69721600	1.43639000	0.59718000
C	3.99939200	1.45664600	-2.30105400
H	4.46064900	1.44636800	-1.32089500
C	0.81695300	-3.35172600	-0.92259200
H	1.75703700	-3.13970600	-0.42444700
C	-1.21997500	-2.05049400	2.59979600
H	-2.15480700	-1.98246000	2.05380300
C	1.19278200	-2.20853400	3.87405100
H	2.16494900	-2.30236200	4.33992700
C	1.94034000	0.33182900	-1.40266700
C	1.05766400	-1.53389400	2.65943600
C	2.16253900	-0.89162600	1.91479100
C	3.50637000	-0.58938400	2.45501500
C	-4.55177700	-2.85974700	-1.54512200
H	-4.10656000	-3.81596400	-1.29960700
C	0.67538800	-4.47205400	-1.73640700
H	1.50840000	-5.15357800	-1.86686700
C	2.69782800	0.94522100	-2.49429200
C	-3.82101800	-1.66944200	-1.42826500
C	-1.57674300	-3.76568500	-2.17514600
H	-2.51231800	-3.88726600	-2.70407800
C	-0.53677200	-4.66850700	-2.38798900
H	-0.67495500	-5.50817100	-3.06129800
C	2.77566900	1.57873500	-4.81986100
H	2.31227400	1.62943600	-5.79966700
C	-2.25732000	2.74319100	0.94056300
C	4.67598400	2.03059200	-3.37924100
C	-1.15685500	-2.69509300	3.83195900
H	-2.05409300	-3.12434200	4.26342800
C	5.74908800	-0.28996600	1.97146300
H	6.52418900	-0.27953200	1.20953600
C	4.05602000	2.08164200	-4.64222700
H	4.60518500	2.53117500	-5.46330100
C	2.08271500	1.01276300	-3.75074400
H	1.08142400	0.61996500	-3.87899600
C	-3.65119700	2.96262800	0.98151100
H	-4.34382100	2.14891900	0.80338500
C	3.72798800	-0.30456000	3.80920200
H	2.90576500	-0.26218200	4.51276200
C	0.07517200	-2.79019200	4.46928900
H	0.17240700	-3.31548900	5.41377800
C	6.61787200	2.57829700	-2.07858300
H	7.57167300	3.06178700	-2.28595500
H	6.79890200	1.55684700	-1.72102600
H	6.07476900	3.15560300	-1.32036100
C	-1.36033400	3.77979000	1.22689600
H	-0.29416200	3.59227300	1.18806000
C	6.06208600	-0.04304300	3.30860500
H	7.08743700	0.15255900	3.60297200
C	-4.13388400	4.23081900	1.31093600
C	-6.45476000	-1.55602700	-2.21403700
H	-7.48459800	-1.46512400	-2.54175000
C	-5.88573100	-2.79616800	-1.94380400
H	-6.47044700	-3.70590400	-2.03669900
C	-1.85806100	5.04343500	1.54159200

H	-1.17346700	5.85782400	1.75474000
C	5.02534600	-0.02803200	4.23598100
H	5.21856000	0.20095800	5.27920600
C	-5.67312900	-0.41569800	-2.02516300
H	-6.08710000	0.57528700	-2.19226200
C	-3.22567600	5.27139300	1.58407500
H	-3.62764900	6.24811400	1.83360400
C	-6.43681300	3.57126600	1.15842100
H	-6.35521800	2.74359100	1.87351500
H	-6.37121700	3.19238000	0.13083600
H	-7.39257900	4.07515100	1.29659400

^{LS}[3OMe]$_{Py}$

Fe	-0.00343200	-0.32028600	0.64884700
O	0.75647600	-0.94223200	-1.05819100
O	-0.57512700	1.39227000	-0.21200500
N	-1.79459100	-0.76809900	0.22642000
N	-0.04031400	-2.19413400	1.29194900
N	1.78094600	0.22800600	0.86619100
O	6.20332300	-1.56217900	-3.59046000
N	-0.16813200	0.45216900	2.46773600
N	-2.49377400	0.22303800	-0.39276500
H	-3.34813500	-0.08460900	-0.88505800
N	4.24859900	1.62679100	1.04267000
O	-5.64997500	3.91306800	-2.29999600
N	2.63906500	-0.01251700	-0.13571200
C	-2.27641700	-1.96498700	0.47260700
C	-1.22059000	-2.83982000	1.02792600
N	-4.29018200	-1.70546200	-0.80935300
C	-1.76099400	1.36265700	-0.62648600
C	4.16766300	-1.08601000	-2.33339400
H	4.70305800	-0.83076800	-1.42850000
C	0.99247000	-2.89392500	1.78173200
H	1.90126800	-2.33380600	1.97314500
C	-1.21824600	0.36682600	3.29794900
H	-2.12161700	-0.06578000	2.88131400
C	1.12662300	1.38169500	4.25859700
H	2.07887300	1.71346900	4.65051000
C	1.99431200	-0.67850600	-1.14909500
C	1.00355400	0.99686600	2.91928900
C	2.07793300	1.01880000	1.90767200
C	3.25670000	1.86843900	1.95382400
C	-4.35676800	-3.31595400	0.97353100
H	-3.88692200	-3.77688500	1.83353700
C	0.93120100	-4.26389600	2.01924100
H	1.79574200	-4.78206400	2.41850500
C	2.75700000	-1.06724500	-2.34041300
C	-3.67764300	-2.36283300	0.20210900
C	-1.32486600	-4.22140600	1.20053400
H	-2.22952000	-4.74067300	0.91455400
C	-0.24213800	-4.93939200	1.70384700
H	-0.31669100	-6.01374800	1.83664700
C	2.74863900	-1.80719900	-4.63772000
H	2.20870000	-2.08246500	-5.53787800
C	-2.38294800	2.48048600	-1.33745900
C	4.85516400	-1.48028200	-3.48193000
C	-1.17284500	0.79101400	4.62079400
H	-2.05319300	0.70902800	5.24791600
C	5.37662700	2.35940100	0.94287600
H	6.07059100	2.06355200	0.16466500
C	4.13634900	-1.83207200	-4.63881300
H	4.69573500	-2.12678000	-5.52086900

C	2.04818400	-1.43517400	-3.49148100
H	0.96511500	-1.41781900	-3.48079400
C	-3.78510200	2.59566900	-1.44833100
H	-4.43716100	1.87884000	-0.96397400
C	3.43628300	2.98197900	2.79689200
H	2.65145000	3.27555000	3.47848400
C	0.03101600	1.28578300	5.11223200
H	0.12478800	1.58318400	6.15167700
C	7.01511500	-1.26109200	-2.45955800
H	8.04350600	-1.41852900	-2.78309700
H	6.79130900	-1.93038800	-1.61955800
H	6.89033400	-0.21458300	-2.15086000
C	-1.53767600	3.43699200	-1.91264100
H	-0.46383700	3.32845700	-1.81990400
C	5.59643400	3.42211100	1.79141500
H	6.50843300	4.00165200	1.71572800
C	-4.32897900	3.67900100	-2.14180700
C	-6.27526100	-3.00463400	-0.43747300
H	-7.29163100	-3.23806000	-0.73530700
C	-5.67229200	-3.63737800	0.64464500
H	-6.21697300	-4.37023900	1.23148900
C	-2.09603800	4.50499100	-2.61380100
H	-1.45184900	5.24639000	-3.07505400
C	4.59337500	3.74158200	2.71733500
H	4.71275900	4.60181700	3.36855800
C	-5.54713900	-2.03134200	-1.12242600
H	-5.99038600	-1.48802400	-1.95292500
C	-3.47272900	4.62906200	-2.72992900
H	-3.92152500	5.45840200	-3.26711900
C	-6.59711100	3.01218100	-1.72636000
H	-6.49583600	2.97407000	-0.63489300
H	-6.49180200	2.00640700	-2.15186500
H	-7.57681700	3.41219500	-1.98457000
H	3.99940400	0.87933400	0.34516700