Electronic Supplementary Material (ESI) for *Chem. Commun.*

Spin canting, metamagnetism, and single-chain magnetic behaviour in the cyano-bridged homospin Iron(II) compound

Dong Shao, Shao-Liang Zhang, Xin-hua Zhao, Xin-Yi Wang*

† State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China. *Email: wangxy66@nju.edu.cn

Supporting Information

Table of contents:

1. Physical Measurements

IR data were measured on KBr pellets using a Bruker Vector 22 FT-IR spectrometer in the 4000-400 cm^{-1} range. Elemental analyses for C, H, and N were performed at Elementar Vario MICRO analyzer. Magnetic susceptibility measurements were performed using a Quantum Design SQUID VSM magnetometer on the microcrystalline sample of **1**. Direct current (dc) measurements were conducted from 300 to 2 K under an external magnetic field of 1000 Oe. The field dependences of the magnetization were measured at 2 K with dc magnetic field between 0 and 7 T. All magnetic data were corrected for the diamagnetism of the sample holder. The data were corrected for the sample holder and for the diamagnetic contribution of the sample.

2. Synthesis

[Fe(L_{N5})(CN)$_2$] was prepared according to literature.[S1]

[Fe(L_{N5})(CN)][BF_4](**1**): A solution of $NaBF_4$ (55 mg, 0.5 mmol) in 1 mL of water was added to a solution of [Fe(L_{N5})$(CN)_2$] (25 mg, 0.05 mmol) in 6 mL of methanol under nitrogen atmosphere. The dark violet solution was filtrated to a vial and was then kept in the dark place for one week. Dark blue rhombus single crystals formed after evaporation. Yield: ~16 mg, 72%. The crystals are quite stable in the air. Anal: Calcd for $C_{16}H_{21}BF_4FeN_6$ (%): C, 43.67; H, 4.81; N, 19.09. Found (%): C, 43.50, H, 4.55; N, 18.89. IR (KBr, cm^{-1}) : 2100 (vs), 1642 (s), 1585 (m), 1435 (s), 1200 (s),1048 (vs), 819 (s), 520 (s).

3. X-ray crystallography

3.1 X-ray data collection, structure solution and refinement for **1**

X-ray Diffraction Single crystal X-ray crystallographic data were collected on a Bruker APEX SMART diffractometer with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å). The APEX II program was used to determine the unit cell parameters and for data collection. The crystal is naturally twined and a twin routine was applied for the structure determination. The program CELL_NOW[S2] was used to identify the matrices of the twin components which were then used for integration of the data frames, and the program TWINABS was then applied to scale the data.[S3] The twin structure was solved by using data from one of the components by direct method but refined using the data from both of them by full matrix least squares based on F^2 using the SHELXTL program (HKLF 5).[S4] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Additional details of the data collection and structural refinement parameters are provided in Table **1**. Selected bond lengths and angles of **1** are listed in Table **2**. CCDC-1030844 (**1**) contains 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.

Table S1. Crystallographic Data and Structure Refinement Parameters for **1**

Formula	$C_{16}H_{23}BF_4FeN_6$
Mr /gmol^{-1}	440.06
Crystal system	Monoclinic
Space group	*P*2(1)/n
a /Å	13.0808(11)
b /Å	10.6982(9)
c /Å	14.0524(12)
α /deg	90
β /deg	96.336(2)
γ /deg	90
V /Å^3	1954.5(3)
Z	4
d_{calc}/g cm^{-1}	1.502
μ(Mo–*K*α) (mm^{-1})	0.822
F (000)	912.0
Refl.collected/unique/obseved	6062 / 4439 / 3659
T_{max}/T_{min}	0.8866/ 0.5591
data/restraints/parameters	4439 / 0 / 254
R_1^a/wR_2^b ($I > 2\sigma(I)$) [a]	0.0438 / 0.1227
R_1/wR_2 (all data)	0.0551 / 0.1302
GOF^c on F^2	1.043
Max/min /e Å^{-3}	0.646 / -0.427

[a]R1 = $[\Sigma||Fo| - |Fc||]/\Sigma|Fo|$; wR_2 = $\{[\Sigma w[(Fo)^2 - (Fc)^2]^2]/[\Sigma w(Fo^2)^2]\}$ 1/2; w = $[\sigma^2(Fo)^2 + (AP)^2 + BP]$-1 where P = $[(Fo)^2 + 2(Fc)^2]/3$

Table S2. Selected Bond Lengths (Å) and Bond Angles (deg) in **1**.

Fe(1)-N(1)	2.183(2)	Fe(1)-N(5)	2.265(8)
Fe(1)-N(2)	2.234(3)	Fe(1)-N(6)	2.199(2)
Fe(1)-N(3)	2.299(3)	Fe(1)-C(16)	2.190(2)
Fe(1)-N(4)	2.309(3)	C(16)-N(6)	1.142(3)
N(1)-Fe(1)-C(16)	91.67(2)	N(6)-Fe(1)-N(5)	91.77(9)
C(16)-Fe(1)-N(6)	169.46(9)	N(6)-Fe(1)-N(3)	88.75(9)
N(1)-Fe(1)-N(6)	98.30(8)	N(6)-Fe(1)-N(4)	80.24(9)

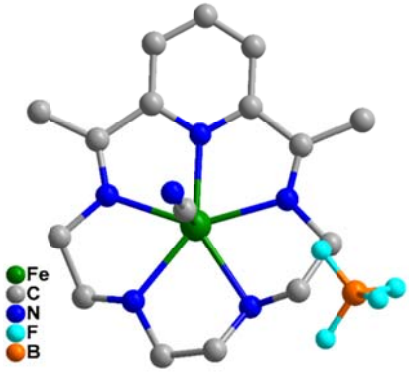

Fig. S1 The asymmetric unit of **1**.

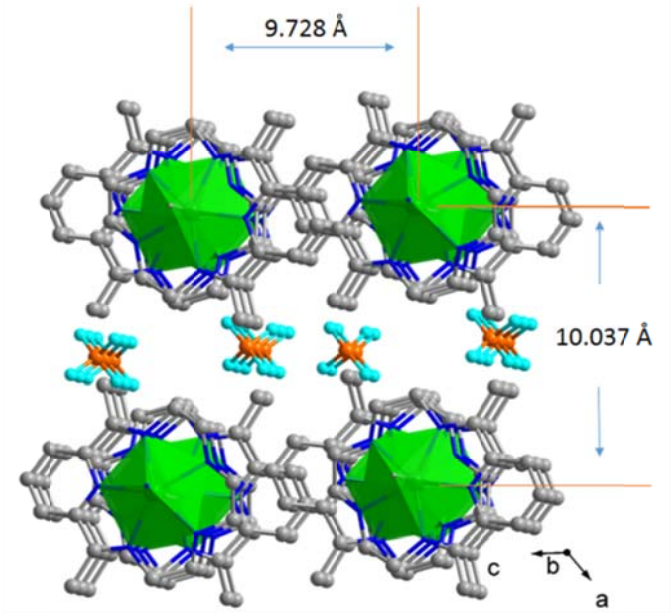

Fig. S2 The packing diagram of **1** showing the interchain distances.

4. Magnetic properties

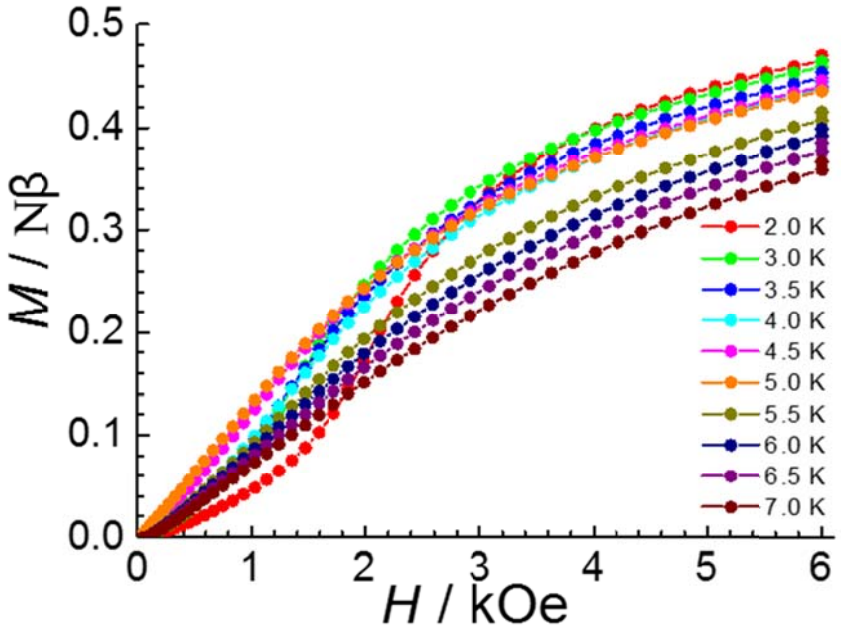

Fig. S3 Field-dependent isothermal magnetization curve for **1** below 7 K.

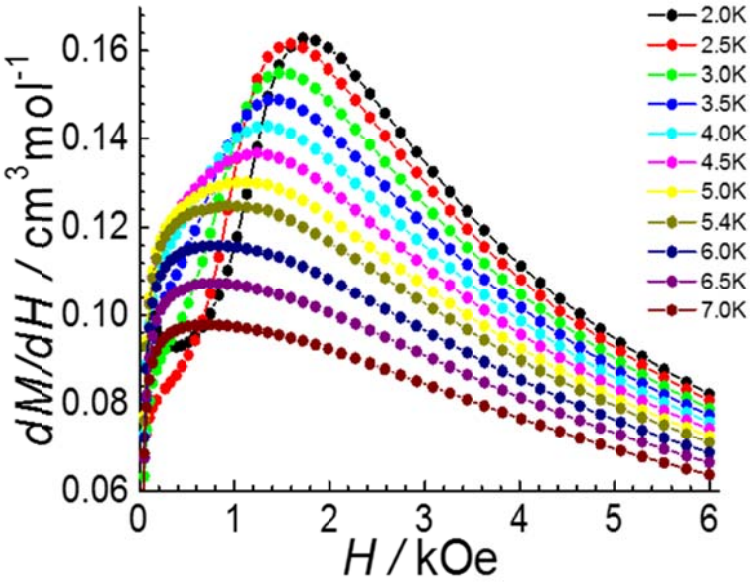

Fig. S4 The derivatives of the magnetization (d*M /dH vs H)* of **1**.

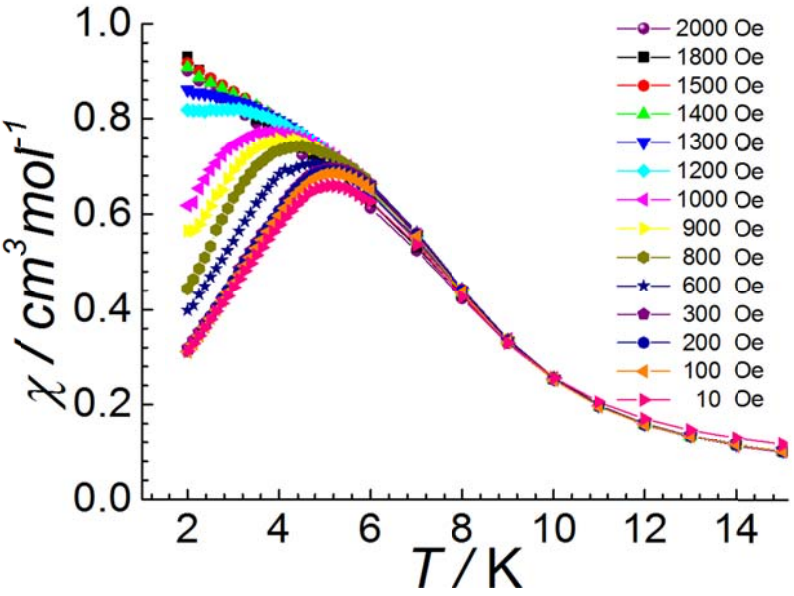

Fig. S5 A series of magnetic susceptibility curves of **1** measured at different dc fields.

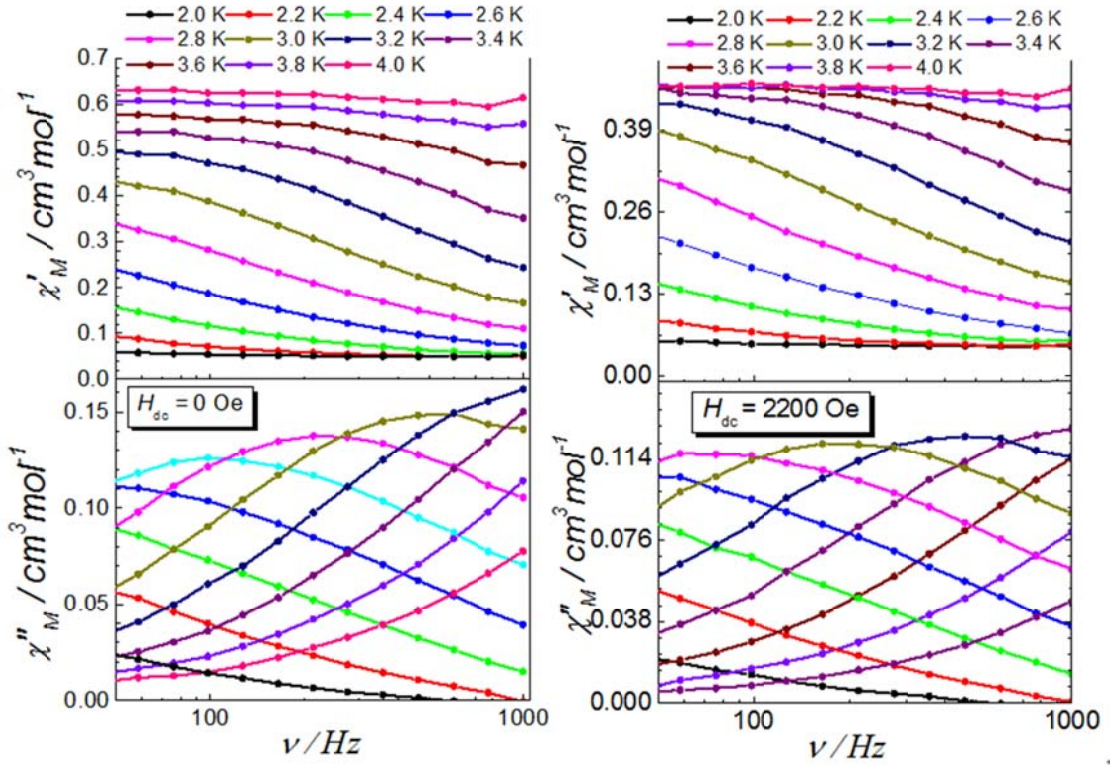

Fig. S6 Frequency dependence of χ' and χ'' of the ac susceptibility for **1** at different temperatures at 0 or 2200 Oe dc fields.

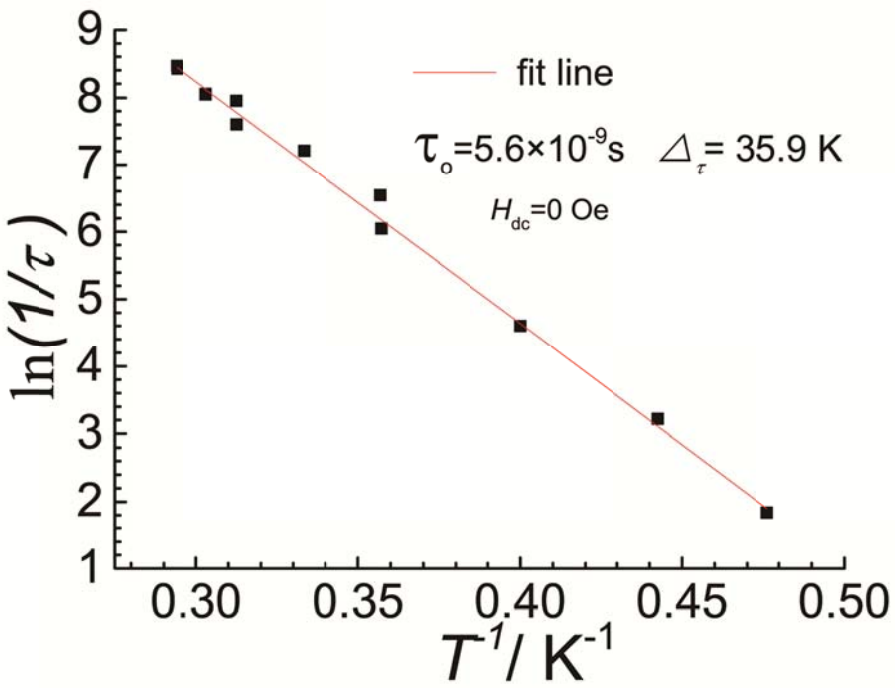

Fig. S7 The ln(1/τ) vs. 1/T plot for **1** under zero dc field. The line is the Arrhenius law fit of the data. The relaxation time data were obtained from the temperature dependent ac data and the Cole-Cole fitting (Table S3).

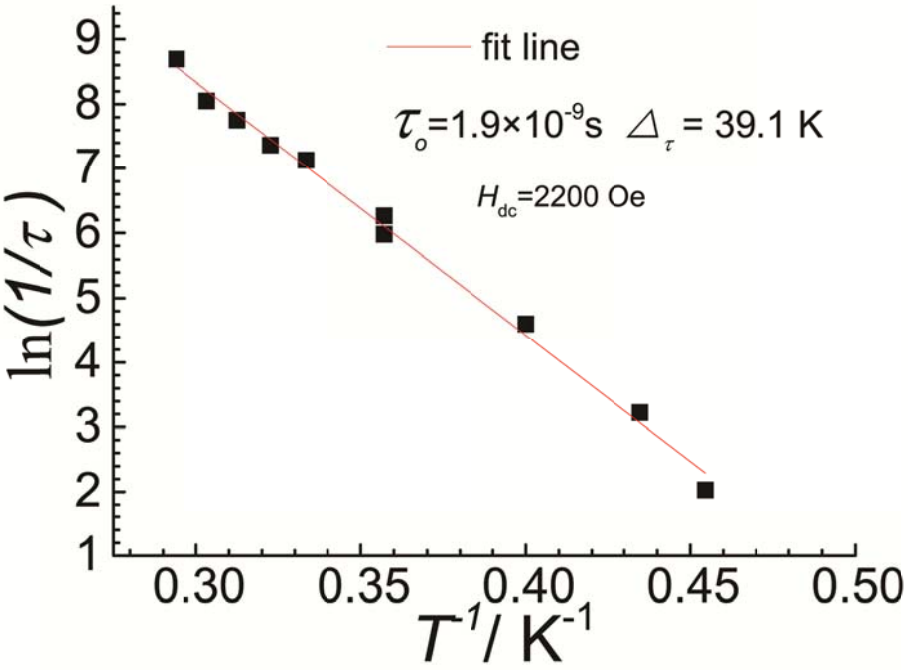

Fig. S8 The ln(1/τ) vs. 1/T plot for **1** under 2200 Oe dc field. The line is the Arrhenius law fit of the data. The relaxation time data were obtained from the temperature dependent ac data and the Cole-Cole fitting (Table S3).

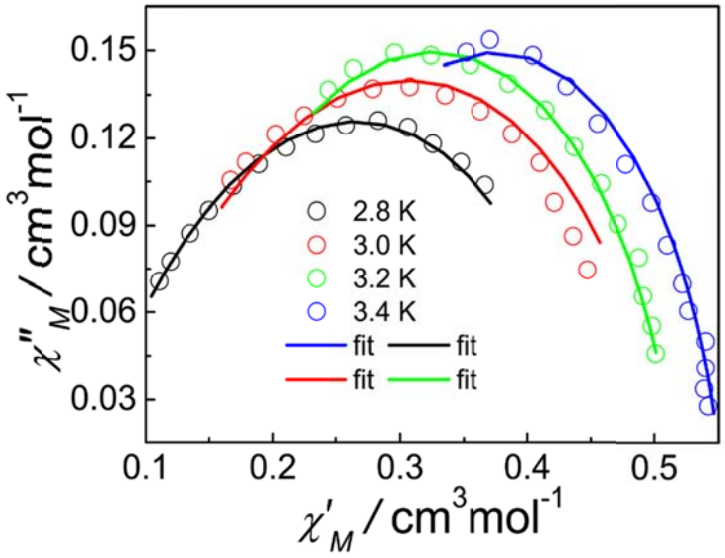

Fig. S9 Cole-Cole plots of **1** at 2.8, 3.0, 3.2 and 3.4 K (H_{dc} = 0 Oe and H_{ac} = 2 Oe). Solid lines represent best fits to the experimental data according to the generalized Debye model.

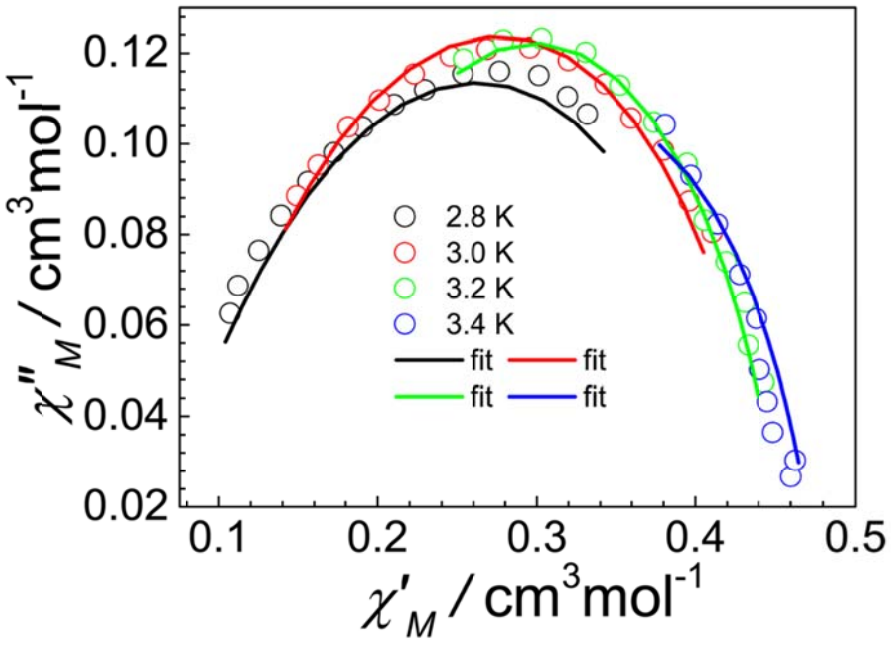

Fig. S10 Cole-Cole plots of **1** at 2.8, 3.0, 3.2 and 3.4 K (H_{dc} = 2200 Oe and H_{ac} = 2 Oe). Solid lines represent best fits to the experimental data according to the generalized Debye model.

Table S3 Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **1** according to the generalized Debye model.

H_{dc} / Oe	T / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
0	2.8	0.04702	0.45118	0.00130	0.29122
	3.0	0.06385	0.51304	0.00074	0.29078
	3.2	0.10742	0.51877	0.00035	0.19970
	3.4	0.18253	0.55223	0.00022	0.13490
2200	2.8	0.05047	0.44123	0.00167	0.32970
	3.0	0.06478	0.45554	0.00080	0.28132
	3.2	0.11711	0.45798	0.00043	0.20792
	3.4	0.16676	0.47704	0.00026	0.23752

5 References

S1 S. M. Nelson, P. D. A. Mcllroy, C. S. Stevenson, E. Konig, G. Ritter and J. Waigel, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 991.

S2 Sheldrick, G. M. CELL_NOW, University of Göttingen, Germany, 2006.

S3 Sheldrick, G. M. TWINABS, University of Göttingen, Germany, 2006.

S4 Sheldrick, G. M. SHELXTL, Version 6.14, Bruker AXS, Inc.; Madison, WI 2000-2003.