Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Hysteretic Spin Crossover in a Hofmann-type Metal-Organic Framework Constructed from the $[Mo^{III}(CN)_7]^{4-}$ unit

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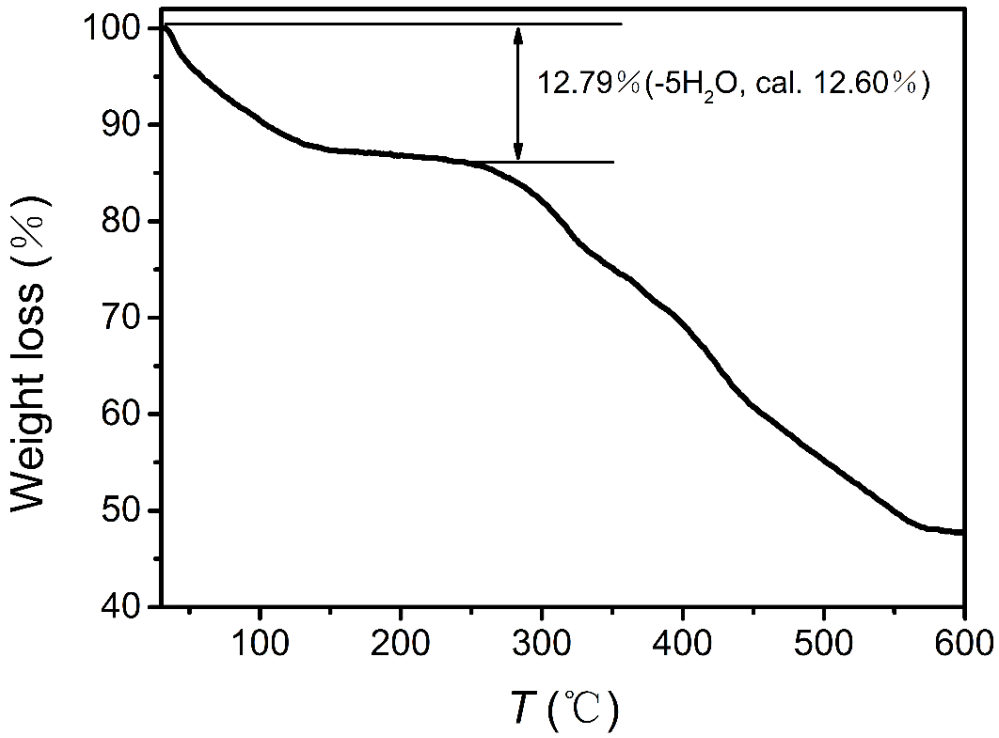

Figure S1. Thermogravimetric analysis (TGA) curve of **1** at a heating rate of 10 K/min.

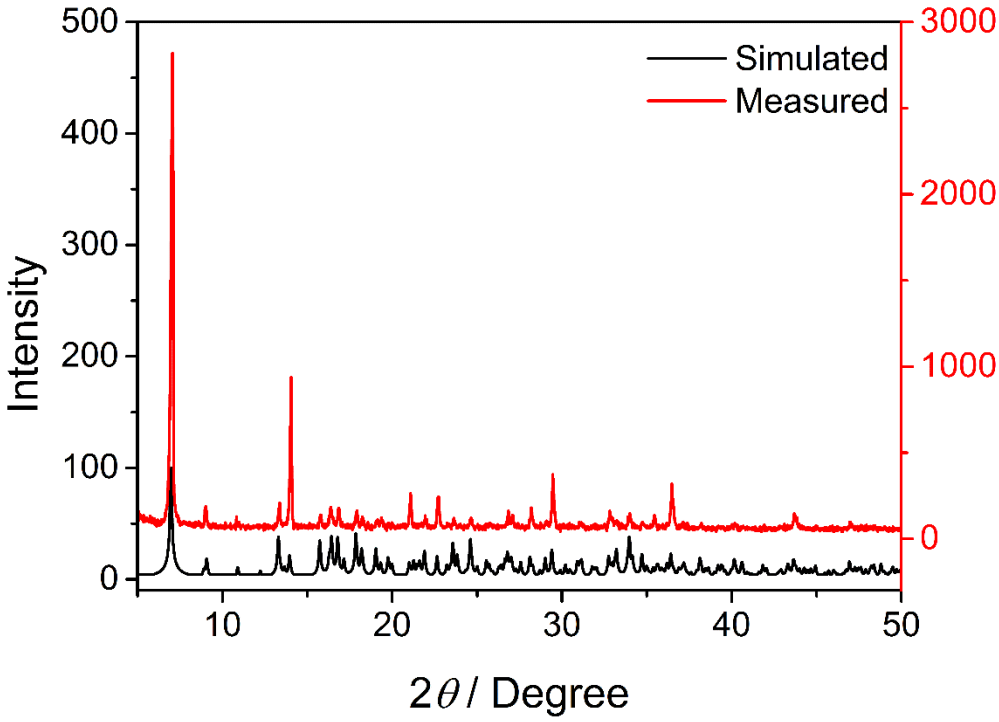

Figure S2. The experimental and simulated PXRD patterns for **1**.

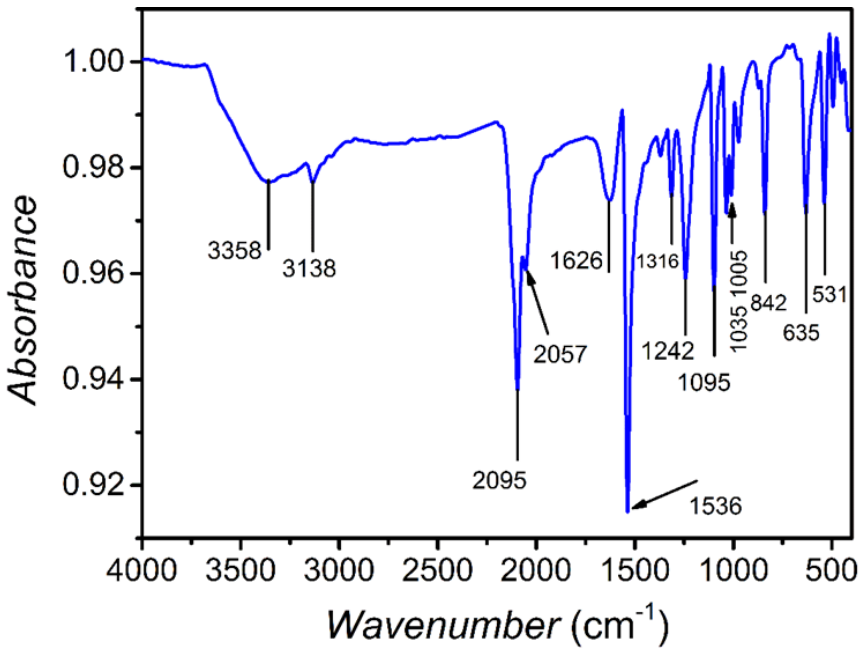

Figure S3. The IR spectra for **1** at 298 K.

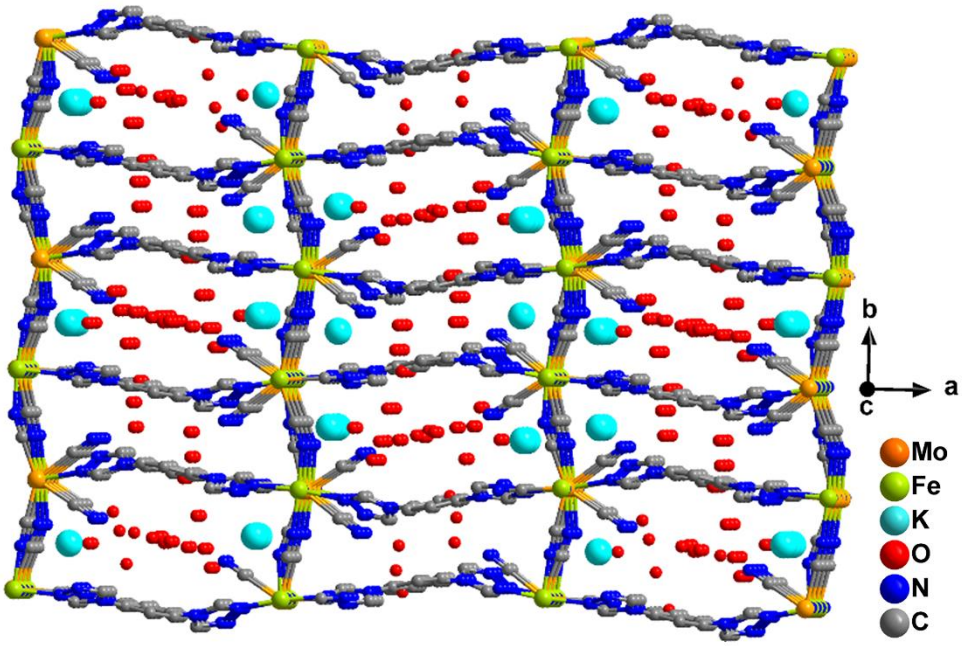

Figure S4. The 3D supramolecular network with K^+ ions and H_2O molecules of **1** viewed along the *c* axis.

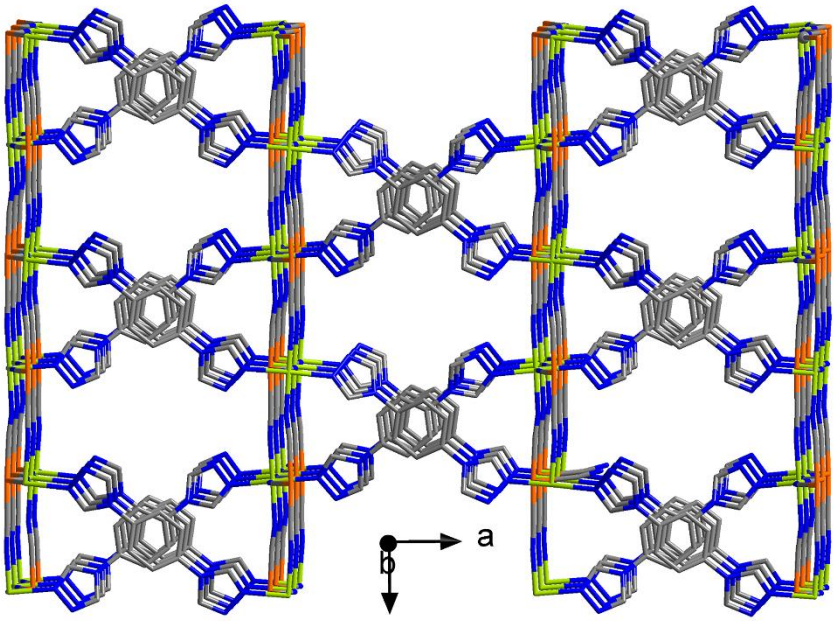

Figure S5. The 3D packing structure of **1** viewed along the *b* axis. Orange, green, blue, and gray represent Mo, Fe, N, and C atoms, respectively.

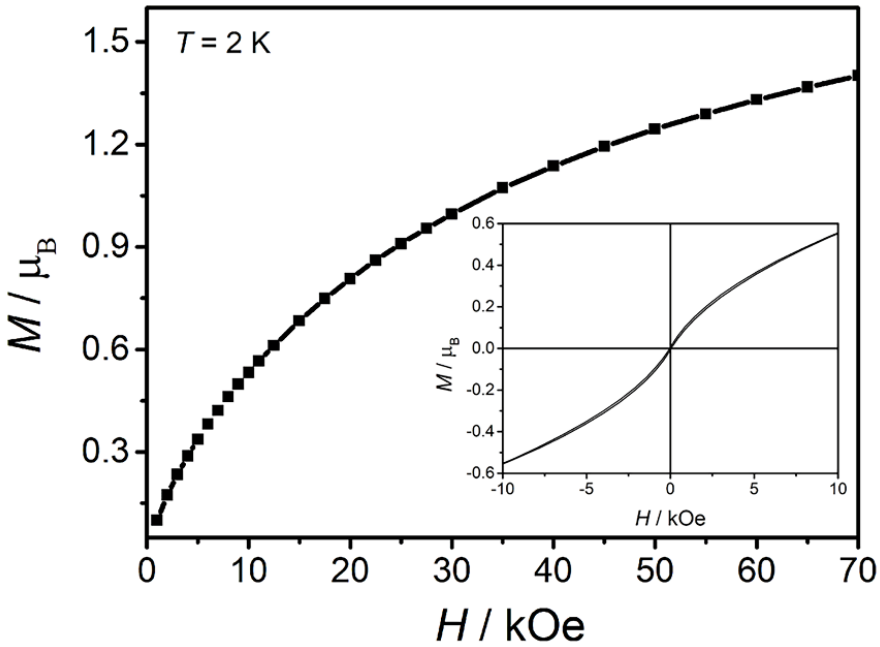

Figure S6. The field-dependent magnetization curve for the crystal sample of **1** measured at 2 K. Insert: magnetic hysteresis loop measured on the crystal sample at 2 K.

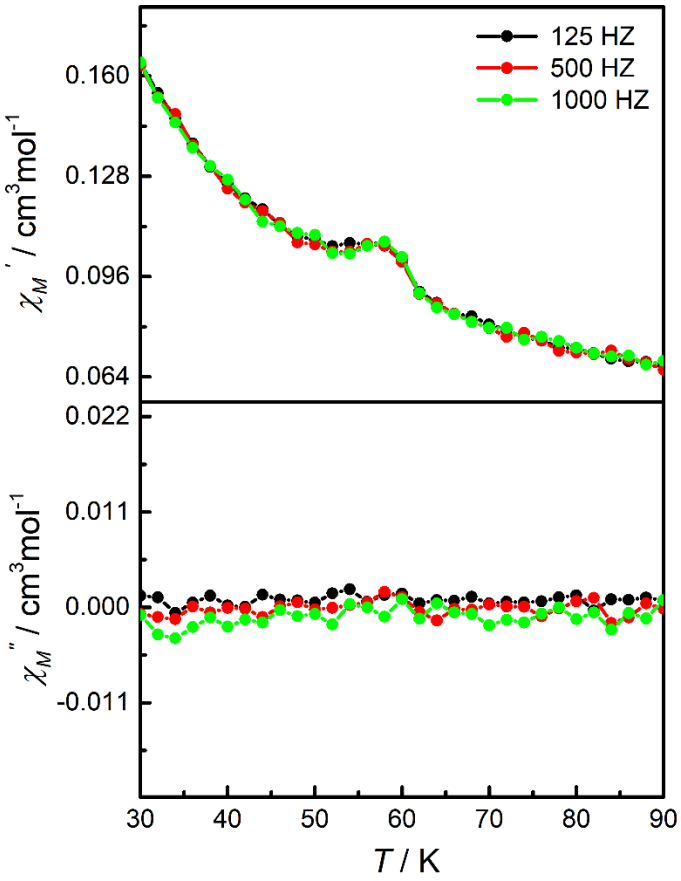

Figure S7. Temperature dependent in-phase (χ'_M) and out-of-phase (χ''_M) signals of the ac susceptibility for **1** collected under H_{ac} = 2 Oe and H_{dc} = 0 Oe.

Table S1. Selected bond lengths [Å] and angles [º] of complex **1**.

Bond lengths [Å]	**193 K**	**Bond lengths [Å]**	**100 K**
Fe(1)-N(1)	2.127(10)	Fe(1)-N(1)	2.113(11)
Fe(1)-N(2)^4	2.144(5)	Fe(1)-N(2)^4	2.129(6)
Fe(1)-N(4)^3	2.159(5)	Fe(1)-N(4)^3	2.153(6)
Fe(1)-N(7)^6	2.113(10)	Fe(1)-N(7)^6	2.104(12)
Fe(1)-N(9)	2.213(5)	Fe(1)-N(9)	2.207(6)
Fe(1)-N(13)^5	2.194(5)	Fe(1)-N(13)^5	2.186(6)
Mo(1)-C(1)	2.134(12)	Mo(1)-C(1)	2.127(14)
Mo(1)-C(2)	2.142(5)	Mo(1)-C(2)	2.137(6)
Mo(1)-C(3)	2.175(8)	Mo(1)-C(3)	2.190(10)
Mo(1)-C(4)	2.147(5)	Mo(1)-C(4)	2.151(7)
Mo(1)-C(5)	2.159(6)	Mo(1)-C(5)	2.160(7)
Mo(1)-C(6)	2.156(6)	Mo(1)-C(6)	2.170(8)

Mo(1)-C(7)	2.147(13)	Mo(1)-C(7)	2.143(15)
Mo(1)-Fe(1) (C1N1)	5.392	Mo(1)-Fe(1) (C1N1)	5.379
Mo(1)-Fe(1) (C2N2)	5.424	Mo(1)-Fe(1) (C2N2)	5.408
Mo(1)-Fe(1) (C4N4)	5.361	Mo(1)-Fe(1) (C4N4)	5.345
Mo(1)-Fe(1) (C7N7)	5.411	Mo(1)-Fe(1) (C7N7)	5.393
Bond angles [º]	**193 K**	**Bond angles [º]**	**100 K**
C(1)-N(1)-Fe(1)	169.2(8)	C(1)-N(1)-Fe(1)	168.9(9)
C(2)-N(2)-Fe(1)[2]	175.5(5)	C(2)-N(2)-Fe(1)[2]	175.5(6)
C(4)-N(4)-Fe(1)[1]	157.1(4)	C(4)-N(4)-Fe(1)[1]	156.6(5)
C(7)-N(7)-Fe(1)[9]	174.5(7)	C(7)-N(7)-Fe(1)[9]	174.4(8)
C(1)-N(1)-Mo(1)	174.1(8)	C(1)-N(1)-Mo(1)	174.2(9)
C(2)-N(2)-Mo(1)	177.6(7)	C(2)-N(2)-Mo(1)	177.3(8)
C(4)-N(4)-Mo(1)	178.5(8)	C(4)-N(4)-Mo(1)	178.6(8)
C(7)-N(7)-Mo(1)	177.7(8)	C(7)-N(7)-Mo(1)	177.7(9)

[1]1/2-X,-1/2+Y,1/2+Z; [2]1/2-X,1/2+Y,1/2+Z; [3]1/2-X,1/2+Y,-1/2+Z; [4]-1/2+X,1/2-Y,1/2+Z; [5]1/2-X,-1/2+Y, 1/2+Z; [6]+X,+Y,-1+Z; [9]+X,+Y,1+Z

Table S2. The hydrogen bonds for **1** at 193 K.

D-H...A	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**＜D-H-A/ º**
O(3)-H(3A)...O(4)	0.87	2.03	2.850(14)	156
O(3)-H(3B)...N(11)	0.87	2.47	3.331(12)	170
O(4)-H(4A)...N(4)	0.87	2.53	3.329(11)	153
O(4)-H(4B)...N(6)	0.87	2.45	3.156(17)	139
O(5)-H(5B)...N(6)	0.87	1.91	2.769(16)	168
C(12)-H(12)...O(2B)	0.95	2.43	3.37(2)	176
C(16)-H(16)...O(2A)	0.95	2.49	3.14(3)	126

Table S3. Continuous Shape Measures (CShMs) calculation for **1**.

Shape	**CShMs**	
	Mo	
	193 K	**100 K**
HP-7 Heptagon (D_{7h})	33.717	33.584
HPY-7 Hexagonal pyramid (C_{6v})	25.014	24.954
PBPY-7 Pentagonal bipyramid (D_{5h})	**0.236**	**0.267**
COC-7 Capped octahedron (C_{3v})	7.069	6.958
CTPR-7 Capped trigonal prism (C_{2v})	5.562	5.487
JPBPY-7 Johnson pentagonal bipyramid J13 (D_{5h})	3.730	3.683
JETPY-7 Johnson elongated triangular pyramid J7 (C_{3v})	23.567	23.302
	Fe	
	193 K	**100 K**
HP-6 Hexagon (D_{6h})	31.475	31.560
PPY-6 Pentagonal pyramid (C_{5v})	27.166	27.320
OC-6 Octahedron (O_h)	**0.222**	**0.215**
TPR-6 Trigonal prism (D_{3h})	14.583	14.628
JPPY-6 Johnson pentagonal pyramid J2 (C_{5v})	30.613	30.770