Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Three New Mn^{II}-$[Mo^{III}(CN)_7]^{4-}$ Molecular Magnets Constructed from Chiral Bidentate Chelating Ligands

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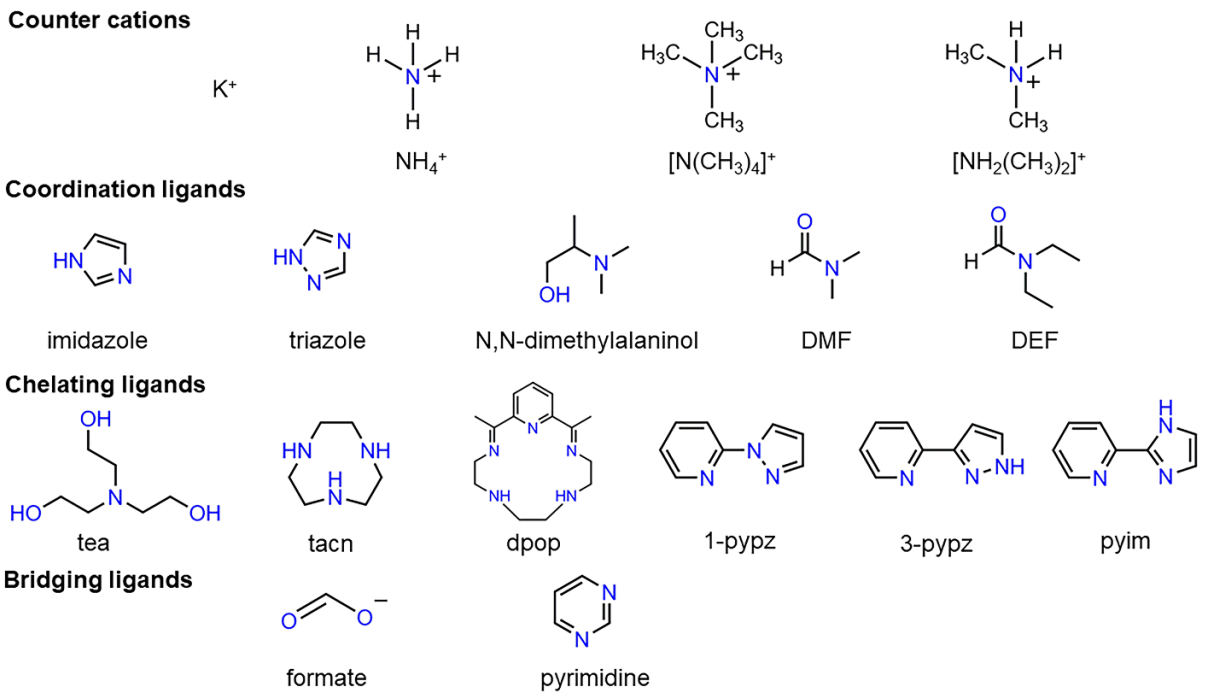

Figure S1. The counter cations and ligands used for the synthesis of compounds based on $[Mo^{III}(CN)_7]^{4-}$.

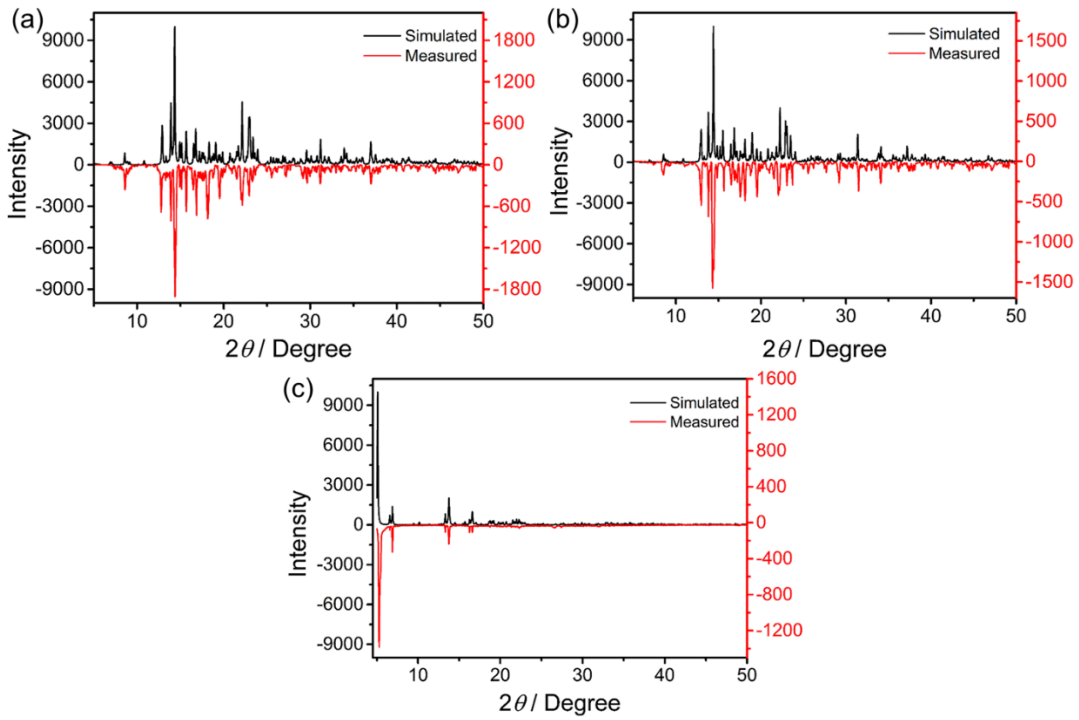

Figure S2. The simulated and measured PXRD patterns for compounds **1-*SS*** (a), **1-*RR*** (b), and **2** (c).

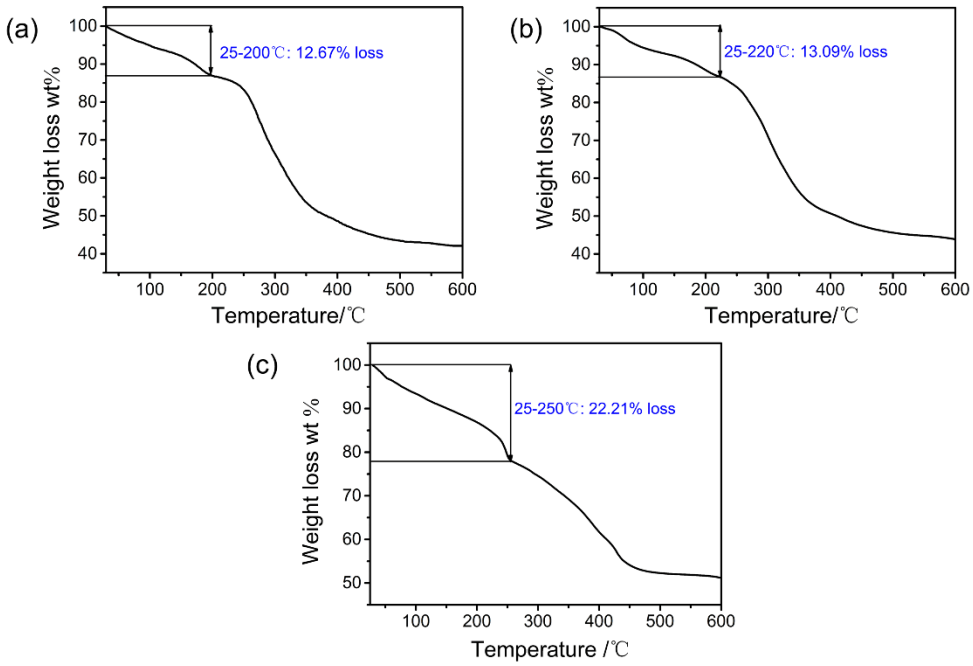

Figure S3. Thermogravimetric analysis of compounds **1-*SS*** (a), **1-*RR*** (b), and **2** (c). The weight losses of **1-*SS***, **1-*RR***, and **2** are 12.67%, 13.09%, and 22.21% below about 200 and 250 ℃, consistent with the calculated values of 12.56% (4 H_2O molecules and 4 MeCN molecules), 12.97% (4.5 H_2O molecules and 4 MeCN molecules), and 22.39% (one H_2O and 4 MeCN molecules) per asymmetric unit, respectively.

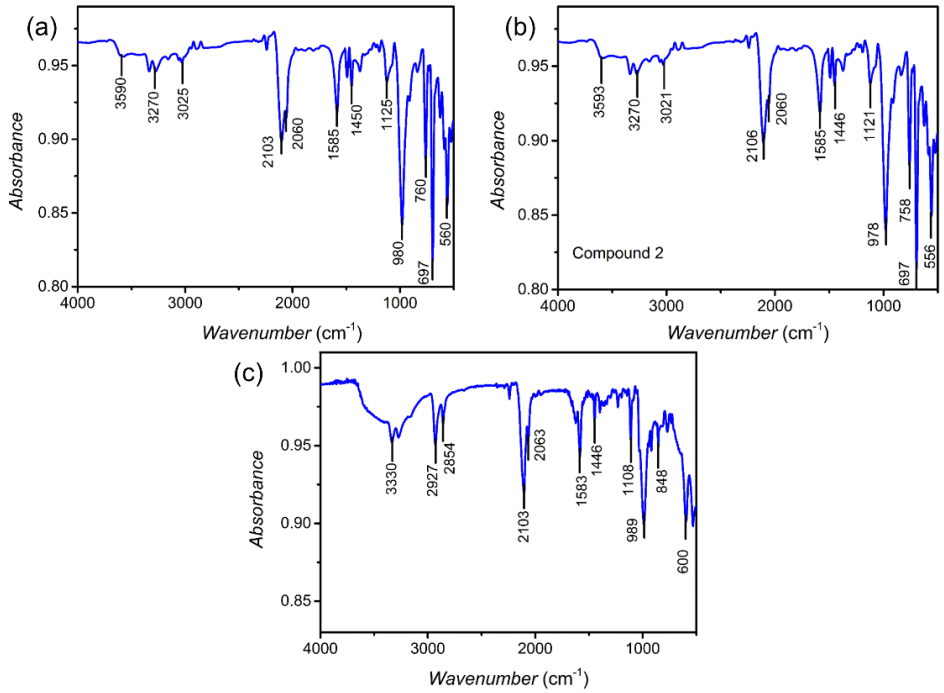

Figure S4. The IR spectra for compounds **1-*SS*** (a), **1-*RR*** (b), and **2** (c).

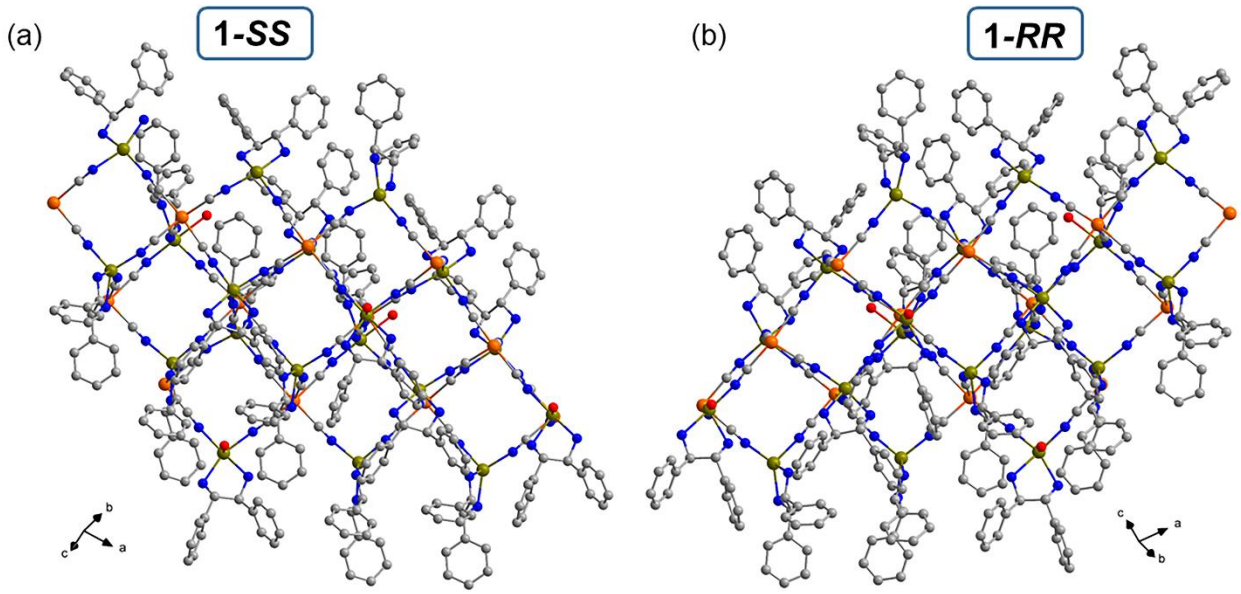

Figure S5. The mirror images of the 2D layers in **1-*SS*** (a) and **1-*RR*** (b). Solvent molecules and all the H atoms have been omitted for clarity. Orange, dark yellow, blue, gray, and red represent Mo, Mn, N, C, and O atoms, respectively.

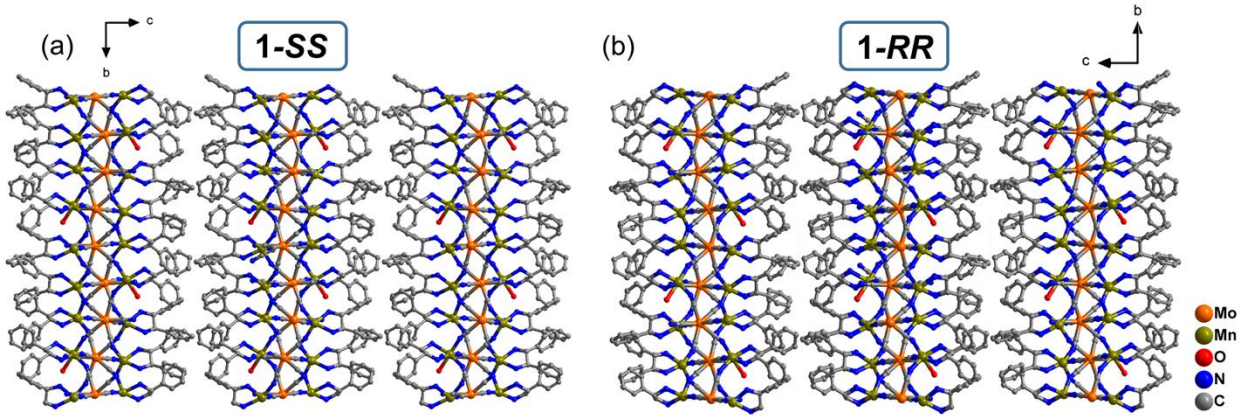

Figure S6. The mirror images of supramolecular networks in **1-*SS*** (a) and **1-*RR*** (b). Solvent molecules and all the H atoms have been omitted for clarity.

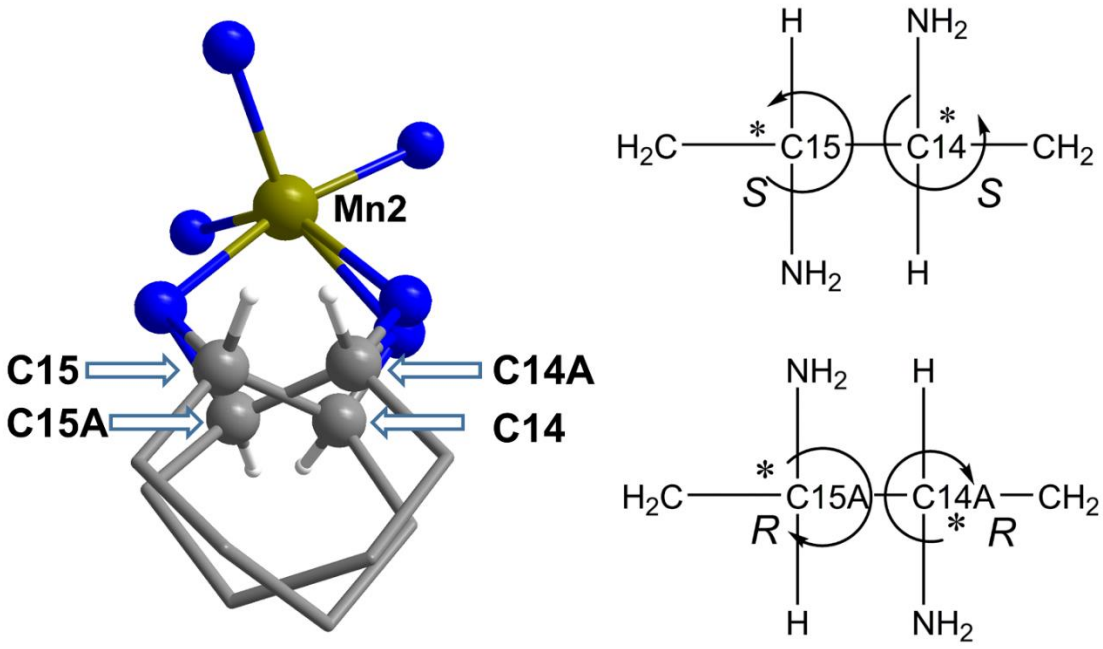

Figure S7. The disordered chiral carbons and the Fischer projections of C14, C15, C14A, and C15A in compound **2**.

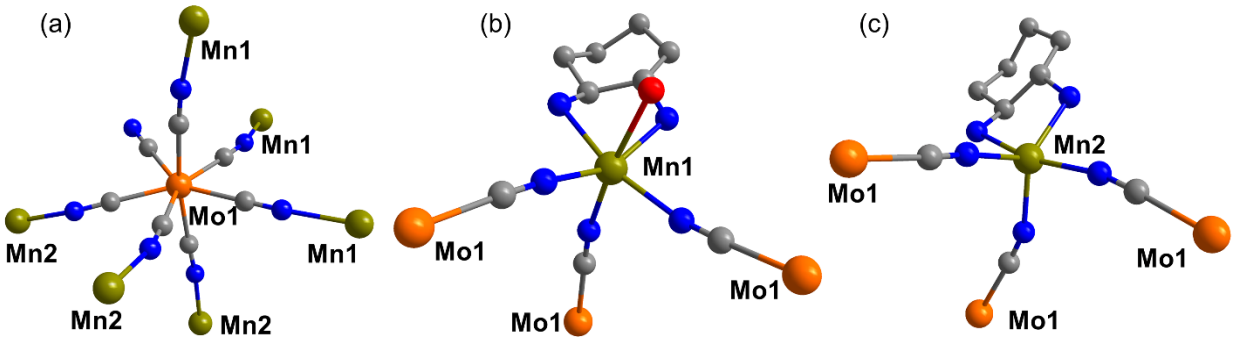

Figure S8. The local structures and CN^- bridged neighbors of the Mo^{III} and Mn^{II} centers in compound **2**.

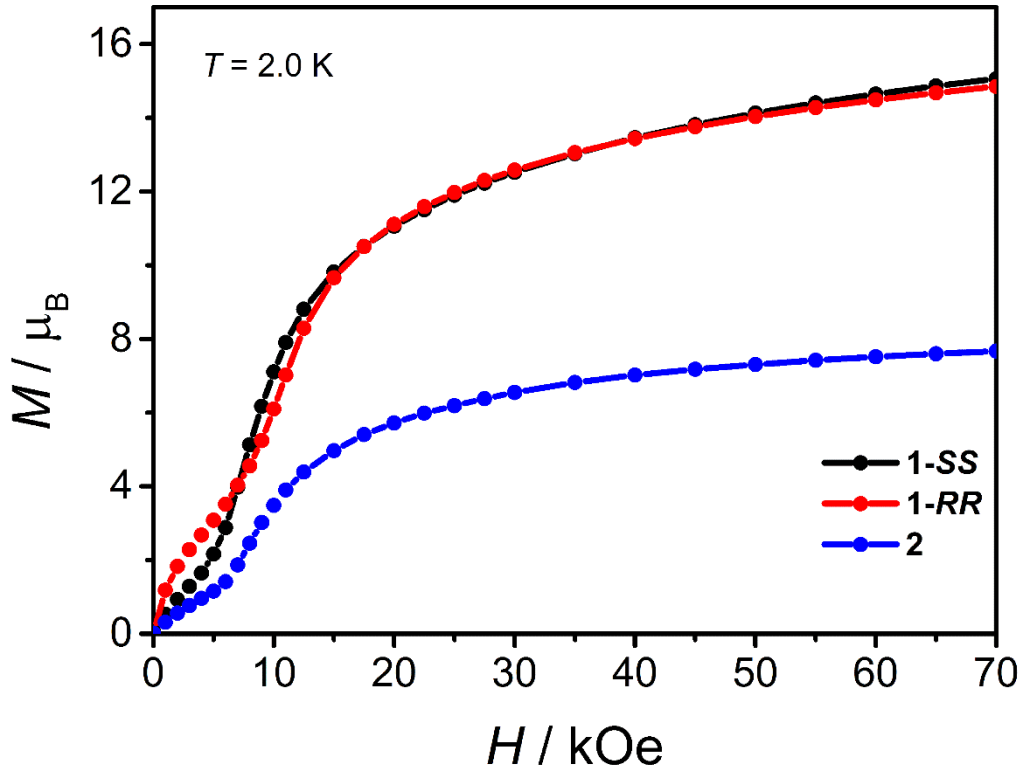

Figure S9. The field-dependent magnetization curves of compounds **1-*SS***, **1-*RR***, and **2** measured at 2 K.

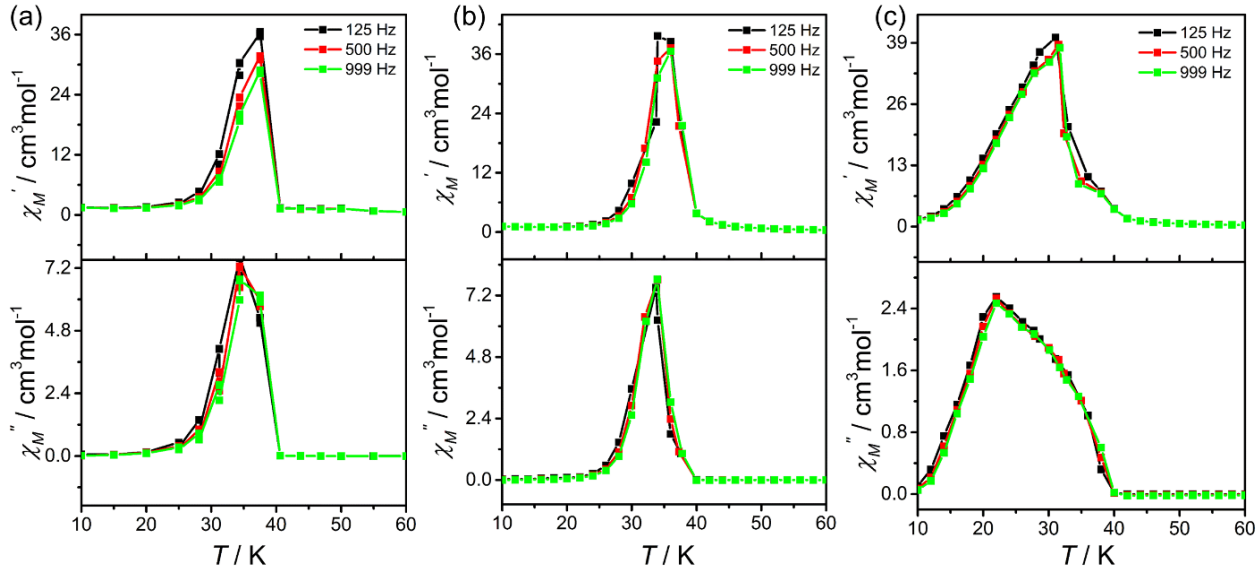

Figure S10. Temperature-dependent ac susceptibilities for compounds **1-*SS*** (a), **1-*RR*** (b), and **2** (c) collected under H_{ac} = 2 Oe and H_{dc} = 0 Oe.

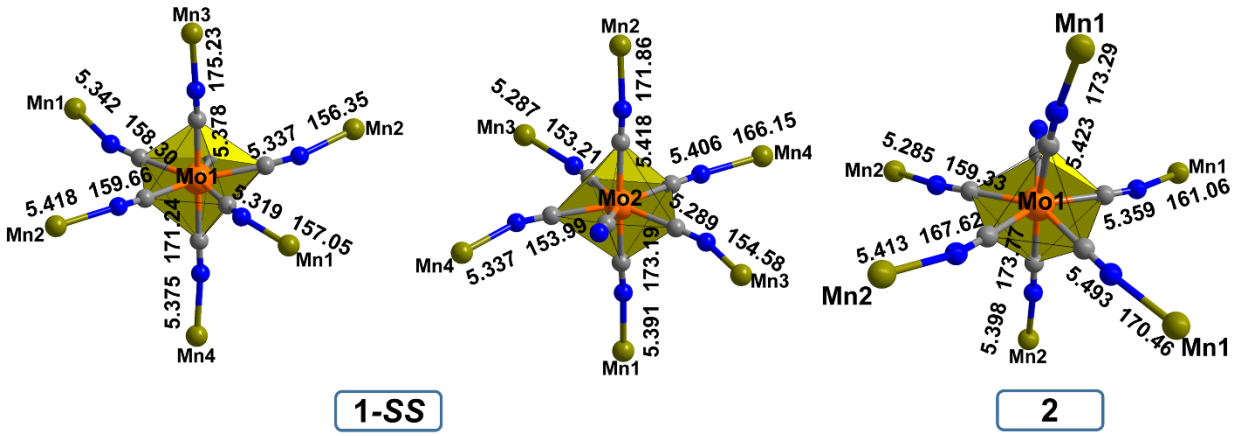

Figure S11. The coordination environment of $[Mo^{III}(CN)_7]^{4-}$, Mn-N-C bond angles, and Mn^{II}-Mo^{III} distances in compounds **1-*SS*** and **2**.

Table S1. The Mn-N-C bond angles and the Mn-N bond lengths in compounds **1-*SS*** and **2**. (the ones in the blue fields denote the axial cyanide bridges)

Mn-N-C angles [º]		Mn-N bond length [Å]	
Complex **1-*SS***			
Mn3-N12-C12	175.2(8)	Mn3-N12	2.075(8)
Mn4-N13-C13	171.2(8)	Mn4-N13	2.080(7)
Mn1-N1-C1	158.3(9)	Mn1-N1	2.149(9)
Mn2-N2-C2	156.4(8)	Mn2-N2	2.182(8)
Mn1[3]-N7-C7	157.0(9)	Mn1-N7[1]	2.125(9)
Mn2[1]-N6-C6	159.7(9)	Mn2-N6[3]	2.167(9)
Mn1-N11-C11	173.2(8)	Mn1-N11	2.118(8)
Mn2[5]-N14-C14	171.9(8)	Mn2-N14[2]	2.143(8)
Mn3-N3-C3	154.6(9)	Mn3-N3	2.166(9)
Mn4[1]-N4-C4	154.0(9)	Mn4-N4[3]	2.200(9)
Mn3[5]-N8-C8	153.2(9)	Mn3-N8[2]	2.105(10)
Mn4[6]-N9-C9	166.2(8)	Mn4-N9[4]	2.137(9)
[1]1-X,1/2+Y,1-Z; [2]2-X,-1/2+Y,1-Z; [3]1-X,-1/2+Y,1-Z; [4]-1+X,+Y,+Z; [5]2-X,1/2+Y,1-Z; [6]1+X,+Y,+Z			
Complex **2**			
Mn1-N1-C1	173.3(5)	Mn1-N1	2.144(4)
Mn2-N6-C6	173.8(5)	Mn2-N6	2.107(4)
Mn1[4]-N3-C3	170.5(4)	Mn1-N3[4]	2.196(5)

Mn1[5]-N4-C4	161.1(4)	Mn1-N4[3]	2.161(4)
Mn2-N2-C2	159.3(4)	Mn2-N2	2.111(4)
Mn2-N7-C7	167.6(4)	Mn2-N7	2.146(4)

[3]-1+X,+Y,+Z; [4]1-X,1-Y,1-Z; [5]1+X,+Y,+Z

Table S2. Selected bond lengths [Å] and angles [⁰] for complexes **1-*SS***, **1-*RR***, and **2**. (the ones in the blue fields denote the axial cyanide bridges)

Complex **1-*SS***			
Bond lengths [Å]		Bond angles [º]	
Mo1-C12	2.141(9)	Mo1-C12-N12	175.4(7)
Mo1-C13	2.152(9)	Mo1-C13-N13	178.5(11)
Mo2-C11	2.143(8)	Mo2-C11-N11	174.9(8)
Mo2-C14	2.143(8)	Mo2-C14-N14	176.8(9)
Mo1-C1	2.156(12)	Mo1-C1-N1	175.1(10)
Mo1-C2	2.175(11)	Mo1-C2-N2	174.7(10)
Mo1-C5	2.142(8)	Mo1-C5-N5	174.5(11)
Mo1-C6	2.193(10)	Mo1-C6-N6	175.4(9)
Mo1-C7	2.169(11)	Mo1-C7-N7	177.5(10)
Mo2-C3	2.131(10)	Mo2-C3-N3	176.3(10)
Mo2-C4	2.161(11)	Mo2-C4-N4	177.2(10)
Mo2-C8	2.145(10)	Mo2-C8-N8	176.7(9)
Mo2-C9	2.149(11)	Mo2-C9-N9	176.3(9)
Mo2-C10	2.164(10)	Mo2-C10-N10	177.5(12)
Complex **1-*RR***			
Bond lengths [Å]		Bond angles [º]	
Mn3-N12[2]	2.100(9)	Mn3[5]-N12-C12	173.3(9)
Mn4-N13	2.112(10)	Mn4-N13-C13	171.6(10)
Mn1-N11A	1.89(2)	Mn1-N11A-C11A	165(4)
Mn1-N11B	2.167(11)	Mn1-N11B-C11B	173.6(13)
Mn2-N14A	2.42(3)	Mn2-N14A-C14A	160(4)
Mn2-N14B	2.054(11)	Mn2-N14B-C14B	173.5(13)
Mo1-C12	2.150(11)	Mo1-C12-N12	176.4(9)
Mo1-C13	2.133(11)	Mo1-C13-N13	176.2(12)
Mo2-C11B	2.155(11)	Mo2-C11B-N11B	175.0(12)
Mo2A-C11A	2.155(17)	Mo2A-C11A-N11A	177(4)
Mo2-C14B	2.162(12)	Mo2-C14B-N14B	175.6(18)

Mo2A-C14A	2.163(19)	Mo2A-C14A-N14A	172(6)
Mn1-N1[4]	2.160(11)	Mn1[6]-N1-C1	156.5(11)
Mn1-N7[3]	2.089(10)	Mn1[1]-N7-C7	158.2(12)
Mn2-N2[2]	2.190(10)	Mn2[5]-N2-C2	154.4(11)
Mn2-N6	2.183(12)	Mn2-N6-C6	162.9(11)
Mn3-N3A[3]	2.268(19)	Mn3[1]-N3B-C3B	154.4(13)
Mn3-N3B[3]	2.129(11)	Mn3-N8A-C8A	153(5)
Mn3-N8A	1.84(3)	Mn3-N8B-C8B	158.5(15)
Mn3-N8B	2.198(14)	Mn4[3]-N4B-C4B	148.6(17)
Mn4-N4A[1]	2.36(2)	Mn4-N9A-C9A	166(5)
Mn4-N4B[1]	2.163(12)	Mn4-N9B-C9B	163.7(14)
Mn4-N9A	1.78(2)	Mo1-C1-N1	178.2(13)
Mn4-N9B	2.252(12)	Mo1-C2-N2	175.3(12)
Mo1-C1	2.112(12)	Mo1-C6-N6	175.3(11)
Mo1-C2	2.129(12)	Mo1-C7-N7	177.1(12)
Mo1-C6	2.159(13)	Mo1-C5-N5	175.6(11)
Mo1-C7	2.172(12)	Mo2-C3B-N3B	176.3(15)
Mo1-C5	2.143(11)	Mo2A-C3A-N3A	170(5)
Mo2-C3B	2.136(11)	Mo2-C4B-N4B	176.9(19)
Mo2A-C3A	2.158(18)	Mo2A-C4A-N4A	170(6)
Mo2-C4B	2.133(12)	Mo2-C8B-N8B	177.8(15)
Mo2A-C4A	2.165(18)	Mo2A-C8A-N8A	176(5)
Mo2-C8B	2.138(12)	Mo2-C9B-N9B	179.4(15)
Mo2A-C8A	2.149(18)	Mo2A-C9A-N9A	171(5)
Mo2-C9B	2.155(11)	Mo2-C10B-N10B	175.7(18)
Mo2A-C9A	2.144(18)	Mo2A-C10A-N10A	169(5)
Mo2-C10B	2.159(10)		
Mo2A-C10A	2.196(17)		

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

Complex **2**

Bond lengths [Å]		Bond angles [º]	
Mo1-C1	2.142(5)	Mo1-C1-N1	176.5(5)
Mo1-C6[1]	2.157(5)	Mo1[1]-C6-N6	177.4(5)
Mo1-C2	2.128(5)	Mo1-C2-N2	176.7(4)
Mo1-C3	2.174(5)	Mo1-C3-N3	179.0(4)
Mo1-C4	2.142(5)	Mo1-C4-N4	175.6(4)
Mo1-C5	2.132(6)	Mo1-C5-N5	178.4(7)
Mo1-C7[2]	2.158(5)	Mo1[2]-C7-N7	177.0(4)

[1]2-X,-Y,1-Z; [2]1-X,-Y,1-Z

Table S3. Continuous Shape Measures (CShMs) of compounds **1-*SS***, **1-*RR***, and **2**.

Shape	CShMs					
	1-*SS*		**1-*RR***			**2**
	Mo1	Mo2	Mo1	Mo2	Mo2A	Mo1
Heptagon (D_{7h})	33.365	33.126	32.930	33.024	31.294	33.409
Hexagonal pyramid (C_{6v})	23.796	23.222	23.608	22.737	22.776	24.095
Pentagonal bipyramid (D_{5h})	**0.785**	**0.964**	**0.884**	**1.808**	**5.458**	**0.840**
Capped octahedron (C_{3v})	4.486	4.056	4.313	2.775	6.716	4.723
Capped trigonal prism (C_{2v})	3.565	3.281	3.152	2.450	5.920	3.014
Johnson pentagonal bipyramid J13 (D_{5h})	4.261	4.530	4.500	5.567	9.517	4.470
Johnson elongated triangular pyramid J7 (C_{3v})	21.790	21.069	21.700	30.635	17.405	22.573

Shape	CShMs						
		1-*SS*			**1-*RR***		**2**
	Mn1	Mn3	Mn4	Mn1	Mn3	Mn4	Mn2
Pentagon (D_{5h})	27.257	29.611	27.438	27.053	27.310	26.698	30.233
Vacant octahedron (C_{4v})	5.217	2.163	4.679	5.393	2.590	5.676	5.218
Trigonal bipyramid (D_{3h})	**2.551**	3.872	2.987	**2.853**	6.187	**3.241**	**1.495**
Spherical square pyramid (C_{4v})	3.086	**1.035**	**2.889**	3.298	**1.093**	4.511	3.892
Johnson trigonal bipyramid J12 (D_{3h})	5.130	6.122	5.449	5.322	9.006	6.029	3.966

Shape	CShMs		
	1-*SS*	**1-*RR***	**2**
	Mn2	Mn2	Mn1
Hexagon (D_{6h})	32.205	32.359	32.706
Pentagonal pyramid (C_{5v})	23.502	22.970	26.169
Octahedron (O_h)	**1.786**	**1.632**	**0.672**
Trigonal prism (D_{3h})	11.384	12.215	14.056
Johnson pentagonal pyramid J2 (C_{5v})	27.191	26.508	30.114

Table S4. Molecular formula, space groups, structures, T_c and H_c values for the structurally characterized compounds based on the $[Mo^{III}(CN)_7]^{4-}$ building block.

Compounds	Space group	Structure	T_c/K	H_c/Oe	Ref*.
$Mn_2(H_2O)_5Mo(CN)_7{\cdot}4H_2O$ (α Phase)	Monoclinic $P2_1/c$	3D	51	-	29a
$K_2Mn_3(H_2O)_6[Mo(CN)_7]_2{\cdot}6H_2O$	Monoclinic $C2$	2D	39	125 (5 K)	30a
$Mn_2(H_2O)_5Mo(CN)_7{\cdot}4.75H_2O$ (β Phase)	Monoclinic $P2_1/c$	3D	51	-	29b
$[\{Mn(dpop)\}_6\{Mo^{III}(CN)_7\}\{Mo^{IV}(CN)_8\}_2]{\cdot}19.5H_2O$	Monoclinic $C2/c$	2D	3	-	37a
$[N(CH_3)_4]_2[Mn(H_2O)]_3[Mo(CN)_7]_2{\cdot}2H_2O$	Monoclinic $C2/c$	3D	86	200 (1.8 K)	32
$[Mn_2(tea)Mo(CN)_7]{\cdot}H_2O$	Orthorhombic $Pbca$	3D	75	70 (5 K)	35
$[Mn_2(tea)Mo(CN)_7]$	Orthorhombic $Pca2_1$	3D	106	200 (5 K)	35
$[NH_4]_2Mn_3(H_2O)_4[Mo(CN)_7]_2{\cdot}4H_2O$	Monoclinic $C2/c$	3D	53	-	31
$[\{Mn(HL)\}_2Mn\{Mo(CN)_7\}_2]{\cdot}2H_2O$ (L = N,N-Dimethylalaninol)	Monoclinic $C2$	3D	85	150 (2 K)	34
$Mn_2[Mo(CN)_7]{\cdot}(pyrimidine)_2{\cdot}2H_2O$	Monoclinic $P2_1/n$	3D	47	60 (2 K)	38
$[K_2(H_2O)_4Mn_5(H_2O)_8(MeCN)\{Mo(CN)_7\}_3]{\cdot}2H_2O$	Monoclinic $P2_1/n$	3D	61	70 (2 K)	30b
$\{[Mn(dpop)]_3[Mn(dpop)(H_2O)][Mo(CN)_7]_2{\cdot}13.5H_2O\}_n$	Trigonal $R\bar{3}$	3D	2.6	90 (1.8 K)	37b
$\{[Mn(dpop)]_2[Mo(CN)_7]{\cdot}2H_2O\}_n$	Trigonal $R3$	3D	24	305 (1.8 K)	37b
$\{[Mn(dpop)]_4[(dpop)Mn(H_2O)]_2[Mo(CN)_7]_3{\cdot}27H_2O\}_n$	Monoclinic $P2_1/c$	2D	2.2	30 (1.8 K)	37c
$[Mn(L_{N5C10})]_2[Mo(CN)_7]{\cdot}2H_2O$	Orthorhombic $Pnma$	1D	5.6	1150 (2 K)	21
$\{Fe_2(H_2O)_5[Mo(CN)_7]{\cdot}5H_2O\}_n$	Monoclinic $P2_1$	3D	65	6000 (2 K)	22
$\{[NH_2(CH_3)_2]_2Fe_5(H_2O)_{10}[Mo(CN)_7]_3{\cdot}8H_2O\}_n$	Orthorhombic $Pnma$	3D	65	1900 (2 K)	22
$Mn_2(3\text{-pypz})(H_2O)(CH_3CN)[Mo(CN)_7]$	Monoclinic $C2/m$	3D	64	820 (2 K)	23
$Mn_2(1\text{-pypz})(H_2O)(CH_3CN)[Mo(CN)_7]$	Monoclinic $C2/m$	3D	66	72 (2 K)	23
$Mn_2(pyim)(H_2O)(CH_3CN)$	Monoclinic $C2/m$	3D	62	146 (2 K)	23

$[Mo(CN)_7]$					
$\{(NH_4)_3[(H_2O)Mn_3(HCOO)][Mo(CN)_7]_2{\cdot}4H_2O\}_n$	Orthorhombic *Pbam*	3D	70	1500 (2 K)	25
$Mn_2(DMF)(H_2O)_2[Mo(CN)_7]{\cdot}H_2O{\cdot}CH_3OH$	Triclinic $P\bar{1}$	3D	80	250 (2 K)	24
$Mn_2(DEF)(H_2O)[Mo(CN)_7]$	Monoclinic $P2_1/n$	3D	80	200 (2 K)	24
$\{[Mn(imH)_2]_2[Mn(H_2O)(imH)_3][Mn(imH)_4][Mo(CN)_7]_2{\cdot}6H_2O\}_n$	Monoclinic $C2/c$	3D	29	5000 (1.8 K)	33
$\{[Mn(H_2O)_2(imH)]_3[Mn(H_2O)(imH)_2][Mo(CN)_7]_2{\cdot}5H_2O\}_n$	Triclinic $P\bar{1}$	3D	45	4500 (1.8 K)	33
$\{[Mn(Htrz)(H_2O)_2][Mn(Htrz)_{0.7}(H_2O)_{2.3}][Mo(CN)_7]{\cdot}5.6H_2O\}_n$	Triclinic $P\bar{1}$	3D	45	710 (1.8 K)	33
$\{[Mn(H_2O)_2]_3[Mn(H_2O)_4][Mo(CN)_7]_2{\cdot}6H_2O{\cdot}2urea\}_n$	Triclinic $P\bar{1}$	3D	59	110 (1.8 K)	33
$[Mn(bida)(H_2O)]_2[Mo(CN)_7]{\cdot}6H_2O$	Triclinic $P\bar{1}$	1D	5.8	15000 (2 K)	20
$\{[Mn(Dpen)]_3[Mn(Dpen)(H_2O)][Mo(CN)_7]_2{\cdot}4.5H_2O{\cdot}4C_2H_3N\}_n$	Monoclinic $P2_1$	2D	40	8000 (2 K)	This work
$\{[Mn(Chxn)][Mn(Chxn)(H_2O)][Mo(CN)_7]{\cdot}H_2O{\cdot}4C_2H_3N\}_n$	Triclinic $P\bar{1}$	2D	40	2000 (2 K)	This work

*The reference numbers refer to the references in the main text.