Electronic supplementary information (ESI)

Exploring catecholase activity in dinuclear Mn(II) and Cu(II) complexes: An experimental and theoretical approach

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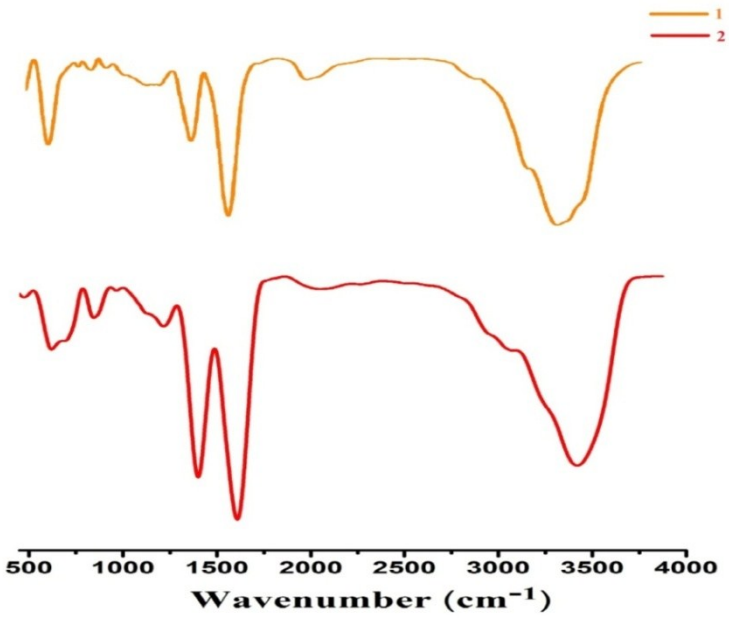

Fig. S1. FTIR spectra of **1** and **2**.

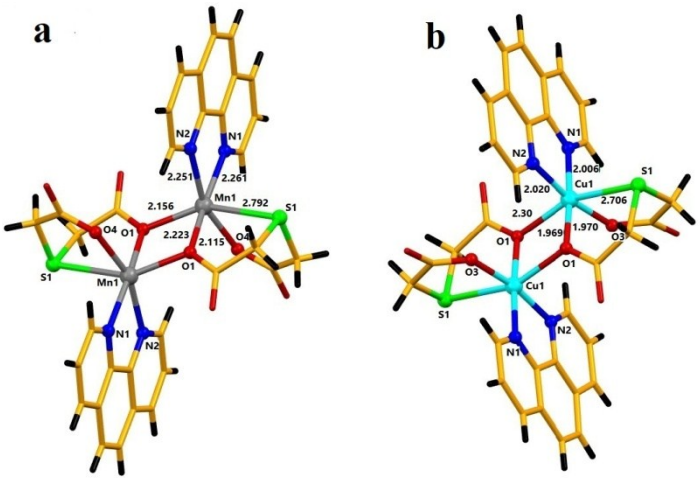

Fig. S2. Selected bond distances and bond angles for **1** and **2**.

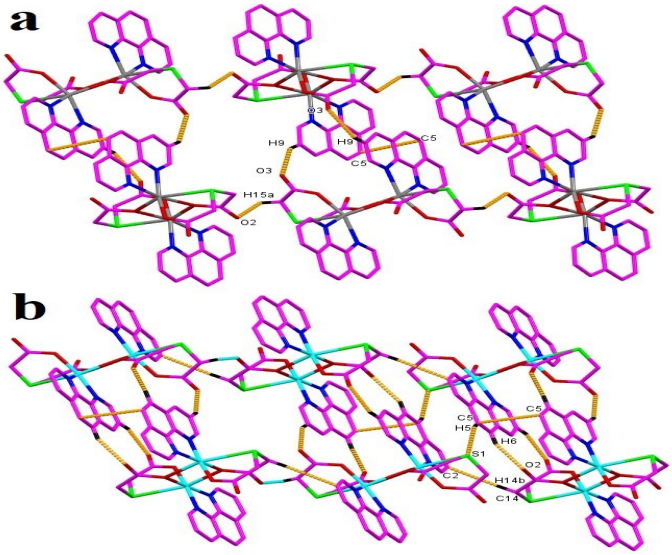

Fig. S3. (a) Formation of a 2D sheet network as a result of O···H and π···π interactions in **1**. (b) Formation of a 2D sheet network through O···H, S···H, C–H···π and π···π interactions in **2**.

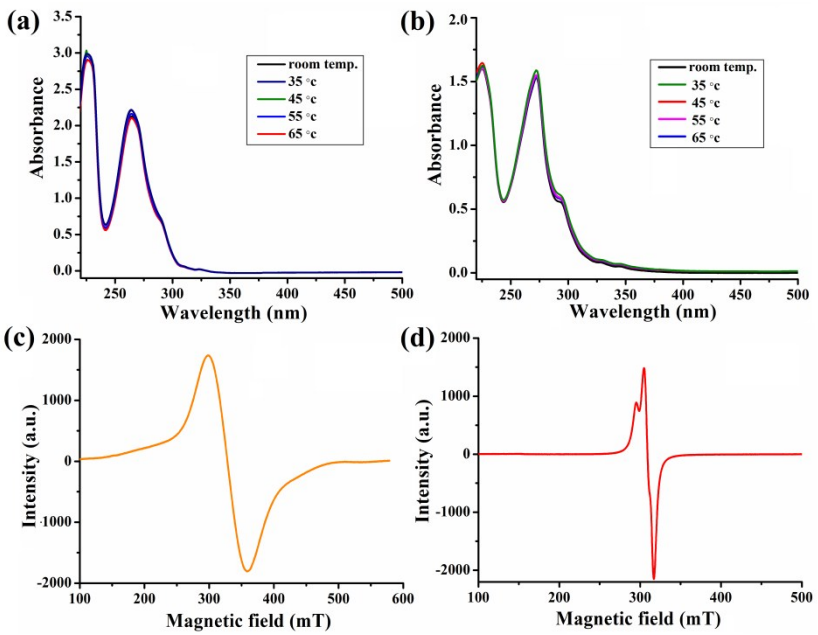

Fig. S4. Thermal UV-visible spectra of **1** (a) and **2** (b) and EPR spectra for **1** (c) and **2** (d).

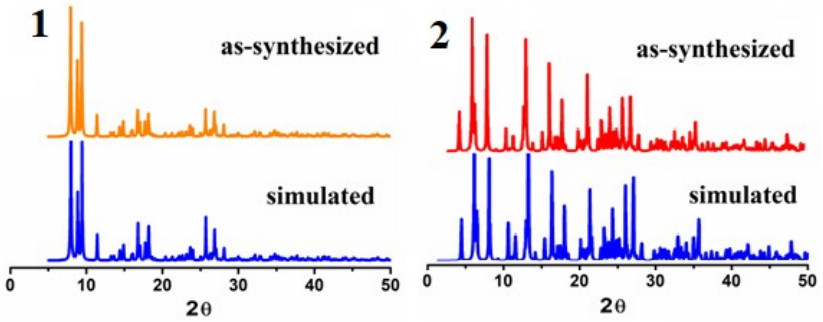

Fig. S5. As-synthesized and simulated PXRD patterns for **1** and **2**.

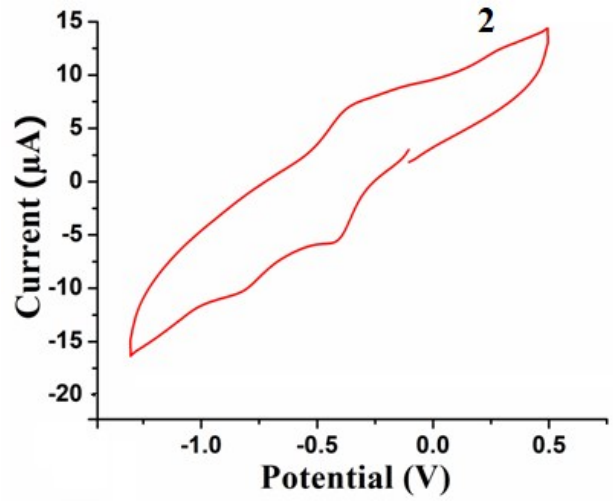

Fig. S6. Cyclic voltammogram of **2** obtained at a 100 mVs^{-1} scan rate.

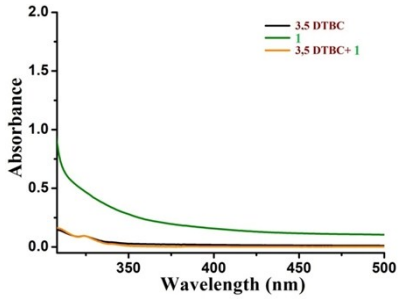

Fig. S7. Time-dependent UV–vis spectra for **1** (10^{-4} M) upon the addition of (100-fold) 3,5-DT BC (10^{-2} M) in MeOH at 298 K.

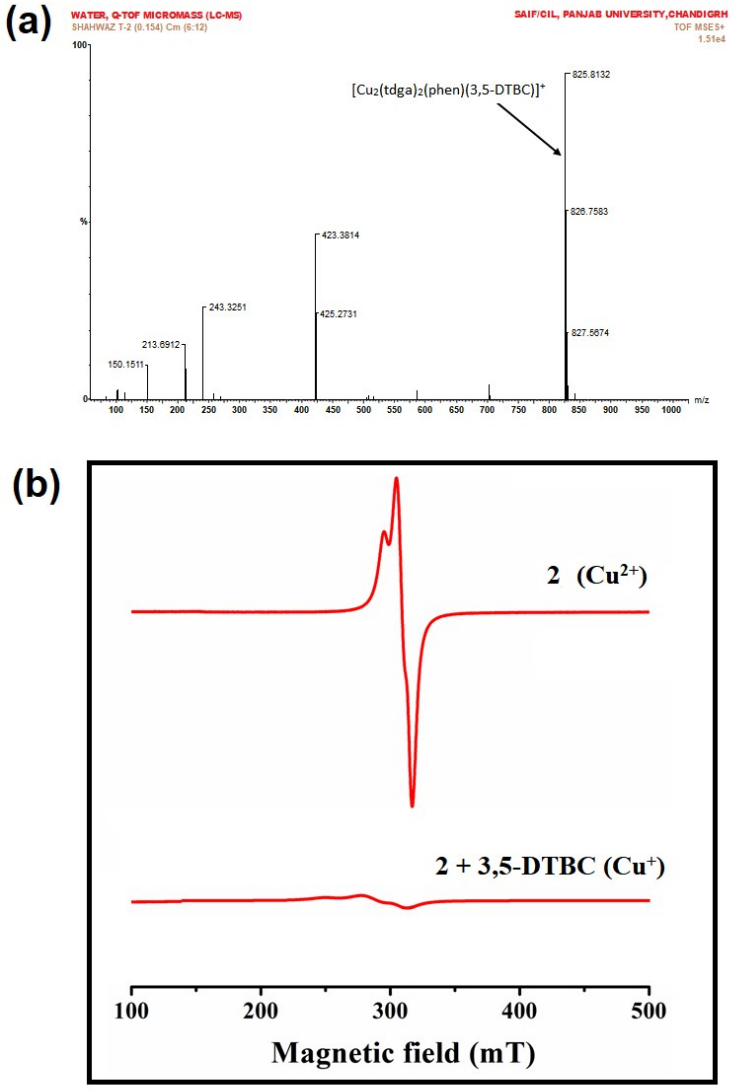

Fig. S8. (a) ESI-MS spectrum (positive mode) of a mixture of **2** and 3,5-DTBC recorded in methanol. (b) EPR spectrum of the complex and before and after mixing 3,5-DTBC.

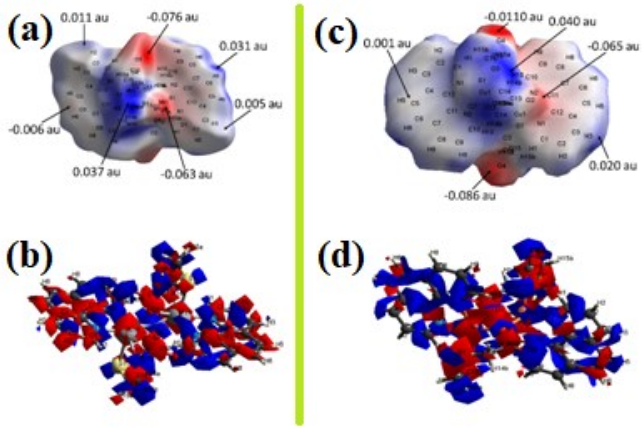

Fig. S9. The ESP map front view and 3D-deformation density map showing the presence of CD regions (in red) and CC regions (in blue). The iso surfaces are drawn at 0.008 for **1** (a, b), **2** (c, d).

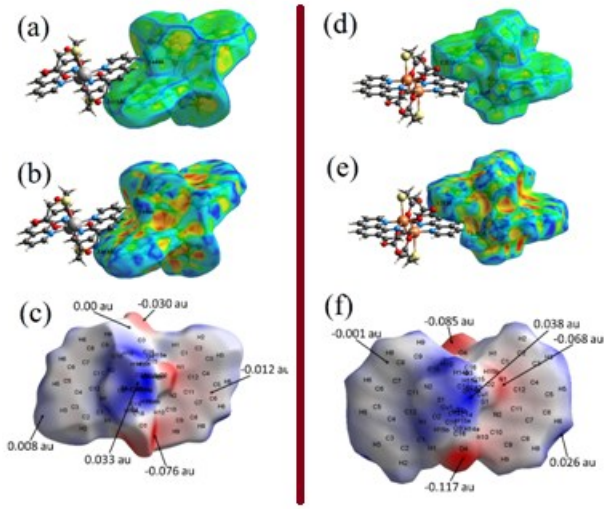

Fig. S10. Intermolecular O···H interactions through red spots shown by Hirshfeld surface mapping over (a) curvedness, (b) shape index and the ESP back view for **1** (a), (b) and (c) and **2** (d), (e) and (f).

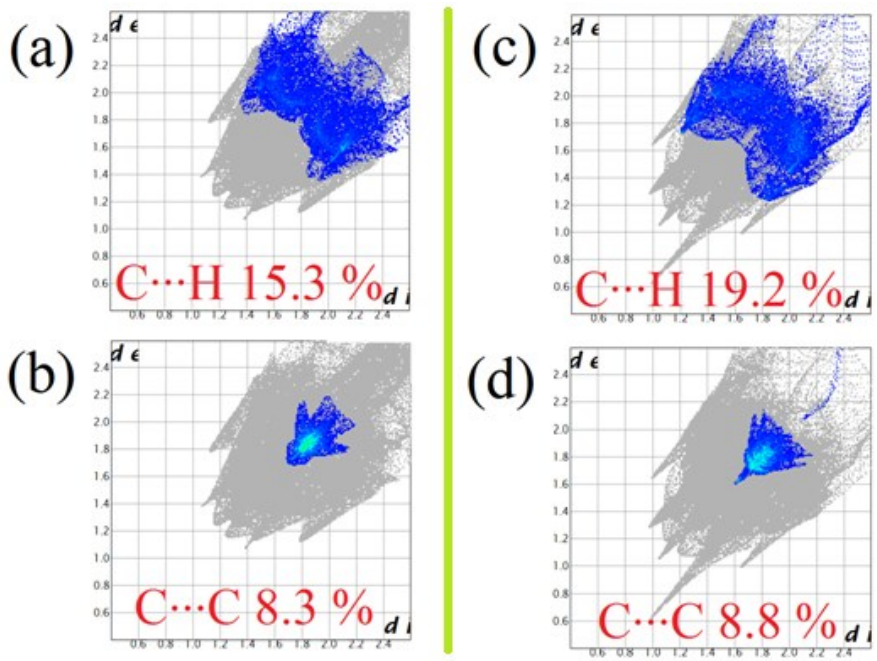

Fig. S11. The 2D-fingerprint plots of **1** (a) and (b), **2** (c), and (d) for showing different interactions.

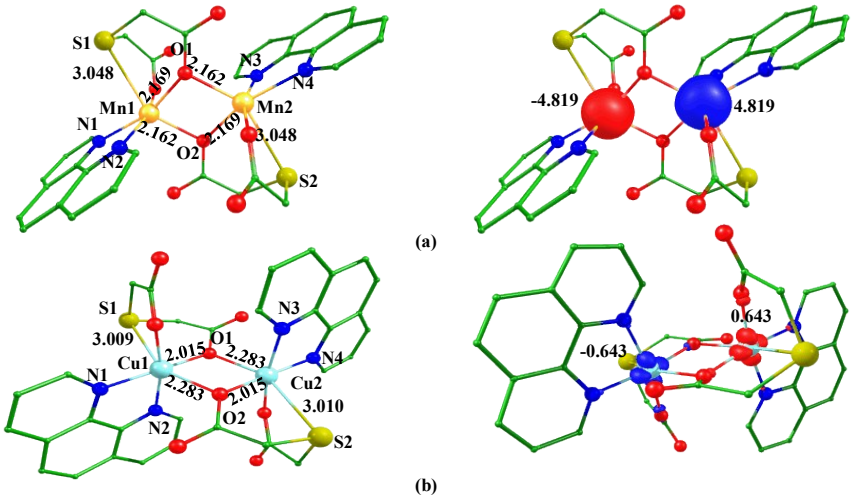

Fig. S12. B3LYP (a) optimized structure (left) and its spin density (right) plot of $^{1}\mathbf{1}_{(hs,hs)}$ and (b) optimized structure (left) and its spin density plot (right) of the $^{1}\mathbf{2}$.

Table. 1S Bond Lengths for **1.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	S1	2.793(4)	C1	C2	1.384(12)
Mn1	O1[1]	2.155(6)	C3	C2	1.376(13)
Mn1	O1	2.223(6)	C4	C3	1.411(13)
Mn1	O4	2.115(7)	C4	C5	1.440(11)
Mn1	N1	2.260(7)	C6	C5	1.336(13)
Mn1	N2	2.251(6)	C7	C6	1.445(12)
S1	C14	1.837(10)	C7	C8	1.411(13)
S1	C15	1.777(12)	C8	C9	1.366(14)
O1	C13	1.276(11)	C10	C9	1.391(13)
O3	C16	1.248(13)	C11	C7	1.429(10)
O4	C16	1.292(14)	C11	C12	1.443(10)
N1	C1	1.353(10)	C12	C4	1.419(10)
N1	C12	1.359(9)	C13	O2	1.223(10)
N2	C10	1.341(10)	C13	C14	1.515(14)
N2	C11	1.369(9)	C16	C15	1.516(18)

Table. 2S Bond Lengths for **2.**

Atom	Atom	Length/Å
Cu1	S1	2.7081(7)
Cu1	O1	1.9687(18)
Cu1	O1[1]	2.2997(17)
Cu1	O3	1.9704(18)
Cu1	N1	2.008(2)
Cu1	N2	2.020(2)
S1	C14	1.804(3)
S1	C15	1.802(3)
O1	C13	1.289(3)
O2	C13	1.223(3)
O3	C16	1.264(3)
O4	C16	1.251(3)
N1	C1	1.326(3)
N1	C12	1.354(3)
N2	C10	1.325(3)
N2	C11	1.360(3)
C1	C2	1.401(4)
C2	C3	1.367(4)
C3	C4	1.407(4)
C4	C5	1.431(4)
C4	C12	1.401(4)
C5	C6	1.349(4)
C6	C7	1.436(4)
C7	C8	1.400(4)
C7	C11	1.405(4)
C8	C9	1.370(4)
C9	C10	1.406(4)
C11	C12	1.426(4)
C13	C14	1.526(4)
C15	C16	1.524(4)
S2	C17	1.820(3)
S2	C17[2]	1.820(3)
O5	C18	1.212(3)
O6	C18	1.324(3)
C17	C18	1.499(4)

Table. 3S Bond Angles for **1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Mn1	S1	148.91(17)	C1	C2	C3	119.0(8)
O1	Mn1	S1	74.66(18)	C2	C3	C4	120.0(8)
O1	Mn1	N1	167.9(2)	C3	C4	C12	117.6(7)
O1[1]	Mn1	N1	113.1(3)	C5	C4	C3	123.3(7)
O4	Mn1	S1	75.4(2)	C5	C4	C12	119.1(8)
O4	Mn1	O1[1]	94.9(3)	C6	C5	C4	121.6(7)
O4	Mn1	O1	93.7(3)	C5	C6	C7	121.3(7)
O4	Mn1	N1	92.6(2)	C6	C7	C11	119.1(8)
O4	Mn1	N2	160.0(3)	C8	C7	C6	124.3(7)
N1	Mn1	S1	97.0(2)	C8	C7	C11	116.6(8)
N2	Mn1	S1	90.44(19)	C9	C8	C7	119.6(8)
N2	Mn1	O1	96.1(2)	C10	C9	C8	121.1(9)
N2	Mn1	O1[1]	104.3(2)	C9	C10	N2	121.3(9)
N2	Mn1	N1	74.9(2)	C7	C11	N2	122.3(7)
C14	S1	Mn1	93.8(4)	C7	C11	C12	119.1(7)
C15	S1	Mn1	95.3(5)	C12	C11	N2	118.5(6)
C15	S1	C14	99.9(5)	C4	C12	N1	121.9(7)
C13	O1	Mn1[1]	125.0(5)	C4	C12	C11	119.6(6)
C13	O1	Mn1	127.2(6)	C11	C12	N1	118.4(6)
C16	O4	Mn1	129.1(7)	O2	C13	O1	124.7(10)
C1	N1	Mn1	127.6(5)	C14	C13	O1	116.4(8)
C1	N1	C12	118.4(6)	C14	C13	O2	118.8(10)
C12	N1	Mn1	114.0(5)	C13	C14	S1	114.7(7)
C10	N2	Mn1	127.1(5)	C16	C15	S1	117.1(8)
C10	N2	C11	118.9(7)	O4	C16	O3	121.1(15)
C11	N2	Mn1	113.9(5)	C15	C16	O3	117.0(14)
C2	C1	N1	123.2(8)	C15	C16	O4	121.9(9)

Table. 4S Bond Angles for **2.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Cu1	S1	81.09(5)	C12	C4	C3	117.2(2)
O1[1]	Cu1	S1	157.70(5)	C12	C4	C5	118.4(2)
O3	Cu1	S1	80.90(5)	C6	C5	C4	121.8(2)
O3	Cu1	O1	92.37(8)	C7	C6	C5	120.8(2)
O3	Cu1	O1[1]	91.71(7)	C8	C7	C6	124.6(2)
N1	Cu1	S1	102.06(6)	C11	C7	C6	118.6(2)
N1	Cu1	O1	175.58(8)	C11	C7	C8	116.8(2)
N1	Cu1	O1[1]	99.08(7)	C9	C8	C7	119.8(2)
N1	Cu1	O3	91.19(8)	C10	C9	C8	119.8(3)
N2	Cu1	S1	93.42(6)	C9	C10	N2	121.8(3)
N2	Cu1	O1	94.81(8)	C7	C11	N2	123.3(2)
N2	Cu1	O1[1]	96.47(7)	C12	C11	N2	116.6(2)
N2	Cu1	O3	170.06(8)	C12	C11	C7	120.2(2)
N2	Cu1	N1	81.98(9)	C4	C12	N1	123.1(2)
C14	S1	Cu1	90.24(9)	C11	C12	N1	116.7(2)
C15	S1	Cu1	90.49(9)	C11	C12	C4	120.2(2)
C15	S1	C14	103.25(13)	O2	C13	O1	124.6(2)
C13	O1	Cu1	125.19(16)	C14	C13	O1	117.9(2)
C13	O1	Cu1[1]	126.57(16)	C14	C13	O2	117.3(2)
C16	O3	Cu1	126.68(17)	C13	C14	S1	118.15(19)
C1	N1	Cu1	128.90(18)	C16	C15	S1	118.28(18)
C12	N1	Cu1	112.59(16)	O4	C16	O3	123.0(2)
C12	N1	C1	118.5(2)	C15	C16	O3	121.8(2)
C10	N2	Cu1	129.28(18)	C15	C16	O4	115.2(2)
C11	N2	Cu1	111.92(17)	C17[2]	S2	C17	93.74(18)
C11	N2	C10	118.6(2)	C18	C17	S2	115.3(2)
C2	C1	N1	122.0(3)	O6	C18	O5	124.2(3)
C3	C2	C1	120.0(3)	C17	C18	O5	125.2(3)
C4	C3	C2	119.1(2)	C17	C18	O6	110.5(2)
C5	C4	C3	124.4(2)				

Table S5. Possible spin interactions of the **1.**

	Electronic Configurations	
Spin States	**Metal 1**	**Metal 2**
$^{11}1_{(hs,hs)}$	↑↑↑↑↑	↑↑↑↑↑

Table S6. Computed selected structural parameters of **1** and **2**.

	Bond lengths(Å)											Bond angle (°)			
	Mn1-Mn2	**Mn1-O1**	**O1-Mn2**	**Mn1-O2**	**O2-Mn2**	**Mn1-N1**	**Mn1-N2**	**Mn2-N3**	**Mn2-N4**	**Mn1-S**	**Mn2-S**	**Mn1-O1-Mn2**	**Mn1-O2-Mn2**	**N1-Mn1-N2**	**N1-Mn2-N2**
^{11}1$_{(hs,hs)}$	**3.367**	**2.171**	**2.162**	**2.162**	**2.171**	**2.255**	**2.268**	**2.268**	**2.255**	**3.046**	**3.046**	**101.9**	**101.9**	**74.0**	**74.0**
^{1}1$_{(hs,hs)}$	**3.364**	**2.169**	**2.162**	**2.162**	**2.169**	**2.255**	**2.268**	**2.268**	**2.255**	**3.048**	**3.048**	**101.8**	**101.8**	**74.0**	**74.0**
^{7}1$_{(is,is)}$	**3.384**	**2.301**	**1.999**	**1.999**	**2.301**	**2.025**	**1.997**	**1.997**	**2.025**	**2.926**	**2.926**	**103.5**	**103.5**	**81.0**	**81.0**
^{1}1$_{(is,is)}$	**3.392**	**2.304**	**1.998**	**1.998**	**2.304**	**2.025**	**1.996**	**1.996**	**2.025**	**2.927**	**2.927**	**103.8**	**103.8**	**81.0**	**81.0**
^{3}1$_{(ls,ls)}$	**3.275**	**2.064**	**2.104**	**2.201**	**2.012**	**2.005**	**2.031**	**2.038**	**2.016**	**2.917**	**2.576**	**103.5**	**101.9**	**80.8**	**80.7**
^{1}1$_{(ls,)}$	**3.4**	**2.9**	**2.7**	**2.6**	**2.8**	**2.2**	**2.1**	**2.0**	**2.2**	**2.5**	**2.5**	**15**	**106**	**80.7**	**80.7**

	Cu1-Cu2	**Cu1-O1**	**O1-Cu2**	**Cu1-O2**	**O2_Cu2**	**Cu1_N1**	**Cu1_N2**	**Cu2_N3**	**Cu2_N4**	**Cu1_S**	**Cu2_S**	**Cu1-O1-Cu2**	**Cu1-O2-Cu2**	**N1-Cu1-N2**	**N1-Cu2-N2**
^{3}2	**3.332**	**2.015**	**2.282**	**2.282**	**2.015**	**2.067**	**2.067**	**2.067**	**2.066**	**3.009**	**3.009**	**101.4**	**101.4**	**80.4**	**80.4**
^{1}2	**3.332**	**2.015**	**2.283**	**2.283**	**2.015**	**2.066**	**2.067**	**2.067**	**2.066**	**3.009**	**3.010**	**101.4**	**101.4**	**80.4**	**80.4**

Table S7. Computed spin densities of **1** and **2**.

Spin States	Mn1	Mn2
$^{11}1_{(hs,hs)}$	4.806	4.806
$^{1}1_{(hs,hs)}$	4.819	-4.819
$^{7}1_{(is,is)}$	3.261	3.261
$^{1}1_{(is,is)}$	3.267	-3.267
$^{3}1_{(ls,ls)}$	1.068	1.068
$^{1}1_{(ls,ls)}$	1.075	-1.075

	Cu1	Cu2
$^{3}2$	0.641	0.641
$^{1}2$	-0.643	0.643