Supplementary Information

COMPUTATIONAL METHODS:

All calculations have been performed using density functional methods as implemented in CP2k program package.[1-4] The CP2k package utilizes a hybrid basis set formalism known as Gaussian and Plane Wave Method[1] (GPW) where the Kohn–Sham orbitals are expanded in terms of contracted Gaussian type orbitals (GTOs), while an auxiliary plane wave basis set is used to expand the electronic charge density. A double-ζ GTH basis set and their relativistic norm-conserving pseudo potentials (Goedecker, Teter, and Hutter)[3] optimized for PBE were used in addition to a plane wave basis set with an energy cut-off of 400 Ry. All calculations were carried out with DZVP-MOLOPT-GTH (valence double-zeta (ζ) plus polarization, molecularly optimized, Goedecker-Teter-Hutter) basis set for all atoms (H, C, O, S, Cl) and DZVP-MOLOPT-SR-GTH (valence double-zeta (ζ) plus polarization, molecularly optimized, short-range Goedecker-Teter-Hutter) basis set for Au and Mn as implemented in the CP2k program package.[1-4] And the pseudo-potential used where GTH-pseud-potential (Goedecker-Teter-Hutter). For our calculations, we have employed PBE functional as implemented in CP2k package.[2] The unit cell are designed to obtain in both the cases, a three layered Au(111) surface applying periodic boundary conditions over an orthorhombic simulation cell. The convergence criteria of 1 x 10^{-6} Hartree for the SCF energy had been employed throughout.[2] The simulation cell has been employed such that x and y axes are on the surface plane as reference axes. The size along z-axis is kept more than 60 Å. An empty space is therefore left to prevent inter cells interaction and polarization effects. To account for the dispersion a DFTD2 approach has been used throughout the calculations.

Exchange part of the Hamiltonian adapted for complex **1** is given below,

$$\begin{aligned}\hat{H}_{Ex} = & -J_1\left[\left(\hat{S}_2\hat{S}_5+\hat{S}_3\hat{S}_6+\hat{S}_4\hat{S}_7+\hat{S}_{11}\hat{S}_{15}+\hat{S}_{12}\hat{S}_{16}+\hat{S}_{13}\hat{S}_{14}\right)\right]-J_2\left[\left(\hat{S}_2\hat{S}_6+\hat{S}_3\hat{S}_7+\hat{S}_4\hat{S}_5+\right.\right.\\ & -J_3\left[\left(\hat{S}_5\hat{S}_6+\hat{S}_5\hat{S}_7+\hat{S}_6\hat{S}_7+\hat{S}_{14}\hat{S}_{15}+\hat{S}_{15}\hat{S}_{16}+\hat{S}_{14}\hat{S}_{16}\right)\right]-J_4\\ & \left[\left(\hat{S}_2\hat{S}_3+\hat{S}_2\hat{S}_4+\hat{S}_3\hat{S}_4+\hat{S}_{11}\hat{S}_{12}+\hat{S}_{11}\hat{S}_{13}+\hat{S}_{12}\hat{S}_{13}\right)\right]-J_5\\ & \left[\left(\hat{S}_1\hat{S}_2+\hat{S}_1\hat{S}_3+\hat{S}_1\hat{S}_4+\hat{S}_1\hat{S}_{11}+\hat{S}_1\hat{S}_{12}+\hat{S}_1\hat{S}_{13}\right)\right]-J_6\\ & \left[\left(\hat{S}_5\hat{S}_{10}+\hat{S}_6\hat{S}_8+\hat{S}_7\hat{S}_9+\hat{S}_{14}\hat{S}_{18}+\hat{S}_{15}\hat{S}_{19}+\hat{S}_{16}\hat{S}_{17}\right)\right]-J_7\\ & \left[\left(\hat{S}_2\hat{S}_{10}+\hat{S}_3\hat{S}_8+\hat{S}_4\hat{S}_9+\hat{S}_{11}\hat{S}_{19}+\hat{S}_{12}\hat{S}_{17}+\hat{S}_{13}\hat{S}_{18}\right)\right]-J_8\\ & \left[\left(\hat{S}_5\hat{S}_9+\hat{S}_6\hat{S}_{10}+\hat{S}_7\hat{S}_8+\hat{S}_{14}\hat{S}_{19}+\hat{S}_{15}\hat{S}_{17}+\hat{S}_{16}\hat{S}_{18}\right)\right]\end{aligned}$$

Table S1: Comparison of the magnetic exchange coupling parameters of the {Mn19} as calculated by using PBE functional with those calculated by Ruiz by the Eliseo and PBE and applying both functional.[5] B3LYP

Ruiz etal				This Work	
Exchange Coupling	*bridging ligands*	J_{PBE}	J_{B3LYP}	*bridging ligands*	J_{PBE}
J_1	μ_4-O, μ_3-N_3	9.9	3.0	μ_4-O, μ_3-Cl	9.8
J_2	μ_4-O, μ_3-N_3	15.7	15.2	μ_4-O, μ_3-Cl	17.9
J_3	μ_4-O, μ_3-N_3	16.8	11.3	μ_4-O, μ_3-Cl	29.7
J_4	μ_4-O, μ_3-N_3	22.2	14.0	μ_4-O, μ_3-Cl	0.9
J_5	μ_4-O, μ_2-OR	3.6	1.8	μ_4-O, μ_2-O	1.6
J_6	μ_4-O, μ_2-OR	7.2	5.4	μ_4-O, μ_2-O	7.6
J_7	μ_4-O, μ_2-OR	7.2	3.4	μ_4-O, μ_2-O	4.8
J_8	μ_4-O, μ_2-OR	5.1	1.6	μ_4-O, μ_2-O	0.6

Spin density plots and spin densities: Extent of spin delocalization can be understood by analyzing the computed spin density plot (see Figure 2b). All the Mn^{III} atoms found to possess a net spin density of 3.82 to 3.90 while the Mn^{II} atoms found to be in the range of 4.78 to 4.86. Upon adsorption on the surface, these values are nearly unaltered (See Table S6-S8) and this suggests that the magnetic core is still protected upon adsorption. Most notable changes on the ligand atoms include small variation in the sign as well magnitude of spin density when the Mn^{III} atoms switch its geometry from octahedral in the X-ray to square-pyramidal in end-on/side-on geometries. All the spin density plots of different broken symmetry analysis as calculated by us using CP2k program package have been shown below. The pink color shows positive spin density whereas blue ones show negative spin density.

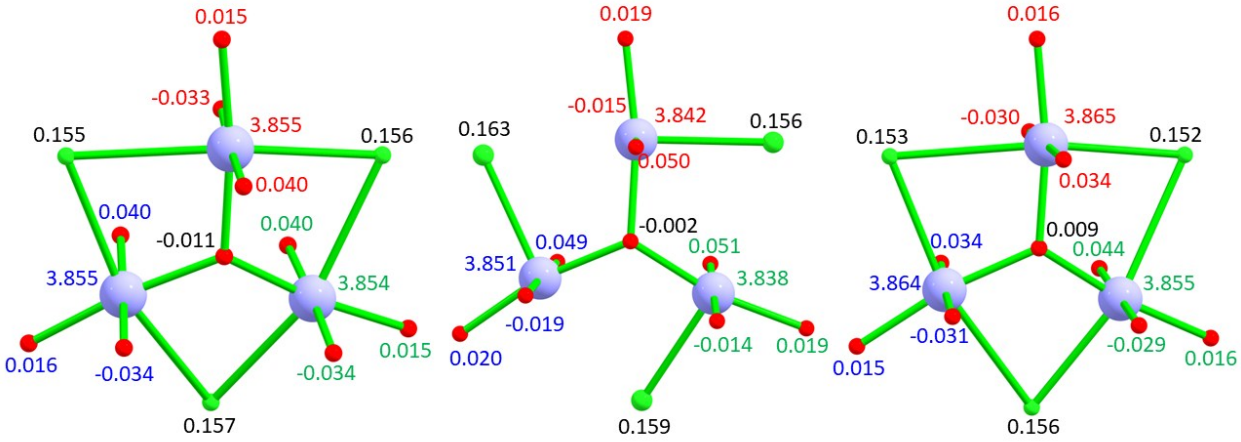

Figure S1: Spin density of individual atoms in a model system of three different geometries of **1**.

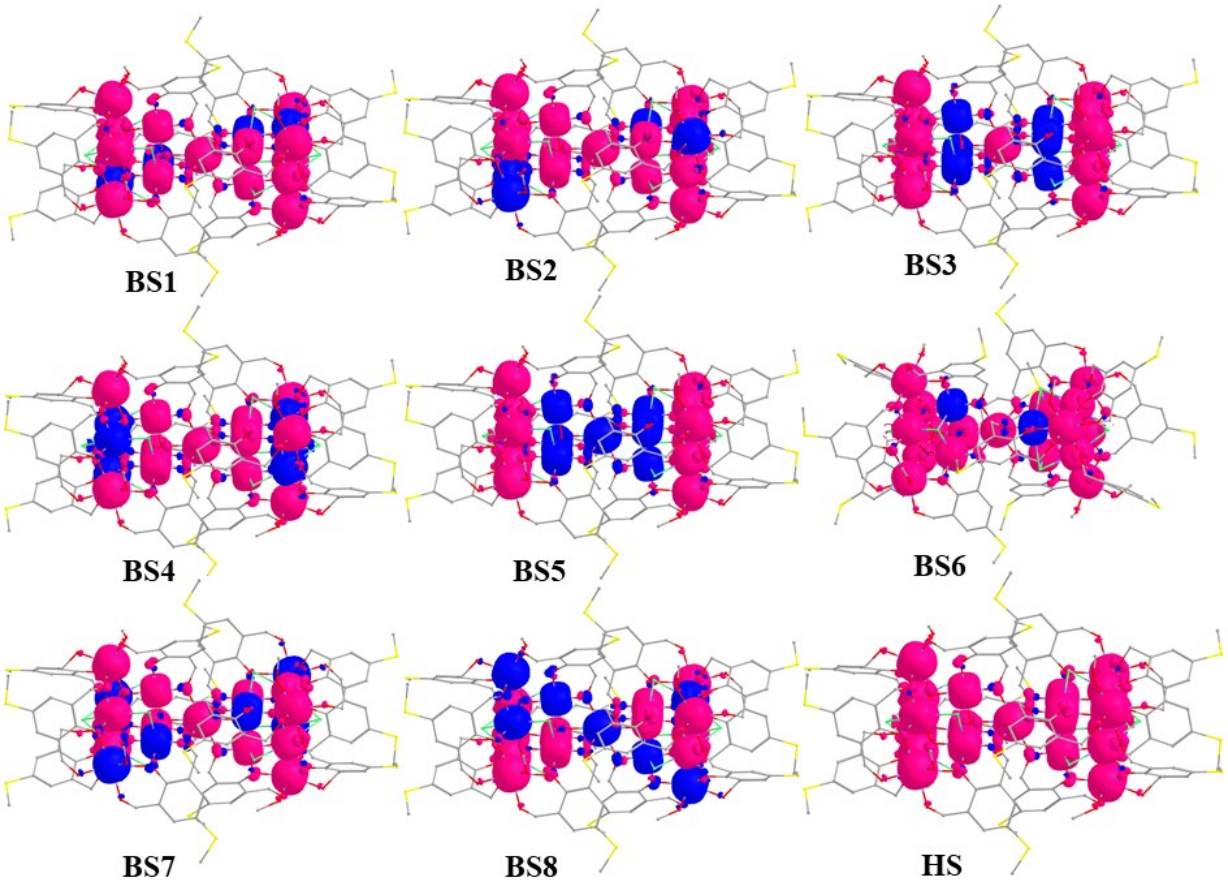

Figure S2: Showing spin density plots of various broken symmetry solution computed for complex **1** using X-ray structure.

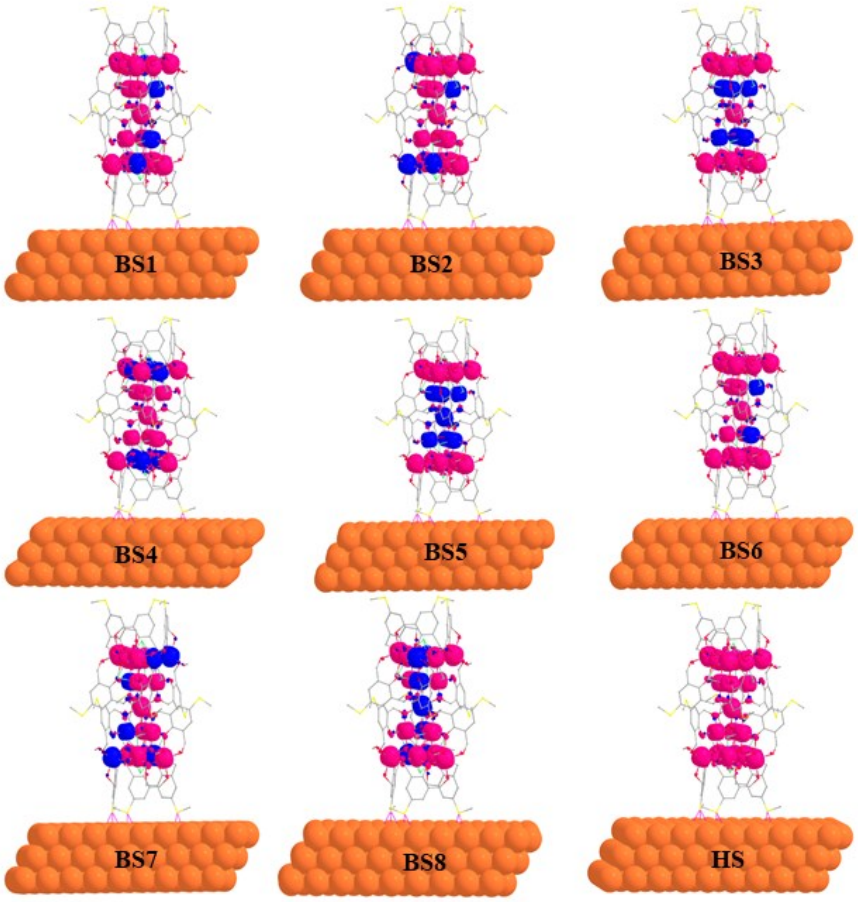

Figure S3: Spin density plots of high-spin and various broken symmetry solution for the optimized geometry of **1** on Au(111) surface (end-on orientation).

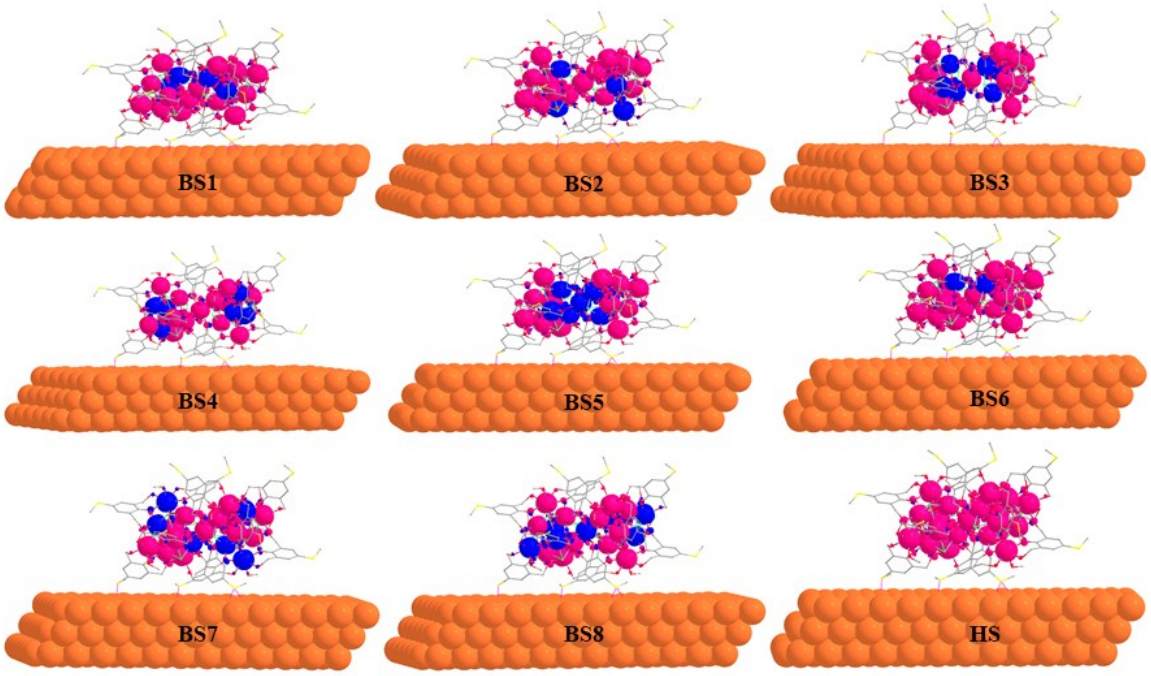

Figure S4: Spin density plots of high-spin and various broken symmetry solutions for optimized geometry of **1** on Au(111) surface (side-on orientation).

Table S2: Selected structural parameter along with the exchange coupling constant of the X-ray structure of complex **1**. Mn atom numbers as per Figure 1b in the main manuscript.

Mn		*bridging ligands*	*M · · · M (Å)*	Mn^{III}	Mn^{III}	Mn^{II}	Mn^{II}		
				Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O-Mn	Mn-O-Mn
2,5	J_1	μ_4-O, μ_3-Cl	3.31612	1.92735	2.66958	1.93155	2.66559	118.486	76.86
3,6	J_1	μ_4-O, μ_3-Cl	3.31612	1.9275	2.66841	1.931	2.66493	118.506	76.891
4,7	J_1	μ_4-O, μ_3-Cl	3.317	1.92801	2.6701	1.93155	2.66559	118.504	76.875
11,15	J_1	μ_4-O, μ_3-Cl	3.31612	1.92683	2.66914	1.93184	2.66573	118.497	76.865
12,16	J_1	μ_4-O, μ_3-Cl	3.31612	1.92801	2.66958	1.9307	2.66559	118.495	76.86
13,14	J_1	μ_4-O, μ_3-Cl	3.317	1.92801	2.66937	1.93155	2.66478	118.504	76.902
2,6	J_2	μ_4-O, μ_3-Cl	3.22394	1.92735	2.76695	1.91068	2.66493	114.279	72.787
3,7	J_2	μ_4-O, μ_3-Cl	3.22443	1.9275	2.76782	1.91032	2.66559	114.316	72.776
4,5	J_2	μ_4-O, μ_3-Cl	3.22356	1.92801	2.76695	1.90977	2.66559	114.27	72.768
11,14	J_2	μ_4-O, μ_3-Cl	3.22307	1.92683	2.76695	1.9094	2.66478	114.314	72.767
12,15	J_2	μ_4-O, μ_3-Cl	3.22443	1.92801	2.76695	1.91068	2.66573	114.275	72.788
13,16	J_2	μ_4-O, μ_3-Cl	3.22443	1.92801	2.76782	1.91068	2.66559	114.275	72.776

5,6	J_3	μ_4-O, μ_3-Cl	3.19197	1.93155	2.65478	1.91068	2.65576	112.353	73.892
6,7	J_3	μ_4-O, μ_3-Cl	3.19155	1.931	2.65576	1.91032	2.65437	112.371	73.888
7,5	J_3	μ_4-O, μ_3-Cl	3.19115	1.90977	2.65478	1.93155	2.65437	112.349	73.893
14,15	J_3	μ_4-O, μ_3-Cl	3.22443	1.92801	2.76695	1.91068	2.66573	114.275	72.788
15,16	J_3	μ_4-O, μ_3-Cl	3.19155	1.91068	2.65485	1.9307	2.65478	112.368	73.896
16,14	J_3	μ_4-O, μ_3-Cl	3.19197	1.93155	2.65528	1.91068	2.65478	112.353	73.9
2,3	J_4	μ_4-O, μ_3-Cl	3.21233	1.8864	2.76695	1.8864	2.66841	116.739	72.431
3,4	J_4	μ_4-O, μ_3-Cl	3.21358	1.8864	2.76782	1.88714	2.6701	116.775	72.425
4,2	J_4	μ_4-O, μ_3-Cl	3.21239	1.8864	2.66958	1.88714	2.76695	116.705	72.415
11,12	J_4	μ_4-O, μ_3-Cl	3.21277	1.88653	2.66914	1.8864	2.76695	116.757	72.432
12,13	J_4	μ_4-O, μ_3-Cl	3.21277	1.8864	2.66958	1.887	2.76782	116.734	72.411
13,11	J_4	μ_4-O, μ_3-Cl	3.21277	1.88653	2.76695	1.887	2.66937	116.727	72.428
1,2	J_5	μ_4-O, μ_2-O	3.43946	2.55189	2.30911	1.8864	1.84769	100.529	111.187

1,3	J_5	μ_4-O, μ_2-O	3.43982	2.55189	2.30845	1.8864	1.84754	100.544	111.239
1,4	J_5	μ_4-O, μ_2-O	3.43946	2.55189	2.30845	1.88714	1.84762	100.508	111.218
1,11	J_5	μ_4-O, μ_2-O	3.44032	2.55189	2.30882	1.88653	1.84877	100.561	111.2
1,12	J_5	μ_4-O, μ_2-O	3.43946	2.55189	2.30874	1.8864	1.84704	100.529	111.228
1,13	J_5	μ_4-O, μ_2-O	3.43896	2.55189	2.30845	1.887	1.84704	100.491	111.215
5,10	J_6	μ_4-O, μ_2-O	3.30559	1.93155	1.90295	2.25516	2.33369	104.019	102.086
6,8	J_6	μ_4-O, μ_2-O	3.30558	1.931	1.90202	2.25584	2.33405	104.011	102.101
7,9	J_6	μ_4-O, μ_2-O	3.30601	1.93155	1.90295	2.25478	2.33478	104.051	102.065
14,18	J_6	μ_4-O, μ_2-O	3.30681	1.93155	1.90295	2.25584	2.33497	104.048	102.093
15,19	J_6	μ_4-O, μ_2-O	3.30518	1.93184	1.90202	2.25516	2.33369	103.99	102.097
16,17	J_6	μ_4-O, μ_2-O	3.30519	1.9307	1.90295	2.25478	2.33387	104.043	102.062
2,10	J_7	μ_4-O, μ_2-O	3.28353	1.92735	1.90482	2.25516	2.31654	103.174	101.682
3,8	J_7	μ_4-O, μ_2-O	3.28309	1.9275	1.90507	2.25584	2.31588	103.125	101.679
4,9	J_7	μ_4-O, μ_2-O	3.28264	1.92801	1.90418	2.25478	2.31527	103.126	101.709

11,19	J_7	μ_4-O, μ_2-O	3.28264	1.92683	1.90482	2.25516	2.31588	103.151	101.667
12,17	J_7	μ_4-O, μ_2-O	3.28264	1.92801	1.90482	2.25478	2.31588	103.126	101.667
13,18	J_7	μ_4-O, μ_2-O	3.28398	1.92801	1.90443	2.25584	2.31593	103.147	101.735
6,10	J_8	μ_4-O, μ_2-O	3.24308	1.91068	1.8716	2.25516	2.21698	101.928	104.656
5,9	J_8	μ_4-O, μ_2-O	3.2423	1.90977	1.8716	2.25478	2.21585	101.937	104.663
7,8	J_8	μ_4-O, μ_2-O	3.2423	1.91032	1.8716	2.25584	2.21585	101.881	104.663
14,19	J_8	μ_4-O, μ_2-O	3.24187	1.9094	1.8716	2.25516	2.21564	101.916	104.652
15,17	J_8	μ_4-O, μ_2-O	3.2427	1.91068	1.8716	2.25478	2.21669	101.925	104.65
16,18	J_8	μ_4-O, μ_2-O	3.24311	1.91068	1.8716	2.25584	2.21635	101.905	104.682

Table S3: Selected structural parameter along with the exchange coupling constant of the end-on geometry of **1** on Au(111) surface. Mn atom numbers as per Figure 1b in the main manuscript.

M		*bridging ligands*	*M · · · M (Å)*	Mn^{III}	Mn^{III}	Mn^{II}	Mn^{II}		
				Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O-Mn	Mn-O-Mn
2,5	J_1	μ_4-O, μ_3-Cl	3.14733	1.91491	2.55721	1.90573	2.54954	110.928	76.094
3,6	J_1	μ_4-O, μ_3-Cl	3.179	1.89837	2.62236	1.90513	2.53422	113.4	76.1
4,7	J_1	μ_4-O, μ_3-Cl	3.15031	1.91217	2.54549	1.9047	2.55178	111.25	76.346
11,15	J_1	μ_4-O, μ_3-Cl	3.17562	1.92067	2.58116	1.90381	2.52947	112.266	76.826
12,16	J_1	μ_4-O, μ_3-Cl	3.1121	1.90284	2.53549	1.88562	2.54393	110.464	75.568
13,14	J_1	μ_4-O, μ_3-Cl	3.15966	1.90689	2.52404	1.89592	2.62137	112.377	75.743
2,6	J_2	μ_4-O, μ_3-Cl	3.2568	1.91491	3.02461	1.9072	2.53422	116.88	71.107
3,7	J_2	μ_4-O, μ_3-Cl	3.21128	1.89837	2.91692	1.89553	2.55178	115.652	71.565
4,5	J_2	μ_4-O, μ_3-Cl	3.26129	1.91217	2.94276	1.90733	2.54954	117.267	72.453
11,14	J_2	μ_4-O, μ_3-Cl	3.26462	1.92067	2.91279	1.89747	2.62137	117.525	72.082
12,15	J_2	μ_4-O, μ_3-Cl	3.26232	1.90284	3.02375	1.88724	2.52947	118.802	71.323
13,16	J_2	μ_4-O, μ_3-Cl	3.27424	1.90689	3.06507	1.89436	2.54393	118.939	70.734

5,6	J_3	μ_4-O, μ_3-Cl	3.20913	1.90573	2.64992	1.9072	2.64769	114.628	74.568
6,7	J_3	μ_4-O, μ_3-Cl	3.24417	1.90513	2.64769	1.89553	2.65306	117.207	75.472
7,5	J_3	μ_4-O, μ_3-Cl	3.21344	1.90733	2.64992	1.9047	2.65306	114.911	74.597
14,15	J_3	μ_4-O, μ_3-Cl	3.19521	1.89747	2.59893	1.90381	2.67941	114.399	74.49
15,16	J_3	μ_4-O, μ_3-Cl	3.1861	1.88724	2.67941	1.88562	2.63908	115.232	73.601
16,14	J_3	μ_4-O, μ_3-Cl	3.16562	1.89592	2.59893	1.89436	2.63908	113.272	74.361
2,3	J_4	μ_4-O, μ_3-Cl	3.22894	1.89354	3.02461	1.88215	2.62236	117.562	69.332
3,4	J_4	μ_4-O, μ_3-Cl	3.17814	1.89409	2.54549	1.88215	2.91692	114.622	70.785
4,2	J_4	μ_4-O, μ_3-Cl	3.24782	1.89354	2.55721	1.89409	2.94276	118.07	72
11,12	J_4	μ_4-O, μ_3-Cl	3.23989	1.89852	2.58116	1.89365	3.02375	117.379	70.118
12,13	J_4	μ_4-O, μ_3-Cl	3.24339	1.89365	2.53549	1.89473	3.06507	117.772	70.048
13,11	J_4	μ_4-O, μ_3-Cl	3.1809	1.89852	2.91279	1.89473	2.52404	113.979	71.207
1,2	J_5	μ_4-O, μ_2-O	3.30136	2.3738	2.22363	1.89354	1.8312	100.761	108.627
1,3	J_5	μ_4-O, μ_2-O	3.28871	2.3738	2.26192	1.88215	2.26192	100.564	107.065

1,4	J_5	μ_4-O, μ_2-O	3.28809	2.3738	2.2089	1.89409	1.83316	100.178	108.516
1,11	J_5	μ_4-O, μ_2-O	3.29991	2.33636	2.25389	1.89852	1.82476	101.881	107.545
1,12	J_5	μ_4-O, μ_2-O	3.27984	2.33636	2.24715	1.89365	1.82528	101.162	106.837
1,13	J_5	μ_4-O, μ_2-O	3.26021	2.33636	2.22543	1.89473	1.82284	100.283	106.865
5,10	J_6	μ_4-O, μ_2-O	3.24212	1.90573	1.91517	2.23853	2.23451	102.65	102.486
6,8	J_6	μ_4-O, μ_2-O	3.27361	1.90513	1.9031	2.21956	2.32987	104.802	100.832
7,9	J_6	μ_4-O, μ_2-O	3.24423	1.9047	1.91089	2.22117	2.2631	103.419	101.687
14,18	J_6	μ_4-O, μ_2-O	3.24492	1.89592	1.91212	2.25055	2.20385	102.658	103.842
15,19	J_6	μ_4-O, μ_2-O	3.21485	1.90381	1.9076	2.21637	2.21098	102.304	102.376
16,17	J_6	μ_4-O, μ_2-O	3.249	1.88562	1.92793	2.26616	2.20319	102.605	103.513
2,10	J_7	μ_4-O, μ_2-O	3.44285	2.23853	2.66175	1.91491	1.8806	111.739	97.067
3,8	J_7	μ_4-O, μ_2-O	3.20041	1.89837	1.88514	2.21956	2.20867	101.724	102.559
4,9	J_7	μ_4-O, μ_2-O	3.36798	1.91217	1.88137	2.22117	2.56822	108.913	97.181
11,19	J_7	μ_4-O, μ_2-O	3.36572	1.92067	1.92067	2.21637	2.54124	108.68	97.86

12,17	J_7	μ_4-O, μ_2-O	3.3732	1.90284	1.89129	2.26616	2.48978	107.701	99.797
13,18	J_7	μ_4-O, μ_2-O	3.37196	1.90689	1.89645	2.25055	2.5165	108.117	98.682
6,10	J_8	μ_4-O, μ_2-O	3.14443	1.9072	1.89237	2.23853	2.06997	98.343	104.954
5,9	J_8	μ_4-O, μ_2-O	3.15035	1.90733	1.89514	2.22117	2.0542	99.19	105.75
7,8	J_8	μ_4-O, μ_2-O	3.18418	1.89553	1.8896	2.21956	2.12831	101.097	104.683
14,19	J_8	μ_4-O, μ_2-O	3.14494	1.89747	1.8807	2.21637	2.1013	99.429	104.195
15,17	J_8	μ_4-O, μ_2-O	3.18574	1.88724	1.88287	2.26616	2.0855	99.772	106.682
16,18	J_8	μ_4-O, μ_2-O	3.16116	1.89436	1.88312	2.25055	2.06634	99.038	106.245

Table S4: Selected structural parameter along with the exchange coupling constant of the side-on geometry of **1** on Au(111) surface. Mn atom numbers as per Figure 1b in the main manuscript.

Mn		*bridging ligands*	*M · · · M (Å)*	*Mn^{III}*	*Mn^{III}*	*Mn^{II}*	*Mn^{II}*		
				Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O-Mn	Mn-O-Mn
2,5	J_1	μ_4-O, μ_3-Cl	3.20276	1.91238	2.60212	1.90713	2.63383	113.969	75.42
3,6	J_1	μ_4-O, μ_3-Cl	3.28356	1.92099	2.63097	1.93805	2.61112	116.613	77.567
4,7	J_1	μ_4-O, μ_3-Cl	3.2403	1.9309	2.61903	1.91789	2.60808	114.683	76.618
11,15	J_1	μ_4-O, μ_3-Cl	3.23079	1.91801	2.6078	1.91274	2.64356	114.998	75.934
12,16	J_1	μ_4-O, μ_3-Cl	3.21793	1.9172	2.61316	1.90983	2.60788	114.458	76.098
13,14	J_1	μ_4-O, μ_3-Cl	3.24247	1.91501	2.59568	1.9194	2.64705	115.477	76.402
2,6	J_2	μ_4-O, μ_3-Cl	3.25845	1.91238	2.77367	1.90339	2.63097	117.286	74.103
3,7	J_2	μ_4-O, μ_3-Cl	3.24017	1.93805	2.83225	1.91404	2.60808	114.521	72.977
4,5	J_2	μ_4-O, μ_3-Cl	3.29832	1.9309	2.79245	1.91319	2.63383	118.19	74.803
11,14	J_2	μ_4-O, μ_3-Cl	3.27485	1.91801	2.845	1.91366	2.64705	117.449	73.109
12,15	J_2	μ_4-O, μ_3-Cl	3.27532	1.9161	2.64356	1.9172	2.81093	117.396	73.737
13,16	J_2	μ_4-O, μ_3-Cl	3.24344	1.91501	2.83282	1.90587	2.60788	116.178	73.056

5,6	J_3	μ_4-O, μ_3-Cl	3.19547	1.90713	2.61858	1.90339	2.61183	113.983	75.315
6,7	J_3	μ_4-O, μ_3-Cl	3.19803	1.92099	2.61183	1.91404	2.6191	113.002	75.377
7,5	J_3	μ_4-O, μ_3-Cl	3.16284	1.91319	2.61858	1.91789	2.6191	111.294	74.294
14,15	J_3	μ_4-O, μ_3-Cl	3.15963	1.91366	2.59558	1.91274	2.61015	111.328	74.738
15,16	J_3	μ_4-O, μ_3-Cl	3.18538	1.9161	2.61015	1.90983	2.61714	112.729	75.088
16,14	J_3	μ_4-O, μ_3-Cl	3.17441	1.9194	2.59558	1.90587	2.61714	112.166	75.029
2,3	J_4	μ_4-O, μ_3-Cl	3.15781	1.84813	2.77367	1.84745	2.61112	117.405	71.736
3,4	J_4	μ_4-O, μ_3-Cl	3.19912	1.84745	2.83225	1.85301	2.61903	119.656	71.747
4,2	J_4	μ_4-O, μ_3-Cl	3.13706	1.84813	2.60212	1.85301	2.79245	115.901	71.015
11,12	J_4	μ_4-O, μ_3-Cl	3.2016	1.87301	2.6078	1.86512	2.81093	117.845	72.323
12,13	J_4	μ_4-O, μ_3-Cl	3.18167	1.86512	2.61316	1.86519	2.83282	117.062	71.367
13,11	J_4	μ_4-O, μ_3-Cl	3.19412	1.87301	2.845	1.86519	2.59568	117.399	71.734
1,2	J_5	μ_4-O, μ_2-O	3.41394	2.60463	2.15481	1.84813	1.85846	98.694	116.374
1,3	J_5	μ_4-O, μ_2-O	3.42062	2.60463	2.2412	1.84745	1.84153	98.988	113.462

1,4	J_5	μ_4-O, μ_2-O	3.42431	2.60463	2.2121	1.85301	1.84857	98.989	114.683
1,11	J_5	μ_4-O, μ_2-O	3.42803	2.55377	2.24576	1.87301	1.85035	100.367	113.276
1,12	J_5	μ_4-O, μ_2-O	3.38762	2.55377	2.2215	1.86512	1.84268	98.911	112.594
1,13	J_5	μ_4-O, μ_2-O	3.38108	2.55377	2.16965	1.86519	1.85491	98.64	114.076
5,10	J_6	μ_4-O, μ_2-O	3.26384	1.90713	1.8918	2.21888	2.26109	104.311	103.253
6,8	J_6	μ_4-O, μ_2-O	3.2256	1.92099	1.90214	2.13986	2.37963	105.054	97.131
7,9	J_6	μ_4-O, μ_2-O	3.27035	1.91789	1.8944	2.17476	2.28253	105.914	102.668
14,18	J_6	μ_4-O, μ_2-O	3.2584	1.9194	1.89378	2.19385	2.27	104.581	102.616
15,19	J_6	μ_4-O, μ_2-O	3.2735	1.91274	1.88524	2.21559	2.29602	104.683	102.61
16,17	J_6	μ_4-O, μ_2-O	3.2316	1.90983	1.89374	2.18678	2.26796	103.951	101.505
2,10	J_7	μ_4-O, μ_2-O	3.27927	1.91238	1.90348	2.21888	2.30001	104.835	102.133
3,8	J_7	μ_4-O, μ_2-O	3.1949	1.93805	1.88599	2.13986	2.24067	103.046	101.118
4,9	J_7	μ_4-O, μ_2-O	3.24949	1.9309	1.89914	2.17476	2.38466	104.489	98.034
11,19	J_7	μ_4-O, μ_2-O	3.28306	1.91801	1.90674	2.21559	2.3663	104.938	99.848

12,17	J_7	μ_4-O, μ_2-O	3.25284	1.9172	1.90494	2.18678	2.34231	104.668	99.454
13,18	J_7	μ_4-O, μ_2-O	3.28025	1.91501	1.90512	2.19385	2.39482	105.743	98.796
6,10	J_8	μ_4-O, μ_2-O	3.16238	1.90339	1.88503	2.21888	2.11266	99.914	104.424
5,9	J_8	μ_4-O, μ_2-O	3.13788	1.91319	1.88653	2.17476	2.12928	100.08	102.607
7,8	J_8	μ_4-O, μ_2-O	3.16269	1.91404	1.89424	2.13986	2.1772	102.408	101.712
14,19	J_8	μ_4-O, μ_2-O	3.19949	1.91366	1.88902	2.21559	2.15048	101.329	104.57
15,17	J_8	μ_4-O, μ_2-O	3.17718	1.9161	1.89086	2.18678	2.13694	101.293	103.982
16,18	J_8	μ_4-O, μ_2-O	3.15791	1.90587	1.89353	2.19385	2.11403	100.522	103.86

Table S5: Selected structural parameter along with the exchange coupling constant of the reduced geometry of **1** on Au(111) surface. Mn atom numbers as per Figure 1b in the main manuscript.

Mn		*bridging ligands*	*M · · · M (Å)*	*Mn^{III}*	*Mn^{III}*	*Mn^{II}*	*Mn^{II}*		
				Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O/Mn	Mn-O-Mn	Mn-O-Mn
2,5	J_1	μ_4-O, μ_3-Cl	3.33299	1.99345	2.50476	2.00548	3.05535	112.913	72.901
3,6	J_1	μ_4-O, μ_3-Cl	3.23098	2.04809	2.55796	1.91121	2.66018	109.333	76.485
4,7	J_1	μ_4-O, μ_3-Cl	3.29033	2.00063	2.49093	2.11505	2.7959	106.124	76.737
11,15	J_1	μ_4-O, μ_3-Cl	3.22887	2.08722	2.55786	2.02467	2.5223	103.477	78.923
12,16	J_1	μ_4-O, μ_3-Cl	3.22061	2.02721	2.44135	1.97004	3.07368	107.348	70.396
13,14	J_1	μ_4-O, μ_3-Cl	3.19146	2.04314	2.5349	1.98328	2.72529	104.854	74.607
2,6	J_2	μ_4-O, μ_3-Cl	3.31077	1.99345	2.87149	1.87206	2.66018	117.815	73.415
3,7	J_2	μ_4-O, μ_3-Cl	3.40901	2.04809	2.67609	2.0158	2.7959	114.036	77.036
4,5	J_2	μ_4-O, μ_3-Cl	3.54005	2.00063	3.11558	1.974	3.05535	125.912	70.005
11,14	J_2	μ_4-O, μ_3-Cl	3.31246	2.08722	2.63083	1.92842	2.72529	111.093	76.383
12,15	J_2	μ_4-O, μ_3-Cl	3.27884	2.02721	2.93563	1.9972	2.5223	109.12	73.407
13,16	J_2	μ_4-O, μ_3-Cl	3.55229	2.04314	2.76361	1.94108	3.07368	126.128	74.758

5,6	J_3	μ_4-O, μ_3-Cl	3.23527	2.00548	2.50543	1.87206	3.03991	113.054	70.634
6,7	J_3	μ_4-O, μ_3-Cl	3.3353	1.91121	3.03991	2.0158	2.50143	116.251	73.285
7,5	J_3	μ_4-O, μ_3-Cl	3.05576	1.974	2.50543	2.50543	2.50143	96.654	75.224
14,15	J_3	μ_4-O, μ_3-Cl	3.18746	1.92842	2.98544	2.02467	2.68384	107.451	68.181
15,16	J_3	μ_4-O, μ_3-Cl	3.23503	1.9972	2.68384	1.97004	2.67361	109.259	74.29
16,14	J_3	μ_4-O, μ_3-Cl	3.26585	1.98328	2.98544	1.94108	2.67361	112.646	70.247
2,3	J_4	μ_4-O, μ_3-Cl	3.23549	2.09593	2.87149	2.07585	2.07585	101.712	72.897
3,4	J_4	μ_4-O, μ_3-Cl	3.18288	2.07585	2.67609	2.05253	2.49093	100.882	75.955
4,2	J_4	μ_4-O, μ_3-Cl	3.40505	2.09593	2.50476	2.05253	3.11558	110.326	73.678
11,12	J_4	μ_4-O, μ_3-Cl	3.39712	2.09083	2.55786	2.02177	2.93563	111.375	76.051
12,13	J_4	μ_4-O, μ_3-Cl	3.17269	2.02177	2.44135	2.08973	2.76361	100.994	74.827
13,11	J_4	μ_4-O, μ_3-Cl	3.31213	2.09083	2.63083	2.08973	2.5349	104.796	79.735
1,2	J_5	μ_4-O, μ_2-O	3.19921	1.92893	2.10447	2.09593	2.45852	105.209	88.681
1,3	J_5	μ_4-O, μ_2-O	3.50518	1.92893	2.98944	2.07585	2.29415	122.106	81.98

1,4	J_5	μ_4-O, μ_2-O	3.37034	1.92893	2.74071	2.05253	2.4716	115.633	80.393
1,11	J_5	μ_4-O, μ_2-O	3.42664	1.9253	2.92898	2.09083	2.41181	117.068	79.173
1,12	J_5	μ_4-O, μ_2-O	3.13253	1.9253	2.28831	2.02177	3.23155	105.027	66.63
1,13	J_5	μ_4-O, μ_2-O	3.41526	1.9253	2.9128	2.08973	2.44592	116.499	78.655
5,10	J_6	μ_4-O, μ_2-O	3.26125	2.00548	2.02864	2.22246	2.12846	100.827	103.323
6,8	J_6	μ_4-O, μ_2-O	3.16554	1.91121	1.92777	2.08206	2.31464	104.8	96.09
7,9	J_6	μ_4-O, μ_2-O	3.17831	2.11505	2.04881	2.01896	2.10589	100.47	99.803
14,18	J_6	μ_4-O, μ_2-O	3.17273	1.98328	2.0055	2.14291	2.26734	100.443	95.701
15,19	J_6	μ_4-O, μ_2-O	3.05598	2.02467	2.01624	2.01511	2.19275	98.308	93.019
16,17	J_6	μ_4-O, μ_2-O	3.12008	1.97004	1.97889	2.07014	2.14014	101.086	98.409
2,10	J_7	μ_4-O, μ_2-O	3.46127	1.99345	3.73582	2.22246	2.15597	110.253	65.719
3,8	J_7	μ_4-O, μ_2-O	3.17436	2.04809	2.06611	2.08206	2.1103	100.45	98.935
4,9	J_7	μ_4-O, μ_2-O	3.31214	2.00063	2.01839	2.01896	2.7273	110.973	87.179
11,19	J_7	μ_4-O, μ_2-O	3.52077	2.08722	2.02163	2.01511	2.8832	118.228	89.98

12,17	J_7	μ_4-O, μ_2-O	3.46105	2.02721	1.95586	2.07014	2.97882	115.277	86.458
13,18	J_7	μ_4-O, μ_2-O	3.48325	2.04314	1.99628	2.14291	2.91545	112.61	88.267
6,10	J_8	μ_4-O, μ_2-O	3.13641	1.87206	1.92777	2.08206	2.31464	104.8	96.09
5,9	J_8	μ_4-O, μ_2-O	3.31164	1.974	2.26545	2.01896	2.57674	112.063	86.047
7,8	J_8	μ_4-O, μ_2-O	3.36554	2.0158	2.29656	2.08206	2.86856	110.418	80.494
14,19	J_8	μ_4-O, μ_2-O	3.34372	1.92842	2.83049	2.01511	2.32754	115.951	80.174
15,17	J_8	μ_4-O, μ_2-O	3.41412	1.9972	2.91283	2.07014	2.19388	114.141	82.621
16,18	J_8	μ_4-O, μ_2-O	3.06908	1.94108	1.93837	2.14291	2.05222	97.316	100.504

Table S6: Computed spin densities of various spin states of the **1** (X-ray structure).

Mn (ion) X-ray	HS	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8
Mn1	4.78	4.76	4.77	4.72	4.78	-4.77	4.86	4.77	-4.74
Mn2	3.85	3.83	3.82	-3.76	3.83	-3.82	3.83	-3.72	3.76
Mn3	3.82	3.79	3.79	-3.73	3.80	-3.77	3.82	3.79	-3.75
Mn4	3.84	-3.73	-3.71	-3.75	3.82	-3.80	-3.74	3.79	3.76
Mn5	3.90	-3.77	3.84	3.86	-3.78	3.86	3.84	3.82	-3.75
Mn6	3.89	3.88	3.85	3.86	-3.79	3.86	3.86	3.86	3.83
Mn7	3.88	3.86	3.87	3.85	-3.78	3.85	3.85	-3.77	3.80
Mn8	4.82	4.81	4.82	4.81	4.80	4.81	4.85	4.82	-4.80
Mn9	4.83	4.81	4.82	4.82	4.81	4.82	4.84	-4.81	4.82
Mn10	4.82	4.81	-4.80	4.81	4.81	4.81	4.85	4.81	4.81
Mn11	3.85	3.81	3.82	-3.76	3.83	-3.81	3.83	-3.73	3.77
Mn12	3.84	3.82	3.83	-3.75	3.82	-3.80	3.83	3.80	-3.79
Mn13	3.85	-3.72	3.84	-3.76	3.83	-3.81	-3.74	3.82	3.87
Mn14	3.89	-3.76	-3.78	3.85	-3.77	3.85	3.85	3.81	3.87
Mn15	3.89	3.88	3.85	3.85	-3.77	3.85	3.86	3.82	-3.81
Mn16	3.89	3.86	3.87	3.85	-3.77	3.85	3.84	-3.75	3.83
Mn17	4.82	4.81	4.81	4.81	4.80	4.81	4.85	4.81	-4.81
Mn18	4.82	4.81	4.81	4.81	480	4.81	4.84	4.82	4.81
Mn19	4.82	4.82	-4.81	4.82	481	4.82	4.85	-4.81	4.82

Table S7: Computed spin densities of various spin states of the **1** on Au(111) surface, end-on orientation.

Mn (ion) end-on	HS	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8
Mn1	4.80	4.79	4.79	4.75	4.79	-4.79	4.79	4.79	-4.77
Mn2	3.85	3.83	3.81	-3.76	3.83	-3.81	3.83	-3.72	3.77
Mn3	3.82	3.79	3.79	-3.73	3.79	-3.77	3.79	3.78	-3.75
Mn4	3.84	-3.73	-3.71	-3.75	3.82	-3.80	-3.71	3.79	3.76
Mn5	3.89	-3.76	3.83	3.85	-3.77	3.85	3.87	3.82	-3.74
Mn6	3.88	3.86	3.85	3.85	-3.78	3.85	3.88	3.85	3.82
Mn7	3.88	3.85	3.86	3.84	-3.77	3.84	3.87	-3.77	3.80
Mn8	4.82	4.82	4.82	4.82	4.81	4.82	4.82	4.82	-4.81
Mn9	4.83	4.81	4.82	4.82	4.81	4.82	4.82	-4.81	4.82
Mn10	4.83	4.83	-4.80	4.82	4.81	4.82	4.83	4.82	4.82
Mn11	3.85	3.81	3.82	-3.76	3.83	-3.81	3.82	-3.74	3.78
Mn12	3.83	3.81	3.83	-3.75	3.81	-3.79	3.81	3.80	-3.78
Mn13	3.84	-3.72	3.83	-3.75	3.82	-3.80	-3.71	3.81	3.77
Mn14	3.87	-3.75	-3.76	3.83	-3.76	3.83	3.86	3.80	3.85
Mn15	3.87	3.85	3.83	3.83	-3.76	3.83	3.87	3.80	-3.79
Mn16	3.87	3.83	3.85	3.83	-3.76	3.83	3.85	-3.72	3.81
Mn17	4.84	4.83	4.83	4.82	4.82	4.83	4.84	4.83	-4.83
Mn18	4.83	4.82	4.82	4.82	4.81	4.82	4.82	4.82	4.82
Mn19	4.83	4.82	-4.81	4.83	4.81	4.83	4.83	-4.81	4.83

Table S8: Computed spin densities of various spin states of the **1** on Au(111) surface, side-on orientation.

Mn (ion) side-on	HS	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8
Mn1	4.77	4.74	4.76	4.70	4.76	-4.76	4.73	4.74	-4.73
Mn2	3.86	3.83	3.81	-3.76	3.83	-3.81	3.83	-3.71	3.77
Mn3	3.84	3.81	3.81	-3.75	3.82	-3.79	3.81	3.81	-3.77
Mn4	3.85	-3.73	-3.72	-3.76	3.83	-3.81	-3.72	3.80	3.77
Mn5	3.88	-3.76	3.82	3.85	-3.77	3.84	3.86	3.82	-3.75
Mn6	3.89	3.86	3.84	3.85	-3.78	3.85	3.89	3.85	3.82
Mn7	3.88	3.86	3.87	3.85	-3.77	3.85	3.87	-3.79	3.82
Mn8	4.83	4.83	4.83	4.83	4.82	4.83	4.83	4.82	-4.82
Mn9	4.83	4.82	4.83	4.83	4.81	4.83	4.83	-4.81	4.82
Mn10	4.82	4.82	-4.80	4.81	4.81	4.81	4.82	4.81	4.81
Mn11	3.86	3.82	3.83	-3.77	3.84	-3.82	3.84	-3.75	3.79
Mn12	3.85	3.83	3.85	-3.76	3.83	-3.81	3.83	3.82	-3.80
Mn13	3.86	-3.73	3.85	-3.76	3.84	-3.81	-3.72	3.83	3.79
Mn14	3.89	-3.76	-3.79	3.85	-3.77	3.85	3.87	3.82	3.86
Mn15	3.88	3.87	3.84	3.85	-3.77	3.85	3.88	3.81	-3.81
Mn16	3.88	3.84	3.86	3.84	-3.77	3.84	3.86	-3.75	3.82
Mn17	4.83	4.83	4.83	4.83	4.82	4.83	4.83	4.83	-4.82
Mn18	4.83	4.82	4.83	4.82	4.81	4.82	4.83	4.82	4.83
Mn19	4.84	4.83	-4.82	4.83	4.82	4.83	4.84	-4.82	4.83

Bond Length and Bond Angle Parameters

Selected bond angles and bond lengths of **1** of the optimized structure (bare) as well as with Au(111) surface are given in the following table. Also all the parameters have been shown against the X-ray structure parameters[6]. The Au-S bond lengths have been found to be in the range of 2.72 – 3.87 Å.

Table S9: Bond length and bond angle parameters of **1**.

A	Experimental(Å)	Optimized	End-on	Side-on	Mn19_red
O^{a}–Mn^{II}	2.31	2.25	2.21	2.21	2.13
Mn^{II}–O^{a}–Mn^{III}	101.7	101.5	97.2	97.2	96.1
O^{a}–Mn^{III}	1.9	1.88	1.88	1.88	2.02
O^{b}–Mn^{III}	1.85	1.82	1.83	1.83	2.02
Mn^{III}–O^{b}–Mn^{II}	111.2	109.7	108.5	108.5	88.7
O^{b}–Mn^{II}	2.30	2.22	2.21	2.21	2.10
O^{c}–Mn^{II}	2.21	2.23	2.24	2.24	2.29
B					
O^{a}–Mn^{II}	2.33	2.24	2.21	2.26	2.21
Mn^{II}–O^{a}–Mn^{III}	102.1	100.7	102.4	101.7	99.8
O^{a}–Mn^{III}	1.90	1.91	1.91	1.91	2.05
O^{b}–Mn^{III}	1.87	1.88	1.88	1.89	1.89
Mn^{III}–O^{b}–Mn^{II}	104.7	103.7	106.7	104.7	104.7
O^{b}–Mn^{II}	2.21	2.10	2.08	2.12	2.06
O^{c}–Mn^{II}	2.21	2.18	2.22	2.2	2.17

Table S10: Table showing Au-S bond lengths in Å of **1** on Au(111) after optimization using PBE functional.

Au-S End-on	Bond length (Å)	Au-S Side-on	Bond length (Å)
Au2-S575	3.12	Au34-S657	2.73
Au6-S575	3.10	Au207-S657	3.73
Au253-S575	3.12	Au35-S657	3.71
Au4-S521	3.43	Au282-S547	2.73
Au7-S521	2.91	Au281-S547	3.06
Au78-S521	2.86	Au284-S547	3.14
Au11-S629	3.08	Au71-S770	2.72
Au12-S629	3.17	Au25-S770	3.76
Au182-S629	2.84	Au99-S770	3.87

Adsorption energies:
The Adsorption of **1** on gold surface has been modeled by a three layer of Au(111) with 324 and 432 gold atoms. Table S8 lists the activation energy of S–CH_3 cleavage and reaction energy of the adsorption of **1** on gold surface obtained using theoretical approach as mentioned previously. The adsorption energies, ΔE and ΔE´ were computed using the following equations unless otherwise mentioned,

$$\Delta E \;\; = [E\{Mn_{19}SMe(Au111)\} - E\{Au(111) \; + \; Mn_{19}SMe\}] \qquad \text{I}$$

$$\Delta E^{'} \;\; = [E\{Mn_{19}S^{\bullet}(Au111) + 3CH_3^{\bullet}\} - E\{Au(111) \; + \; Mn_{19}SMe\}] \qquad \text{II}$$

Equation I and II give the energy changes of adsorption of Mn_{19}SMe on Au(111) surface. Where E{Mn_{19}SMe(Au111)} is the total energy of Mn_{19}SMe when adsorbed on Au(111) surface, E{Au(111) + Mn_{19}SMe} is the sum of the energies of Au(111) surface and Mn_{19}SMe optimized structure respectively and E {$Mn_{19}S^{\bullet}$} is the energy of radical state of Mn19.

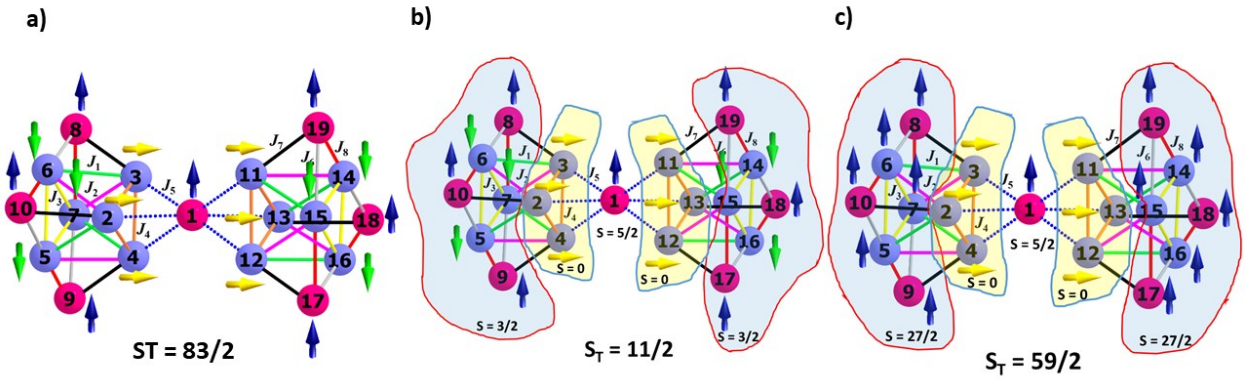

Figure S5: Ground state of **1** on **a**) pristine X-ray structure. **b**) for end-on orientation and **c**) side-on orientations of **1** on Au(111)

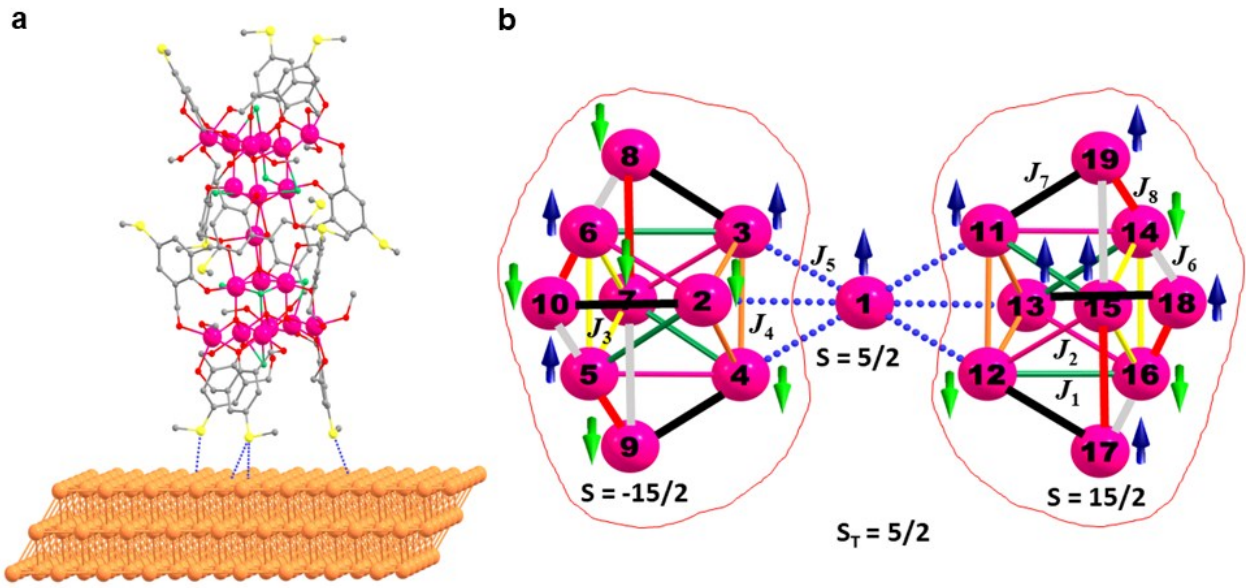

Figure S6: a) Reduced structure of **1** on Au(111) **b**) Ground state of **1** after reduction.

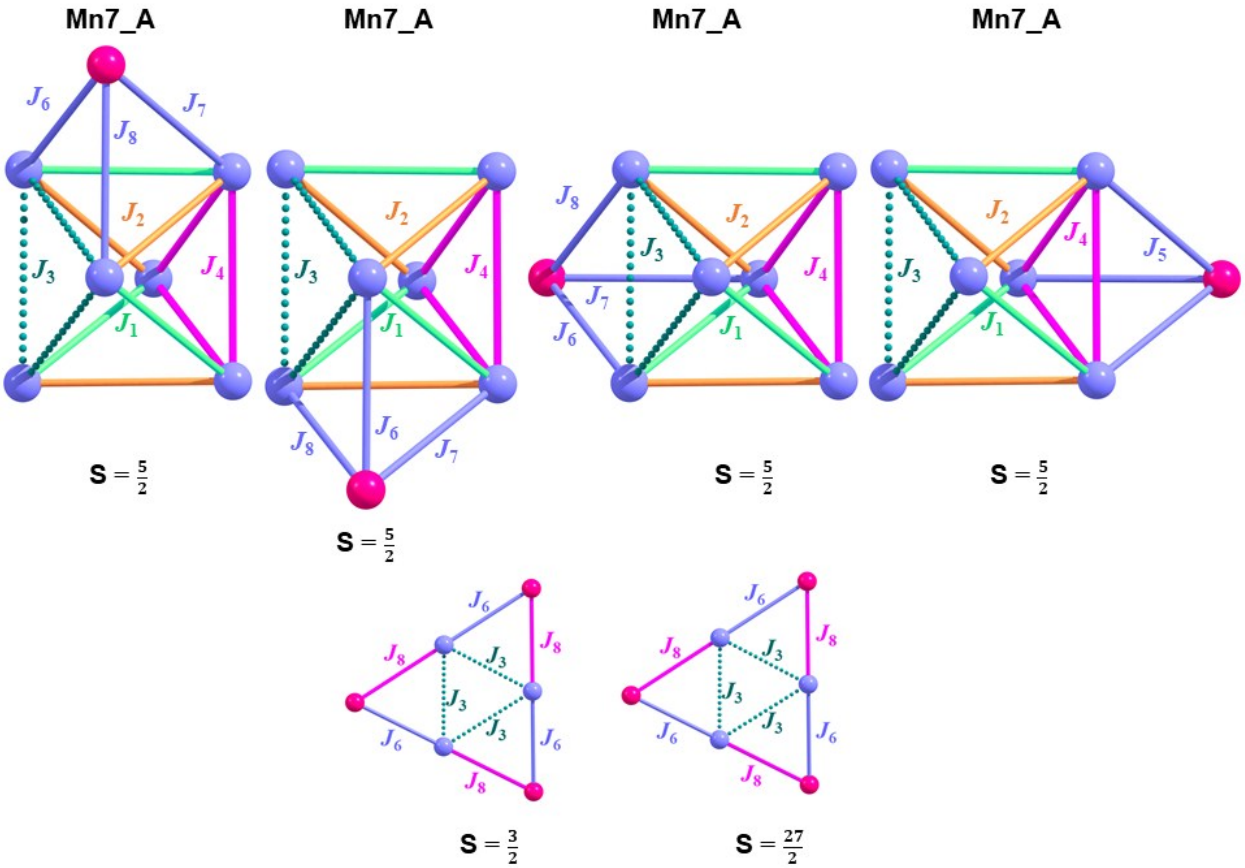

Figure S7. Various small model system constructed based on the exchange topology depicted and three set of computed exchange coupling constants to arrive at the possible ground state spin configuration of **1**.

References:

1. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, **167**, 103-128.
2. J. Paier, R. Hirschl, M. Marsman and G. Kresse, *J. Chem. Phys.*, 2005, **122**, 234102.
3. G. Lippert, J. Hutter and M. Parrinello, *Theor. Chem. Acc.*, 1999, **103**, 124-140.
4. B. G. Lippert, J. H. Parrinello and Michele, *Mol. Phys.*, 1997, **92**, 477-488.
5. E. Ruiz, T. Cauchy, J. Cano, R. Costa, J. Tercero and S. Alvarez, *J. Am. Chem. Soc.*, 2008, **130**, 7420-7426.