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SUPPLEMENTARY INFORMATION

A Systematic Study of Influence of Ligand Substitutions on the Electronic Structure and Magnetic Properties of Mn_4 Single-Molecule Magnets

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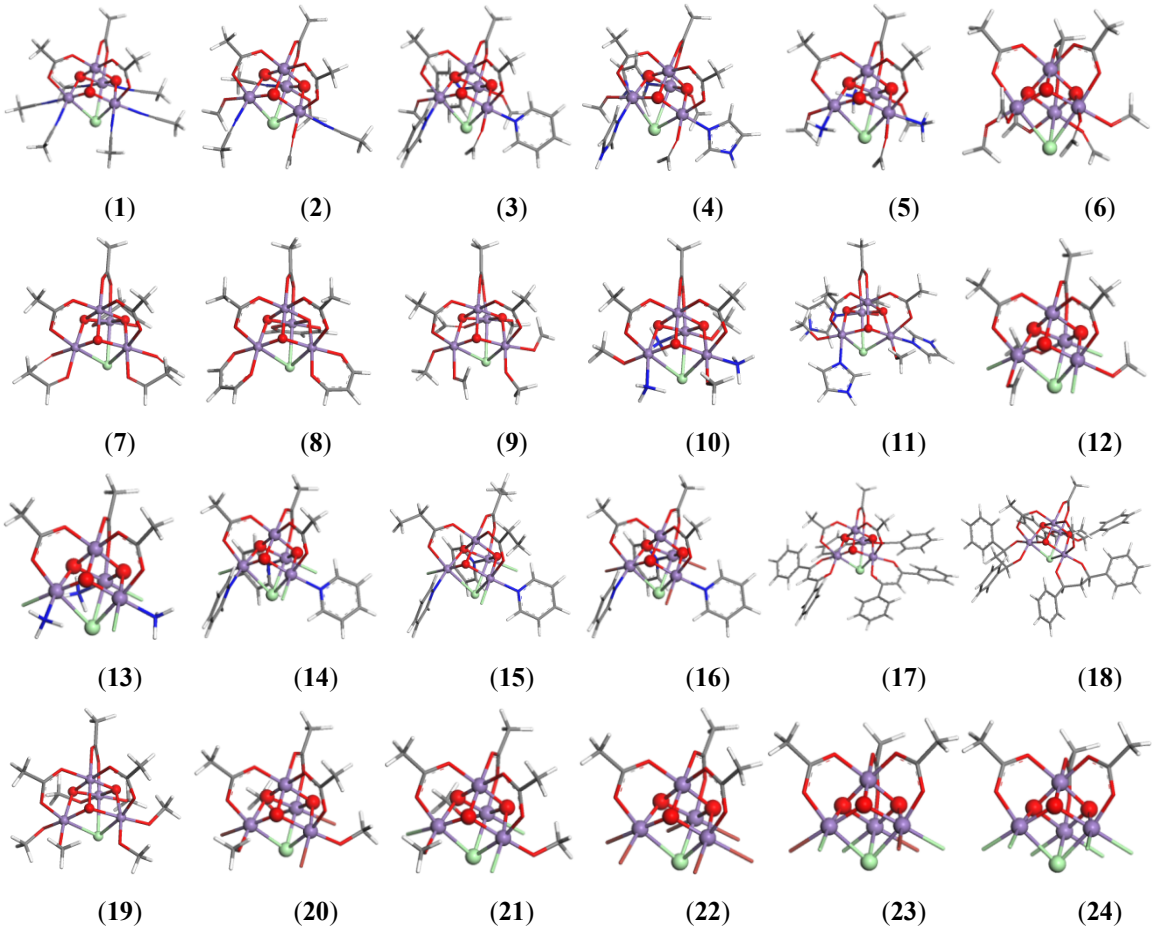

Fig. S1: The geometric structures of the twenty-four Mn_4 molecules.

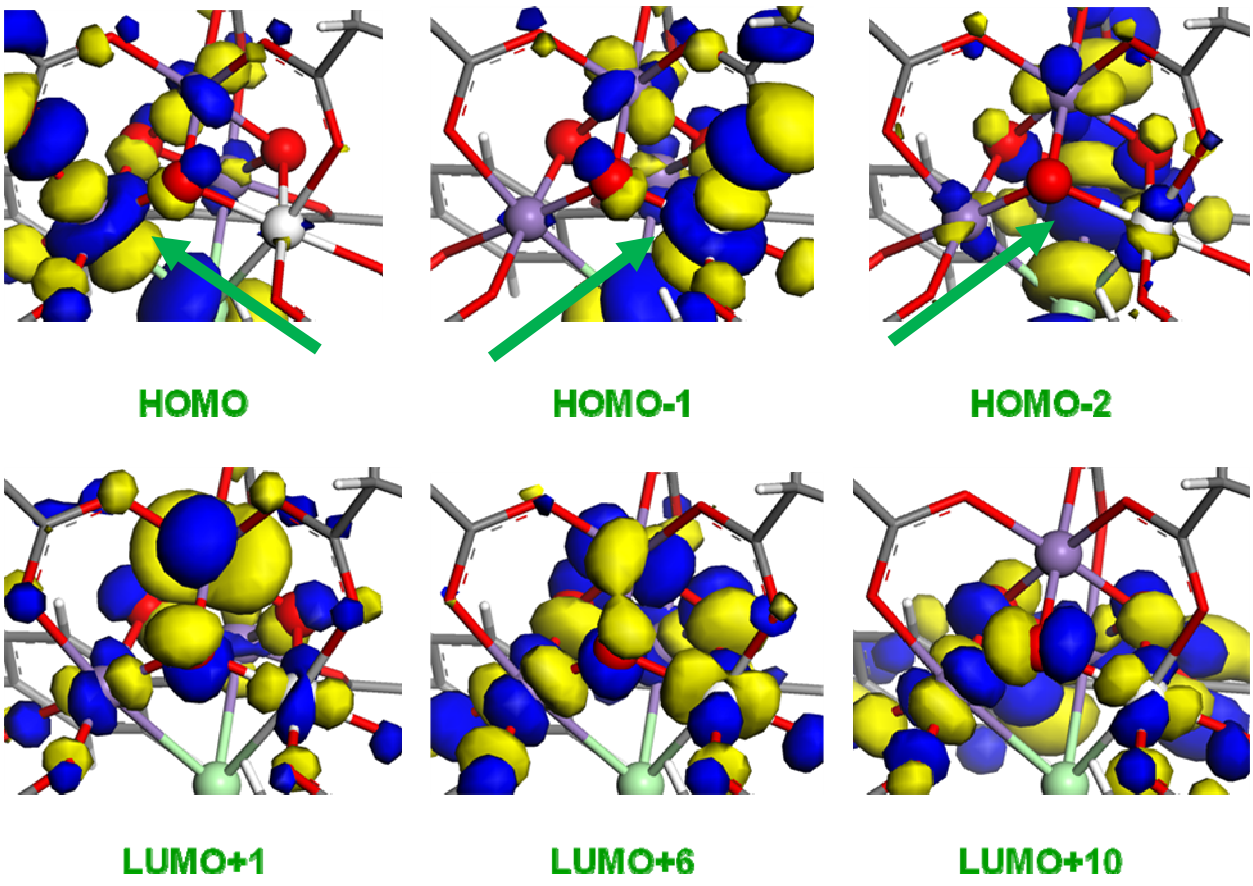

Fig. S2: The selected Kohn-Sham molecular orbitals of (**17**). The HOMO, HOMO-1, and HOMO-2 show that the electron densities of d_{z2} orbitals of Mn^{3+} ions at the B sites, marked by arrows, are directed toward the Cl^{-} ion in the core and the O^{2-} ions in the RCOO groups. The LUMO+1, LUMO+6, and LUMO+10 show that the electron densities of d_{x2-y2} orbitals of Mn^{3+} ions at the B sites are directed toward the four O^{2-} ions in the core and peripheral ligands.

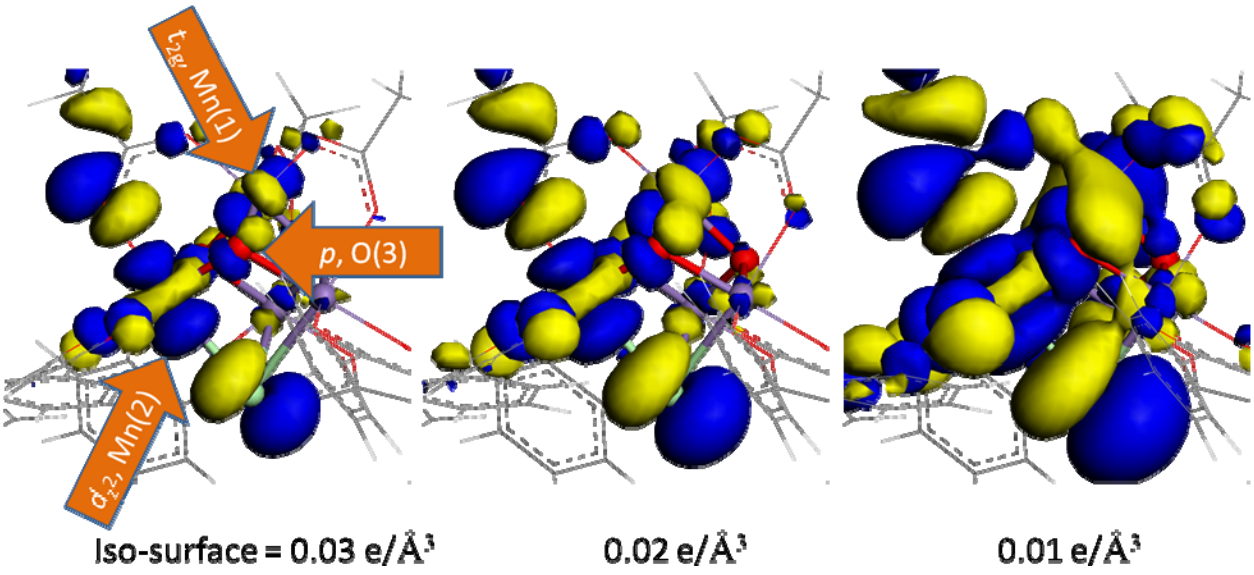

Fig. S3: The HOMO of (**17**) shows the coupling between the occupied d_{z2} orbital of Mn(2) and the unoccupied t_{2g} orbital of Mn(1) through the *p* orbital of O(3). This coupling is similar for other $Mn^{4+}Mn^{3+}{}_3$ molecules.

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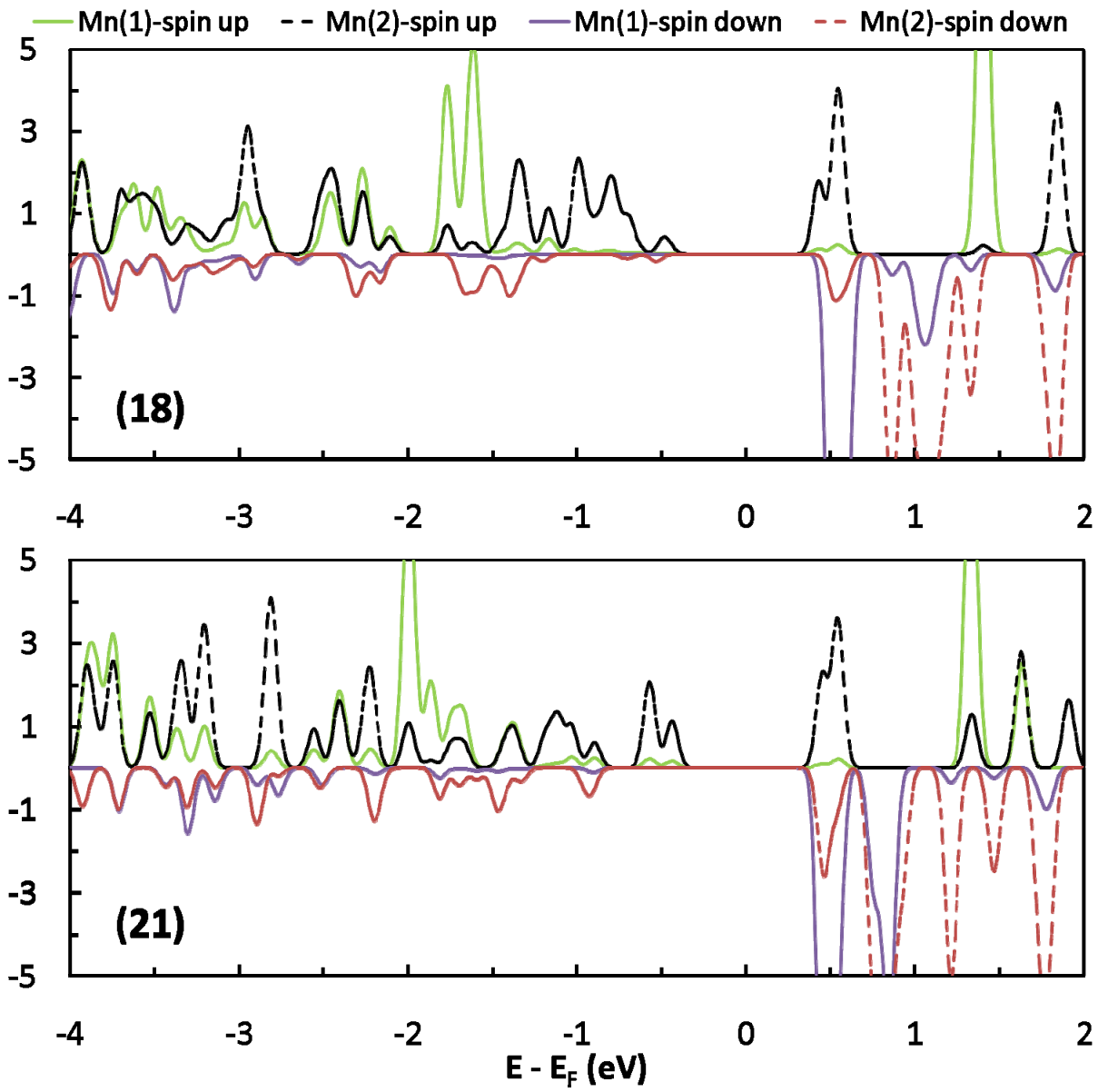

Fig. S4: The projected density-of-state (pDOS) near the Fermi level at the Mn(1) and Mn(2) sites in selected $Mn^{4+}Mn^{4+}_3$ molecules, (**18**) and (**21**), shows the weak coupling between the *d* orbitals of Mn(1) and Mn(2) just below the Fermi level.

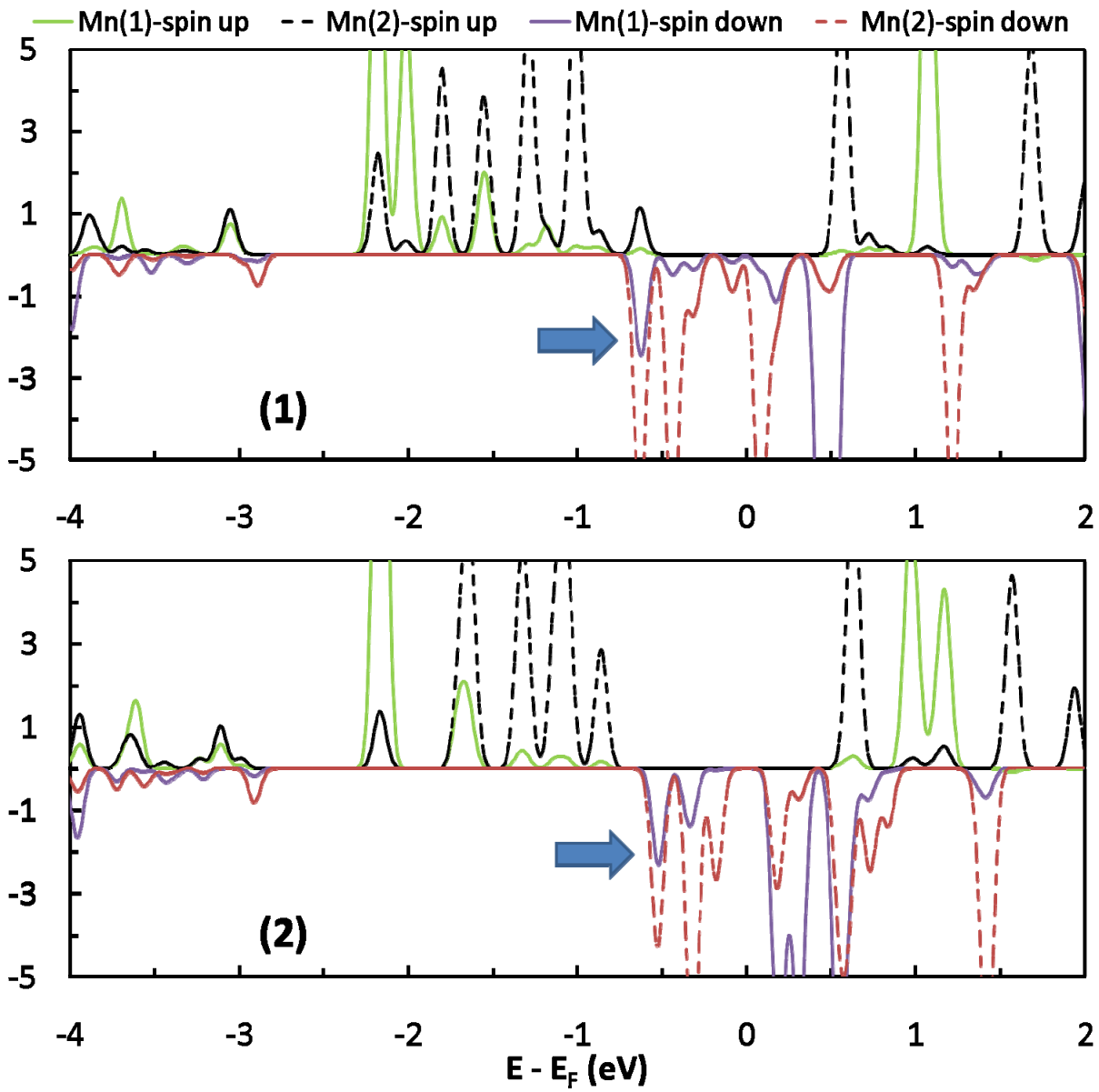

Fig. S5: The projected density-of-state (pDOS) near the Fermi level at the Mn(1) and Mn(2) sites in $Mn^{4+}Mn^{2+}_3$ Type-II molecules, (**1**) and (**2**), shows the strong coupling between the unoccupied t_{2g} spin-down orbitals of Mn(1) and the occupied t_{2g} orbitals of Mn(2) just below the Fermi level, marked by arrows.

Table S1: The magnetic moments at Mn sites, $m_{Mn(1)–(4)}$. The spin polarization on Cl(1) ($m_{Cl(1)}$). The average effective exchange-coupling parameters in Mn_4 J_{AB} refers to the magnetic interaction between Mn(1) and Mn(2), Mn(3), Mn(4) and J_{BB} refers to the magnetic interaction between Mn(2), Mn(3), and Mn(4). (The OpenMX values are shown in italics).

	$m_{Mn(1)}$	$m_{Mn(2)}$	$m_{Mn(3)}$	$m_{Mn(4)}$	$m_{Cl(1)}$	J_{AB}/k_B	J_{BB}/k_B	$\lvert J_{AB}/J_{BB}\rvert$
Group I, n = +2, S_T = 3								
(**1**)	2.797	1.122	1.102	1.123	–0.030	-	-	-
	2.676	*1.292*	*1.169*	*1.215*	*–0.045*	*90.73*	*28.69*	*3.16*
(**2**)	2.742	1.411	1.384	1.401	–0.035	39.20	23.47	1.67
	2.641	*1.488*	*1.479*	*1.523*	*–0.046*	*81.55*	*20.03*	*4.07*
(**3**)	–2.775	3.474	3.472	3.474	0.075	–63.95	35.27	1.81
	–3.070	*3.464*	*3.465*	*3.472*	*0.086*	*–122.89*	*79.39*	*1.55*
(**4**)	–2.768	3.509	3.494	3.487	0.070	–62.75	32.21	1.95
	–3.107	*3.477*	*3.476*	*3.485*	*0.078*	*–128.22*	*79.50*	*1.61*
(**5**)	–2.694	3.511	3.505	3.513	0.083	–59.74	35.04	1.68
	–3.087	*3.470*	*3.470*	*3.472*	*0.099*	*–127.30*	*86.71*	*1.47*
(**6**)	–2.758	3.471	3.471	3.471	0.085	–73.04	41.28	1.77
	–2.971	*3.451*	*3.445*	*3.447*	*0.108*	*–124.31*	*88.08*	*1.41*
(**7**)	–2.679	3.682	3.658	3.652	0.115	–64.06	31.68	2.02
	–2.857	*3.545*	*3.539*	*3.538*	*0.149*	*–94.27*	*68.27*	*1.38*
Group II, n = +3, S_T = 9/2								
(**8**)	–2.697	3.884	3.878	3.879	0.117	–61.93	23.47	2.64
	–2.687	*3.846*	*3.841*	*3.846*	*0.165*	*–84.79*	*54.47*	*1.56*
(**9**)	–2.629	3.813	3.804	3.805	0.073	–72.88	9.82	7.42
	–2.661	*3.770*	*3.768*	*3.770*	*0.108*	*–111.55*	*24.75*	*4.51*
(**10**)	–2.685	3.823	3.816	3.824	0.098	–68.30	10.58	6.46
	–2.705	*3.785*	*3.782*	*3.785*	*0.135*	*–112.05*	*27.77*	*4.04*
(**11**)	–2.669	3.826	3.811	3.834	0.086	–66.98	15.90	4.21
	–2.702	*3.801*	*3.791*	*3.806*	*0.118*	*–112.18*	*30.33*	*3.70*
(**12**)	–2.651	3.860	3.858	3.858	0.105	–70.34	26.81	2.62
	–2.670	*3.822*	*3.821*	*3.822*	*0.178*	*–105.49*	*60.86*	*1.73*
(**13**)	–2.687	3.876	3.871	3.868	0.113	–64.50	23.43	2.75
	–2.708	*3.838*	*3.834*	*3.836*	*0.171*	*–97.94*	*51.22*	*1.91*
(**14**)	–2.708	3.879	3.873	3.872	0.104	–66.10	23.32	2.83
	–2.712	*3.852*	*3.849*	*3.850*	*0.158*	*–99.35*	*51.09*	*1.94*
(**15**)	–2.729	3.888	3.876	3.875	0.106	–64.30	24.78	2.60
	–2.725	*3.855*	*3.850*	*3.853*	*0.160*	*–96.60*	*50.98*	*1.90*
(**16**)	–2.718	3.896	3.890	3.888	0.098	–65.80	23.86	2.76
	–2.718	*3.863*	*3.859*	*3.861*	*0.145*	*–99.95*	*47.91*	*2.09*
(**17**)	–2.687	3.862	3.853	3.863	0.117	–63.28	24.33	2.60
	–2.684	*3.829*	*3.820*	*3.831*	*0.163*	*–101.64*	*49.93*	*2.04*
Group III, n = +4, S_T = 6								
(**18**)	2.913	2.714	2.700	2.685	–0.062	27.14	2.71	10.01
	2.878	*2.711*	*2.696*	*2.700*	*–0.073*	*48.79*	*6.39*	*7.64*
(**19**)	2.888	2.680	2.671	2.677	–0.060	-	-	-
	2.866	*2.681*	*2.678*	*2.689*	*–0.067*	*34.03*	*2.78*	*12.25*
(**20**)	2.893	2.733	2.720	2.727	–0.083	4.88	2.61	1.87
	2.871	*2.733*	*2.724*	*2.736*	*–0.086*	*10.17*	*8.32*	*1.22*
(**21**)	2.901	2.725	2.717	2.720	–0.082	5.52	2.61	1.53
	2.875	*2.728*	*2.723*	*2.733*	*–0.083*	*10.55*	*10.10*	*1.04*
(**22**)	2.883	2.892	2.837	2.874	–0.102	11.91	9.32	1.28
	2.877	*2.778*	*2.765*	*2.779*	*–0.108*	*35.62*	*4.09*	*8.72*
(**23**)	2.908	2.872	2.807	2.821	–0.104	13.25	7.37	1.80
	2.879	*2.784*	*2.774*	*2.785*	*–0.104*	*33.09*	*7.70*	*4.30*
(**24**)	2.921	2.805	2.793	2.802	–0.105	15.32	7.04	2.18
	2.878	*2.791*	*2.783*	*2.793*	*–0.101*	*31.21*	*9.38*	*3.33*

Table S2: The magnetic moments of manganese ions of Mn_4 molecules in the magnetic configurations AFM, FM, and MIX (supporting information for Section 3.3.2).

	AF				FM				MIX			
Mn_4	**$m_{Mn(1)}$**	**$m_{Mn(2)}$**	**$m_{Mn(3)}$**	**$m_{Mn(4)}$**	**$m_{Mn(1)}$**	**$m_{Mn(2)}$**	**$m_{Mn(3)}$**	**$m_{Mn(4)}$**	**$m_{Mn(1)}$**	**$m_{Mn(2)}$**	**$m_{Mn(3)}$**	**$m_{Mn(4)}$**
Group I												
(**1**)	-2.939	1.070	1.063	1.071	2.797	1.122	1.102	1.123	-2.885	-1.078	1.059	1.050
(**2**)	-2.900	1.354	1.341	1.344	2.742	1.411	1.384	1.401	-2.832	-1.378	1.332	1.337
(**3**)	-2.775	3.474	3.472	3.474	2.630	3.536	3.536	3.540	-2.697	-3.471	3.476	3.467
(**4**)	-2.768	3.509	3.494	3.487	2.592	3.579	3.558	3.557	-2.668	-3.506	3.501	3.489
(**5**)	-2.694	3.511	3.505	3.513	2.577	3.574	3.569	3.575	-2.609	-3.514	3.511	3.516
(**6**)	-2.758	3.471	3.471	3.471	2.646	3.540	3.543	3.540	-2.700	-3.477	3.471	3.456
(**7**)	-2.679	3.682	3.658	3.652	2.621	3.712	3.700	3.707	-2.637	-3.723	3.661	3.663
Group II												
(**8**)	-2.697	3.884	3.878	3.879	2.888	3.890	3.883	3.885	-2.768	-3.834	3.857	3.852
(**9**)	-2.629	3.813	3.804	3.805	2.823	3.824	3.815	3.815	-2.699	-3.780	3.774	3.784
(**10**)	-2.685	3.823	3.816	3.824	2.862	3.836	3.828	3.836	-2.748	-3.804	3.794	3.806
(**11**)	-2.669	3.826	3.811	3.834	2.853	3.838	3.819	3.850	-2.735	-3.806	3.788	3.813
(**12**)	-2.651	3.860	3.858	3.858	2.825	3.864	3.862	3.863	-2.712	-3.801	3.823	3.837
(**13**)	-2.687	3.876	3.871	3.868	2.860	3.881	3.877	3.873	-2.747	-3.831	3.844	3.842
(**14**)	-2.708	3.879	3.873	3.872	2.887	3.889	3.882	3.881	-2.770	-3.842	3.846	3.848
(**15**)	-2.729	3.888	3.876	3.875	2.909	3.899	3.885	3.886	-2.793	-3.837	3.866	3.850
(**16**)	-2.718	3.896	3.890	3.888	2.892	3.907	3.898	3.897	-2.777	-3.858	3.865	3.863
(**17**)	-2.687	3.862	3.853	3.863	2.879	3.867	3.856	3.870	-2.755	-3.823	3.826	3.836
Group III												
(**18**)	-2.876	2.686	2.670	2.652	2.913	2.714	2.700	2.685	-2.889	-2.687	2.659	2.637
(**19**)	-2.842	2.668	2.660	2.666	2.888	2.680	2.671	2.677	-2.862	-2.650	2.643	2.653
(**20**)	-2.860	2.736	2.722	2.729	2.893	2.733	2.720	2.727	-2.873	-2.697	2.700	2.714
(**21**)	-2.859	2.717	2.708	2.712	2.901	2.725	2.717	2.720	-2.875	-2.689	2.685	2.697
(**22**)	-2.850	2.930	2.871	2.911	2.883	2.892	2.837	2.874	-2.857	-2.811	2.852	2.892
(**23**)	-2.886	2.826	2.804	2.818	2.908	2.872	2.807	2.821	-2.892	-2.779	2.785	2.798
(**24**)	-2.904	2.781	2.768	2.777	2.921	2.805	2.793	2.802	-2.909	-2.766	2.750	2.758