metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	r(0)	beta
Mn1	2.091	1.976	1.934	1.874	1.947	1.76	0.37
	-0.331	-0.216	-0.174	-0.114	-0.187		
	-0.89459	-0.58378	-0.47027	-0.308108	-0.50541		
	0.408773	0.557784	0.624833	0.7348359	0.603261		
M(Ox.State)	2.929487						

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn2	2.223	2.2277	2.099	2.187	2.152	2.225	1.79	0.37
	-0.433	-0.4377	-0.309	-0.397	-0.362	-0.435		
	-1.17027	-1.18297	-0.83514	-1.072973	0.97838	1.17568		
	0.310283	0.306367	0.433816	0.3419903	0.37592	0.30861		
M(Ox.State)	2.076986							

Table S1. Bond valence sum calculations to confirm the oxidation states of Mn ions in complex **3**.

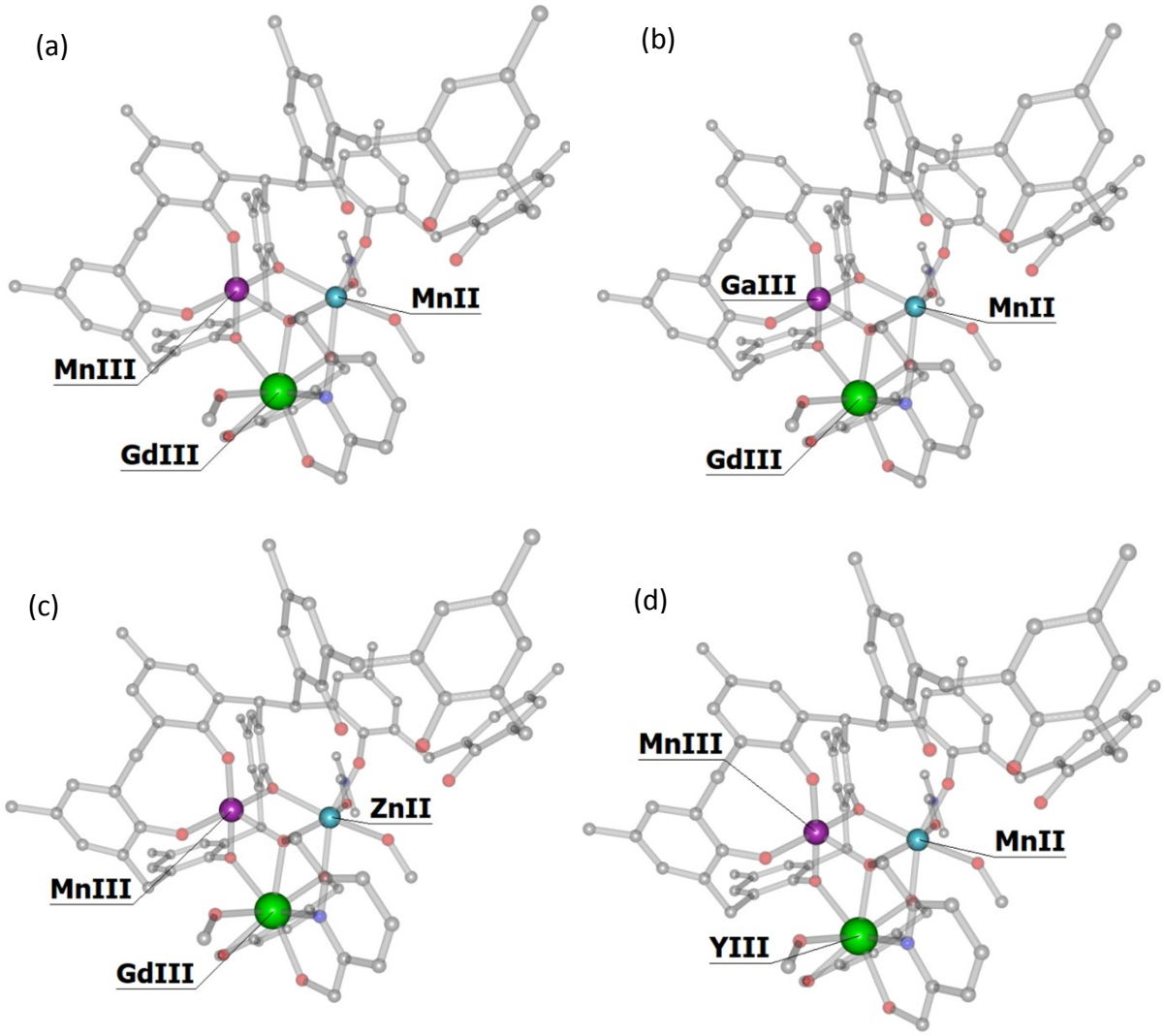


Figure S1. (a) Molecular structure of the model complex **3A**. Figures (b)-(d) show the models used to calculate the $J^{exchange}_{Mn(II)-Gd(III)}$, $J^{exchange}_{Mn(III)-Gd(III)}$ and $J^{exchange}_{Mn(II)-Mn(III)}$ pairwise interactions, respectively. In (b) the Mn(III) ion has been replaced by Ga(III). In (c) the Mn(II) ion has been replaced by Zn(II). In (d) the Gd(III) ion has been replaced with Y(III). Colour code is the same as in Figure 1.

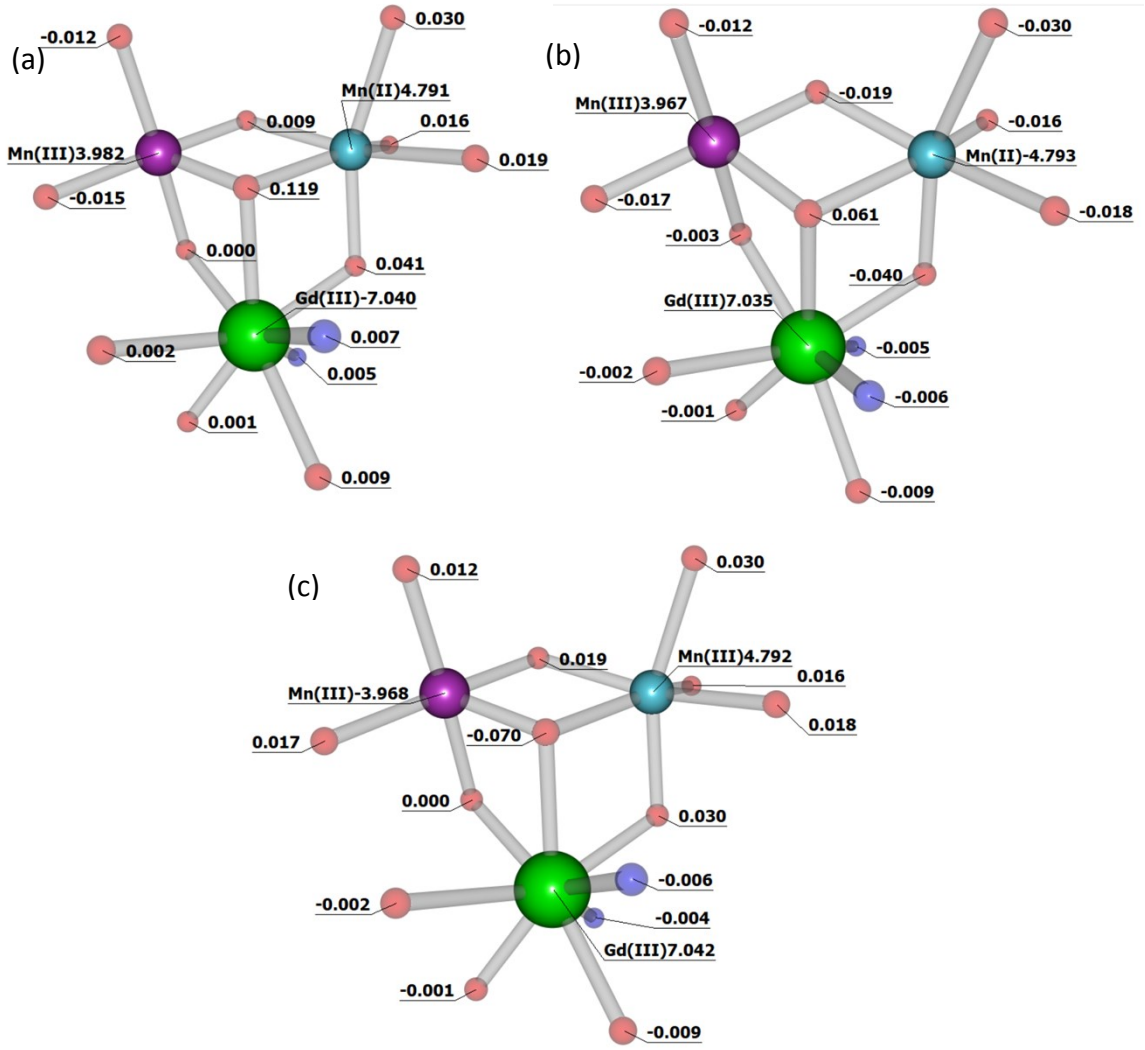


Figure S2. (a)-(c) Spin density values on selected atoms for spin states *S* = 1, 3 and 4, respectively. Note that both experimental and computational studies suggest *S* = 4 as the ground spin state.

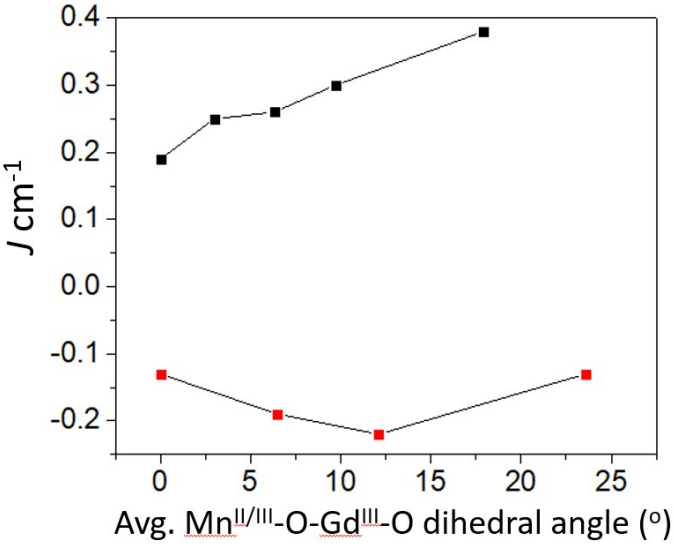


Figure S3. Magneto-structural plots performed by varying the average Mn^{II}/Mn^{III}-O-Gd^{III}–O dihedral angle with respect to the magnetic exchange coupling values ($J^{exchange}_{Mn(II)-Gd(III)}$ = black solid squares and $J^{exchange}_{Mn(III)-Gd(III)} = red\ solid\ squares$). For both models, the change in the magnetic exchange coupling values with respect to the change in $Mn^{III/II}$-O-Gd^{III}-O dihedral angle are minimal.

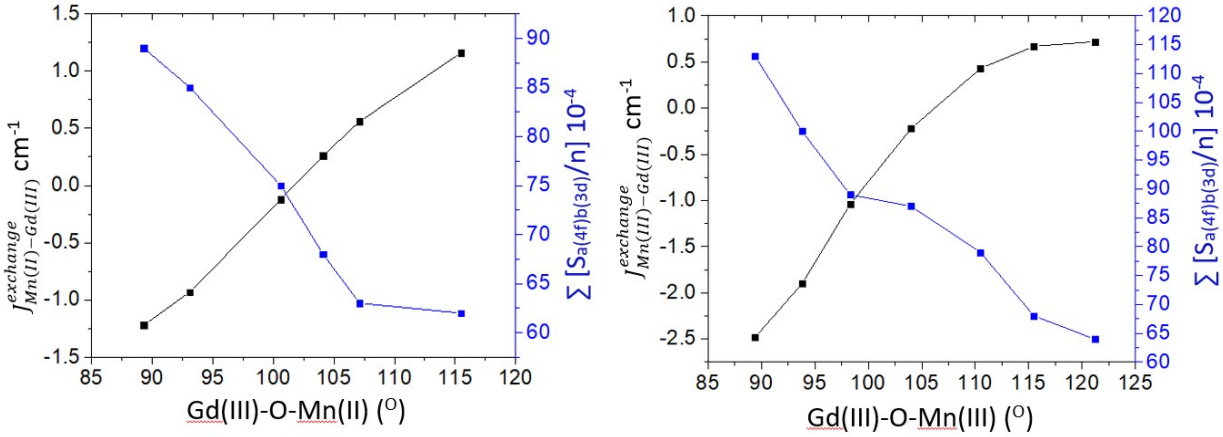
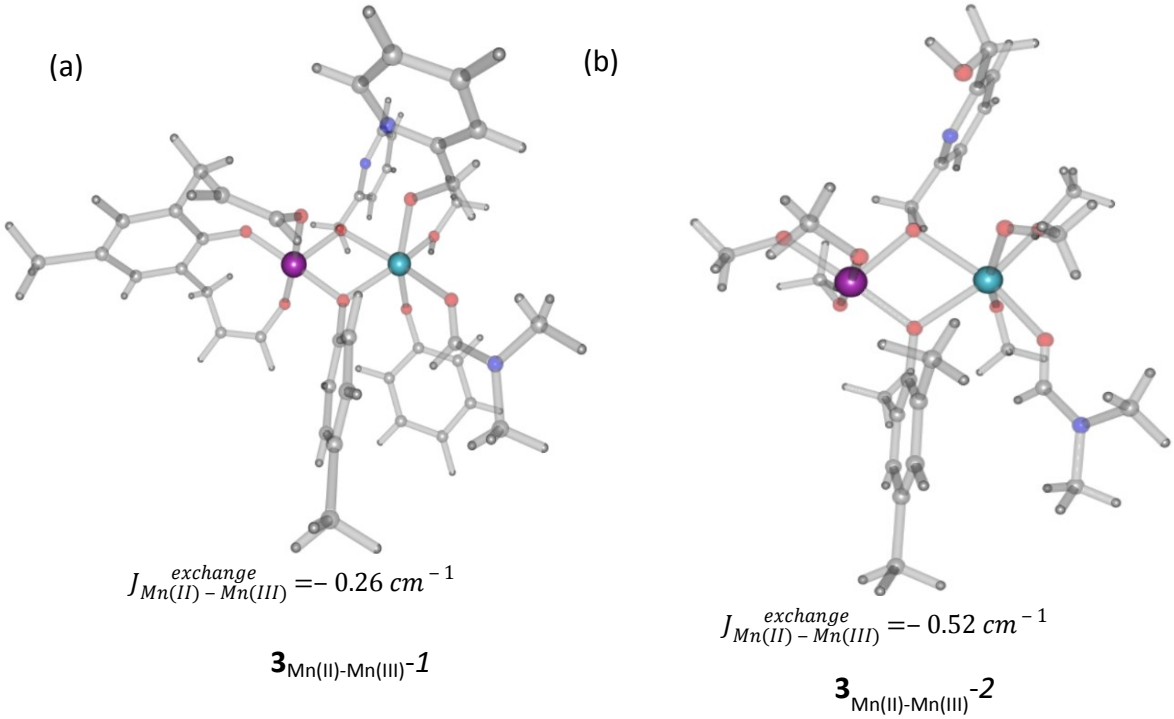


Figure S4. Magneto-structural data calculated by varying the average Mn^{II}/Mn^{III}-O-Gd^{III} angle with respect to the magnetic exchange coupling values, and average overlap integral values between SOMOs of {Mn(III/II)-3d} and {Gd(III)-4f} orbitals. Here, n = number of possible overlap integrals between the SOMOs (for $3d^5$-$4f^7$ systems, n = 35 and for $3d^4$-$4f^7$ systems, n = 28). The larger the average overlap intergral value, the stronger the antiferromagnetic exchange interaction and vice versa.



3$_{Mn(II)-Mn(III)}$-*1*

3$_{Mn(II)-Mn(III)}$-*2*

Figure S5. (a)-(b) Molecular structures for models **3**$_{Mn(II)-Mn(III)}$-*1 and* **3**$_{Mn(II)-Mn(III)}$-*2,* respectively. Colour code is same as in Figure 1.

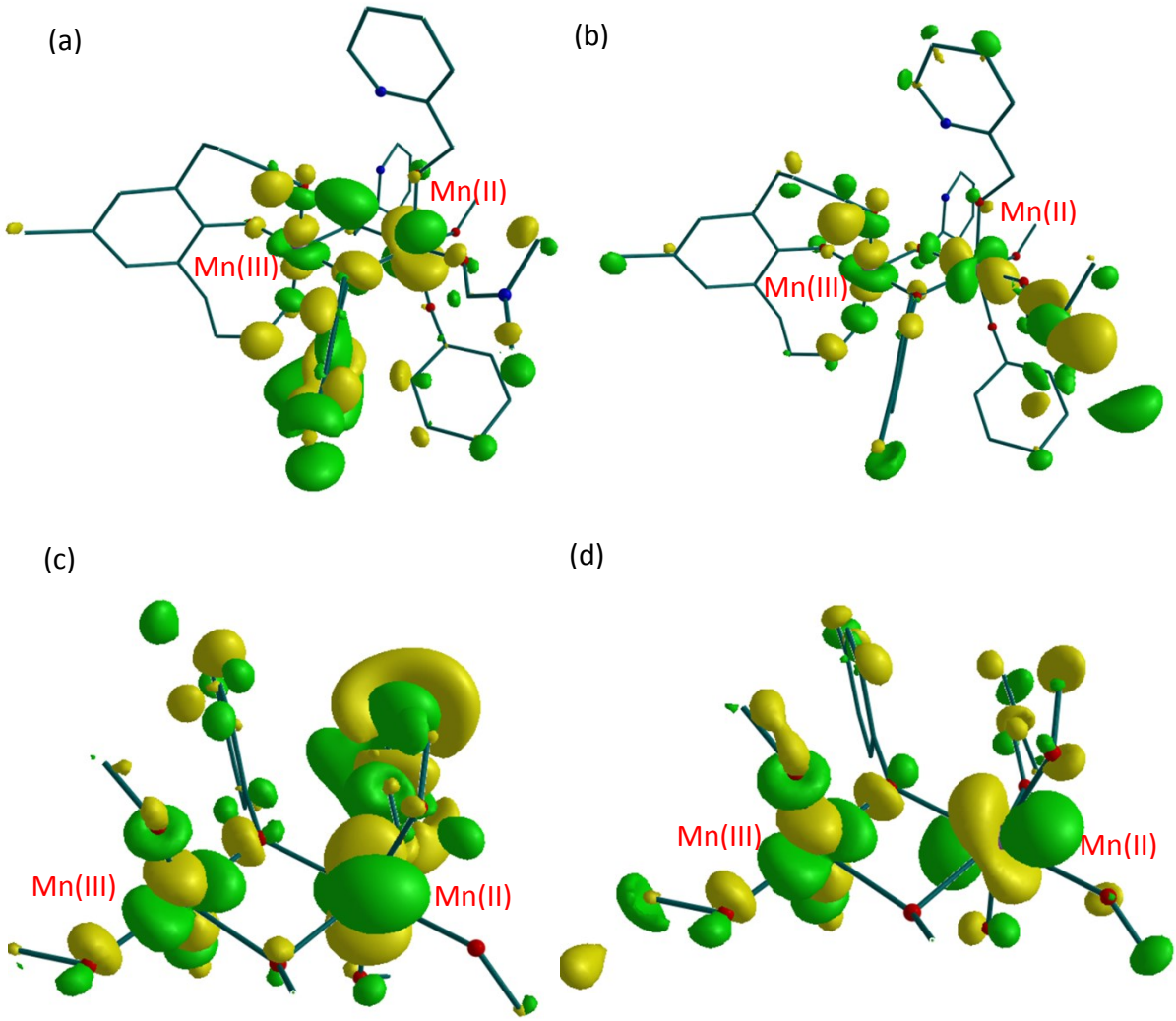


Figure S6. (a)-(b) Representative molecular orbitals showing Mn(II)d_{yz}|p|Mn(III)d_{z^2} and Mn(II)$d_{x^2-y^2}$|p|Mn(III)d_{z^2} for **3**$_{Mn(II)-Mn(III)}$-*1*, and (c)-(d) Mn(II)d_{yz}|p|Mn(III)d_{z^2} and Mn(II)d_{xz}|p|Mn(III)d_{z^2} for **3**$_{Mn(II)-Mn(III)}$-*2*, respectively.

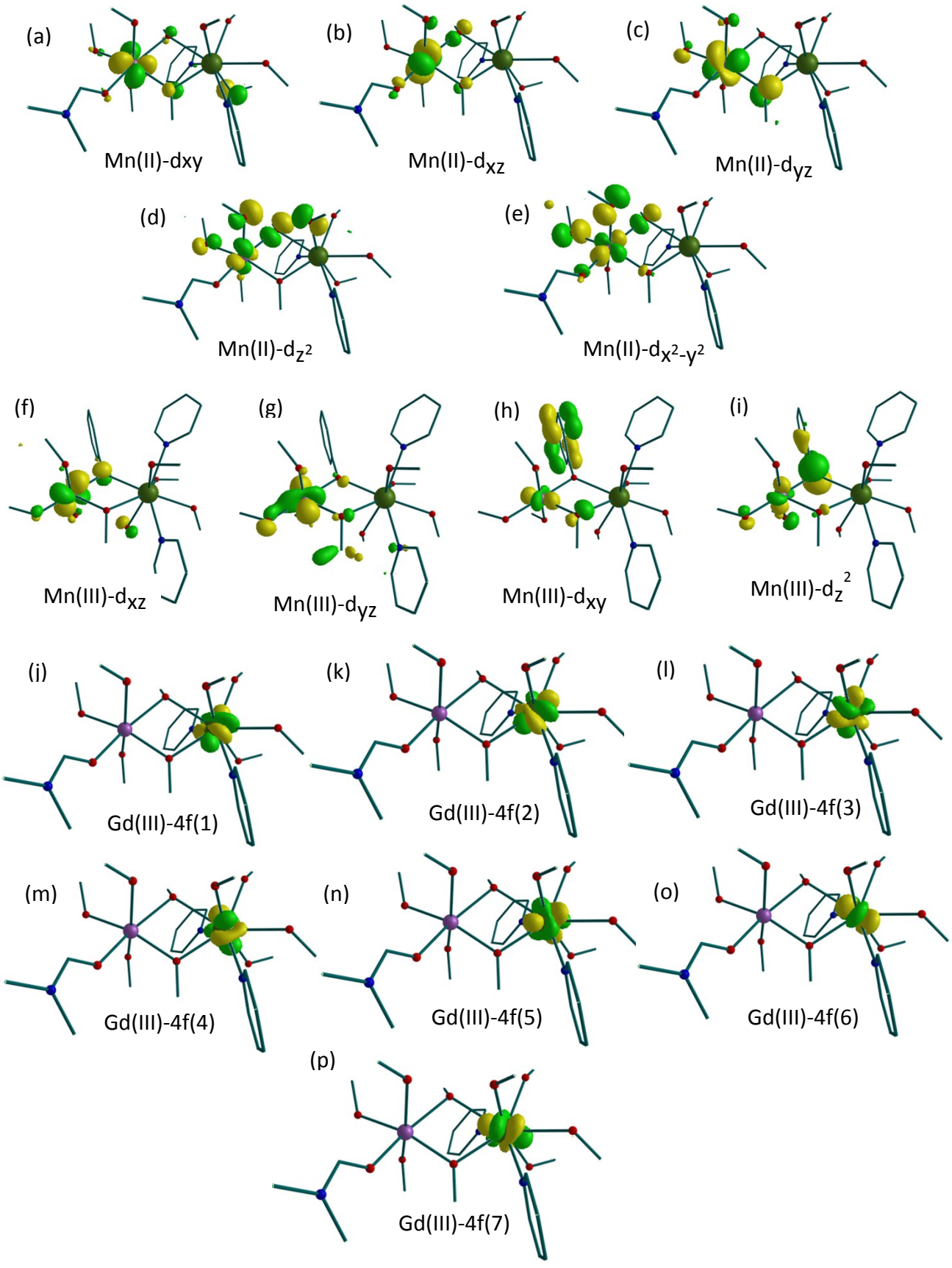

(a)
Mn(II)-dxy
(b)
Mn(II)-dxz
(c)
Mn(II)-dyz
(d)
Mn(II)-dz2
(e)
Mn(II)-dx2-y2
(f)
Mn(III)-dxz
(g)
Mn(III)-dyz
(h)
Mn(III)-dxy
(i)
Mn(III)-dz2
(j)
Gd(III)-4f(1)
(k)
Gd(III)-4f(2)
(l)
Gd(III)-4f(3)
(m)
Gd(III)-4f(4)
(n)
Gd(III)-4f(5)
(o)
Gd(III)-4f(6)
(p)
Gd(III)-4f(7)

Figure S7. Representitive SOMOs for the Mn(II) (a)-(e), Mn(III) (f)-(i) and Gd(III) (j)-(p) ions.

Table S2. DFT computed overlap integral (OI) values corresponding to the $J^{exchange}_{Mn(II)-Gd(III)}$, $J^{exchange}_{Mn(III)-Gd(III)}$ and $J^{exchange}_{Mn(II)-Mn(III)}$ exchange pathways in complex **3**. Here α and β signify spin-up and spin-down orbitals, respectively, with the numbers relating to the corresponding SOMOs.

Gd^{III}-α	Mn^{II}-β	OIs	Gd^{III}- α	Mn^{III}- β	OIs	Mn^{II}- α	Mn^{III}- β	OIs
4f(1)	d_{xz}	0.003	4f(1)	d_{xz}	0.003	d_{xz}	d_{xz}	0.024
	d_{yz}	0.010		d_{yz}	0.001		d_{yz}	0.009
	d_{xy}	0.010		d_{xy}	0.008		d_{xy}	0.090
	$d_{x^2-y^2}$	0.012		d_{z^2}	0.003		d_{z^2}	0.065
	d_{z^2}	0.009	4f(2)	d_{xz}	0.011	d_{yz}	d_{xz}	0.035
4f(2)	d_{xz}	0.001		d_{yz}	0.011		d_{yz}	0.001
	d_{yz}	0.013		d_{xy}	0.005		d_{xy}	0.027
	d_{xy}	0.003		d_{z^2}	0.005		d_{z^2}	0.102
	$d_{x^2-y^2}$	0.002	4f(3)	d_{xz}	0.004	d_{xy}	d_{xz}	0.009
	d_{z^2}	0.014		d_{yz}	0.010		d_{yz}	0.028
4f(3)	d_{xz}	0.001		d_{xy}	0.009		d_{xy}	0.024
	d_{yz}	0.006		d_{z^2}	0.010		d_{z^2}	0.004
	d_{xy}	0.001	4f(4)	d_{xz}	0.010	$d_{x^2-y^2}$	d_{xz}	0.053
	$d_{x^2-y^2}$	0.008		d_{yz}	0.006		d_{yz}	0.043
	d_{z^2}	0.003		d_{xy}	0.005		d_{xy}	0.096
4f(4)	d_{xz}	0.004		d_{z^2}	0.011		d_{z^2}	0.075
	d_{yz}	0.001	4f(5)	d_{xz}	0.011	d_{z^2}	d_{xz}	0.017
	d_{xy}	0.003		d_{yz}	0.003		d_{yz}	0.032
	$d_{x^2-y^2}$	0.007		d_{xy}	0.016		d_{xy}	0.008
	d_{z^2}	0.004		d_{z^2}	0.017		d_{z^2}	0.026
4f(5)	d_{xz}	0.004	4f(6)	d_{xz}	0.004			
	d_{yz}	0.001		d_{yz}	0.009			
	d_{xy}	0.003		d_{xy}	0.019			
	$d_{x^2-y^2}$	0.018		d_{z^2}	0.001			
	d_{z^2}	0.001	4f(7)	d_{xz}	0.000			
4f(6)	d_{xz}	0.002		d_{yz}	0.003			
	d_{yz}	0.016		d_{xy}	**0.200**			
	d_{xy}	0.005		d_{z^2}	0.013			
	$d_{x^2-y^2}$	0.002						
	d_{z^2}	0.011						
4f(7)	d_{xz}	0.001						
	d_{yz}	0.009						
	d_{xy}	0.006						
	$d_{x^2-y^2}$	0.001						
	d_{z^2}	0.006						

Table S3. DFT computed overlap integral (OI) values corresponding to the magneto-structural correlation developed from model $\mathbf{3}_{Mn(II)\text{-}Gd(III)}$ (Figure S1 (b)) with respect to the average Mn^{II}-O-Gd^{III} angle. Here α and β signify spin-up and spin-down orbitals, respectively. with the numbers relating to the corresponding SOMOs. Here, $\sum Sa(4f)b(3d)$ represents the total OIs between {Gd(III)$4f^7$} and {Mn(II)$3d^5$} SOMOs. n = number of possible overlap integrals between the SOMOs (for $3d^5$-$4f^7$ systems, n = 35).

α	β	89.3 °	93.1 °	100.6 °	104.1 °	107.1 °	115.5 °
		OIs	OIs	OIs	OIs	OIs	OIs
4f(1)	d_{xz}	0.002	0.009	0.018	0.018	0.017	0.002
	d_{yz}	0.019	0.021	0.018	0.016	0.015	0.009
	d_{xy}	0.028	0.026	0.022	0.019	0.016	0.007
	$d_{x^2-y^2}$	0.012	0.010	0.007	0.006	0.006	0.000
	d_{z^2}	0.001	0.000	0.002	0.002	0.003	0.003
4f(2)	d_{xz}	0.006	0.003	0.003	0.004	0.006	0.014
	d_{yz}	0.007	0.007	0.005	0.003	0.002	0.001
	d_{xy}	0.002	0.000	0.003	0.003	0.004	0.003
	$d_{x^2-y^2}$	0.010	0.007	0.003	0.002	0.002	0.000
	d_{z^2}	0.003	0.003	0.004	0.005	0.005	0.007
4f(3)	d_{xz}	0.001	0.003	0.008	0.008	0.009	0.016
	d_{yz}	0.002	0.005	0.003	0.002	0.001	0.001
	d_{xy}	0.011	0.012	0.008	0.004	0.001	0.010
	$d_{x^2-y^2}$	0.002	0.003	0.005	0.006	0.006	0.000
	d_{z^2}	0.001	0.002	0.004	0.004	0.005	0.008
4f(4)	d_{xz}	0.010	0.011	0.011	0.019	0.013	0.011
	d_{yz}	0.016	0.011	0.003	0.004	0.008	0.014
	d_{xy}	0.021	0.014	0.001	0.001	0.002	0.006
	$d_{x^2-y^2}$	0.011	0.010	0.009	0.004	0.002	0.000
	d_{z^2}	0.003	0.002	0.001	0.014	0.014	0.013
4f(5)	d_{xz}	0.015	0.025	0.022	0.004	0.004	0.015
	d_{yz}	0.035	0.025	0.002	0.000	0.001	0.002
	d_{xy}	0.016	0.011	0.001	0.006	0.011	0.021
	$d_{x^2-y^2}$	0.006	0.007	0.003	0.007	0.006	0.000
	d_{z^2}	0.008	0.012	0.014	0.003	0.003	0.006
4f(6)	d_{xz}	0.008	0.002	0.006	0.004	0.002	0.008
	d_{yz}	0.002	0.011	0.005	0.004	0.003	0.001
	d_{xy}	0.000	0.007	0.013	0.012	0.010	0.003
	$d_{x^2-y^2}$	0.010	0.003	0.011	0.011	0.010	0.000
	d_{z^2}	0.015	0.012	0.003	0.003	0.003	0.003
4f(7)	d_{xz}	0.002	0.000	0.013	0.013	0.010	0.013
	d_{yz}	0.008	0.007	0.012	0.010	0.008	0.004
	d_{xy}	0.001	0.003	0.007	0.008	0.009	0.012
	$d_{x^2-y^2}$	0.010	0.013	0.006	0.005	0.003	0.000
	d_{z^2}	0.007	0.000	0.005	0.003	0.001	0.005
$\sum Sa(4f)b(3d)$		0.311	0.297	0.261	0.237	0.221	0.218
$\sum Sa(4f)b(3d)/n$		0.0089	0.0085	0.0075	0.0068	0.0063	0.0062

Table S4. DFT computed overlap integral (OI) values corresponding to the magneto-structural correlation developed from model $\mathbf{3}_{Mn(III)\text{-}Gd(III)}$ (Figure S1 (c)) with respect to average Mn^{III}-O-Gd^{III} angle. Here α and β signify spin-up and spin-down orbitals, respectively, with the numbers relating to the corresponding SOMOs. Here, $\sum Sa(4f)b(3d)$ represents the total OIs between {Gd(III)$4f^7$} and {Mn(III)$3d^4$} SOMOs. n = number of possible overlap integrals between the SOMOs (for $3d^4$-$4f^7$ systems, n = 28).

α	β	89.4 °	93.8 °	98.3 °	104.0 °	110.5 °	115.5 °	121.2 °
		OIs	OIs	OIs	OIs	OIs	OIs	OIs
4f(1)	d_{xz}	0.008	0.008	0.010	0.010	0.006	0.003	0.007
	d_{yz}	0.015	0.013	0.007	0.007	0.002	0.002	0.001
	d_{xy}	0.018	0.017	0.015	0.013	0.008	0.002	0.000
	d_z^2	0.013	0.018	0.020	0.021	0.027	0.027	0.025
4f(2)	d_{xz}	0.001	0.012	0.000	0.009	0.007	0.007	0.009
	d_{yz}	0.005	0.001	0.002	0.000	0.003	0.002	0.001
	d_{xy}	0.005	0.006	0.005	0.002	0.002	0.003	0.003
	d_z^2	0.009	0.006	0.001	0.002	0.007	0.007	0.007
4f(3)	d_{xz}	0.015	0.008	0.018	0.008	0.006	0.004	0.004
	d_{yz}	0.026	0.012	0.002	0.008	0.015	0.015	0.012
	d_{xy}	0.012	0.004	0.000	0.002	0.005	0.005	0.004
	d_z^2	0.001	0.006	0.007	0.007	0.011	0.011	0.007
4f(4)	d_{xz}	0.011	0.005	0.006	0.008	0.005	0.004	0.008
	d_{yz}	0.017	0.005	0.004	0.001	0.003	0.002	0.000
	d_{xy}	0.010	0.015	0.015	0.015	0.005	0.000	0.001
	d_z^2	0.014	0.016	0.018	0.019	0.020	0.020	0.017
4f(5)	d_{xz}	0.007	0.004	0.002	0.002	0.004	0.003	0.002
	d_{yz}	0.014	0.013	0.007	0.008	0.004	0.005	0.003
	d_{xy}	0.012	0.006	0.013	0.012	0.004	0.004	0.005
	d_z^2	0.005	0.012	0.009	0.014	0.014	0.013	0.012
4f(6)	d_{xz}	0.010	0.003	0.003	0.002	0.001	0.003	0.011
	d_{yz}	0.004	0.003	0.004	0.005	0.013	0.013	0.014
	d_{xy}	0.009	0.011	0.005	0.002	0.011	0.009	0.009
	d_z^2	0.031	0.022	0.010	0.005	0.008	0.004	0.003
4f(7)	d_{xz}	0.004	0.001	0.009	0.009	0.010	0.009	0.004
	d_{yz}	0.016	0.015	0.010	0.009	0.002	0.003	0.000
	d_{xy}	0.009	0.016	0.022	0.023	0.007	0.003	0.005
	d_z^2	0.016	0.022	0.025	0.021	0.011	0.007	0.004
$\sum Sa(4f)b(3d)$		0.317	0.280	0.249	0.244	0.221	0.190	0.178
$\sum Sa(4f)b(3d)/n$		0.0113	0.0100	0.0089	0.0087	0.0079	0.0068	0.0064

Table S5. DFT computed overlap integral (OI) values corresponding to models $\mathbf{3}_{Mn(II)\text{-}Mn(III)}$-*1 and* $\mathbf{3}_{Mn(II)\text{-}Mn(III)}$-*2*, respectively (Figure S5). Here α and β signify spin-up and spin-down orbitals, respectively, with the numbers relating to the corresponding SOMOs. Here, $\sum Sa(3d)b(3d)$ represents the total OIs between {Mn(II)$3d^5$} and {Mn(III)$3d^4$} SOMOs. n = number of possible overlap integrals between the SOMOs (for $3d^5$-$3d^4$ systems, n = 20).

Mn(III)- β	Mn(II)- α	$\mathbf{3}_{Mn(II)\text{-}Mn(III)}$-*1*	$\mathbf{3}_{Mn(II)\text{-}Mn(III)}$-*2*
		OIs	OIs
d_{xz}	d_{xz}	0.005	0.057
	d_{yz}	0.012	0.004
	d_{xy}	0.047	0.018
	$d_{x^2-y^2}$	0.016	0.013
	d_{z^2}	0.085	0.064
d_{yz}	d_{xz}	0.003	0.028
	d_{yz}	0.049	0.007
	d_{xy}	0.009	0.016
	$d_{x^2-y^2}$	0.004	0.039
	d_{z^2}	0.029	0.026
d_{xy}	d_{xz}	0.001	0.093
	d_{yz}	0.019	0.005
	d_{xy}	0.019	0.019
	$d_{x^2-y^2}$	0.003	0.026
	d_{z^2}	0.010	0.020
d_{z^2}	d_{xz}	0.038	0.017
	d_{yz}	**0.139**	**0.246**
	d_{xy}	0.043	**0.188**
	$d_{x^2-y^2}$	**0.178**	0.016
	d_{z^2}	0.030	0.022
$\sum Sa(3d)b(3d)$		0.739	0.924
$\sum Sa(3d)b(3d)/n$		0.037	0.046