Supporting Information

Distinction between Mn(III) and Mn(II) by using a colorimetric chemosensor in aqueous solution

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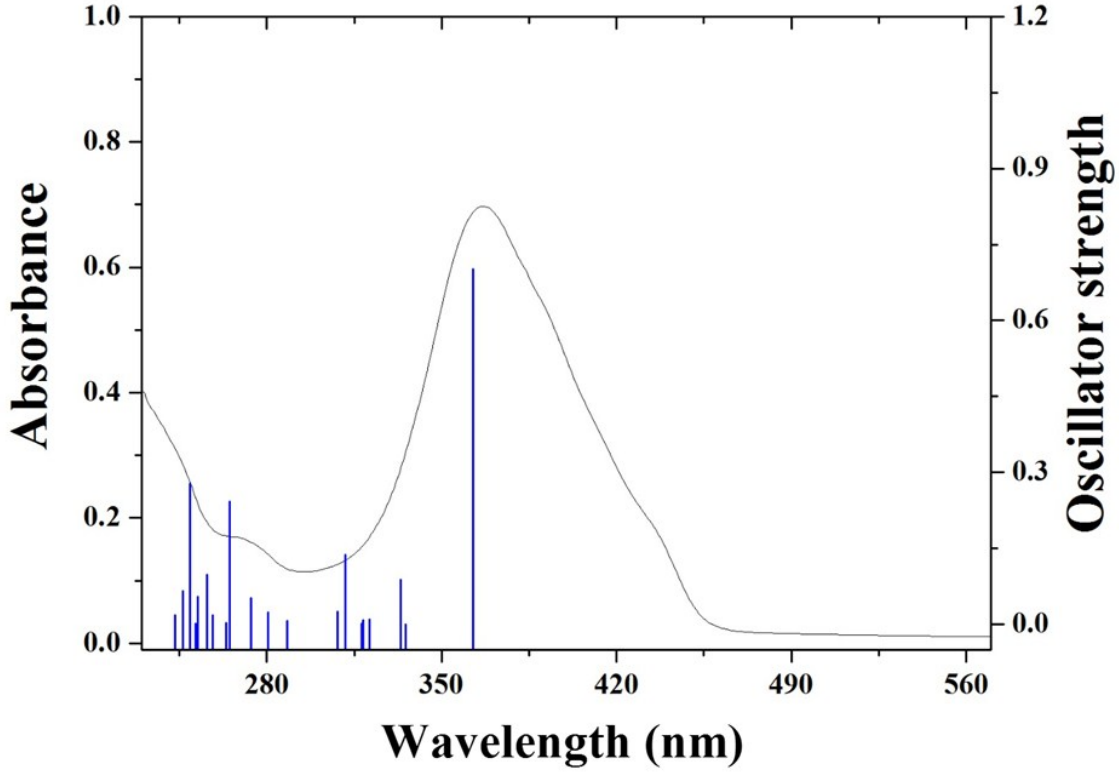
(a)

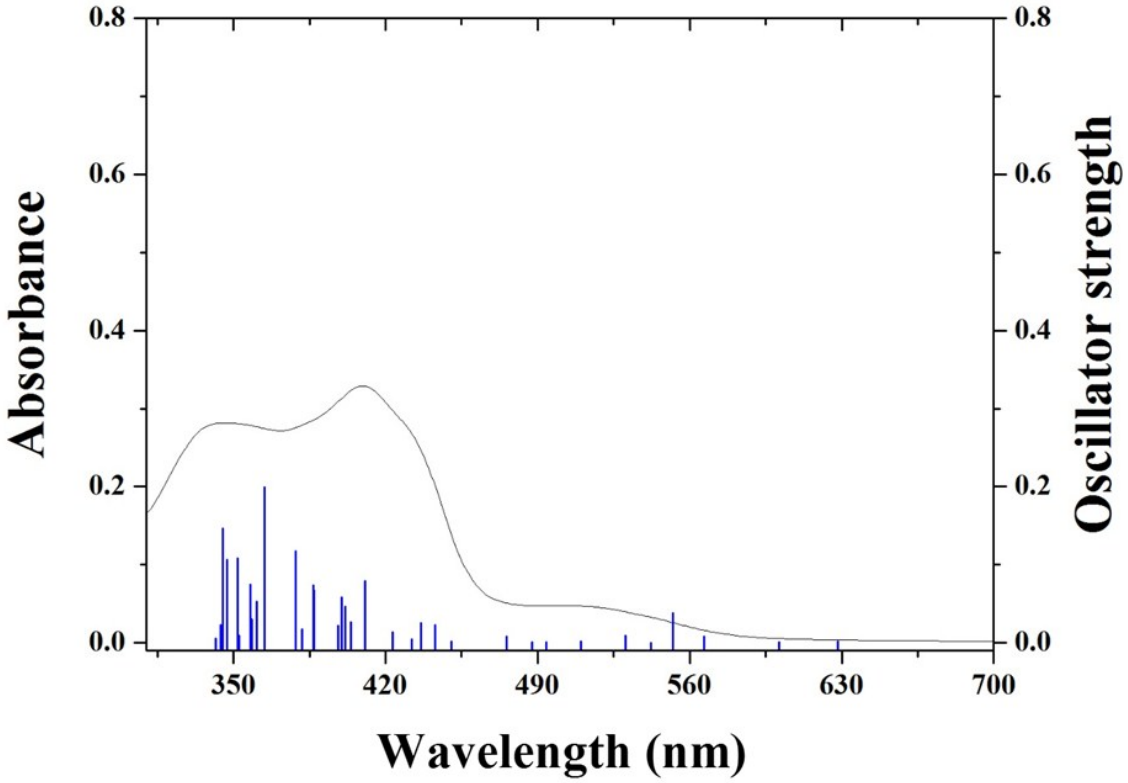


(b)

Excited State 1	Wavelength	Percent (%)	Oscillator strength
H → L	362.50 nm	97 %	0.7023
Excited State 2	**Wavelength**	**Percent (%)**	**Oscillator strength**
H-1 → L+1	335.52 nm	94 %	0.0004
H-1 → L		4 %	

Table S1. (a) The theoretical excitation energies and the experimental UV-vis spectrum of **1**. (b) The major electronic transition energies and molecular orbital contributions for **1** (H = HOMO and L = LUMO).

(a)



(b)

Excited State 10	Wavelength	Percent (%)	Main character	Oscillator strength
H-1 → L (α)	552.33 nm	5 %	LMCT	0.0386
H-2 → L (α)		5 %	LMCT	
H-1 → L+1 (α)		3 %	ICT	
H-6 → L (α)		2 %	LMCT	
H → L (β)		58 %	LMCT	
H-2 → L (β)		18 %	LMCT	
Excited State 22	**Wavelength**	**Percent (%)**	**Main character**	**Oscillator strength**
H-2 → L (α)	410.69 nm	5 %	LMCT	0.0791
H-11 → L (α)		3 %	d-d transition	
H-2 → L+1 (α)		2 %	ICT	
H → L+2 (α)		2 %	ICT	
H → L+2 (β)		22 %	ICT	
H-2 → L (β)		11 %	LMCT	
H-1 → L+2 (β)		11 %	ICT	
H-4 → L (β)		10 %	LMCT	

H-3 → L+2 (β)		2 %	ICT	
H-2 → L+2 (β)		2 %	MLCT	
H-1 → L+3 (β)		2 %	LMCT	
H-1 → L+4 (β)		2 %	ICT	
H → L+3 (β)		2 %	LMCT	
H → L+4 (β)		2 %	ICT	
Excited State 30	**Wavelength**	**Percent (%)**	**Main character**	**Oscillator strength**
H-4 → L (α)	378.60 nm	22 %	LMCT	0.1177
H-2 → L+1 (α)		10 %	ICT	
H-1 → L+1 (α)		5 %	ICT	
H → L+3 (β)		29 %	LMCT	
H-1 → L+3 (β)		3 %	LMCT	
H-1 → L+4 (β)		3 %	ICT	
H → L+4 (β)		3 %	ICT	
H-2 → L+4 (β)		2 %	ICT	
H → L+2 (β)		2 %	ICT	

Table S2. (a) The theoretical excitation energies and the experimental UV-vis spectrum of **1**-Mn^{3+}. (b) The major electronic transition energies and molecular orbital contributions for **1**-Mn^{3+} (H = HOMO and L = LUMO).

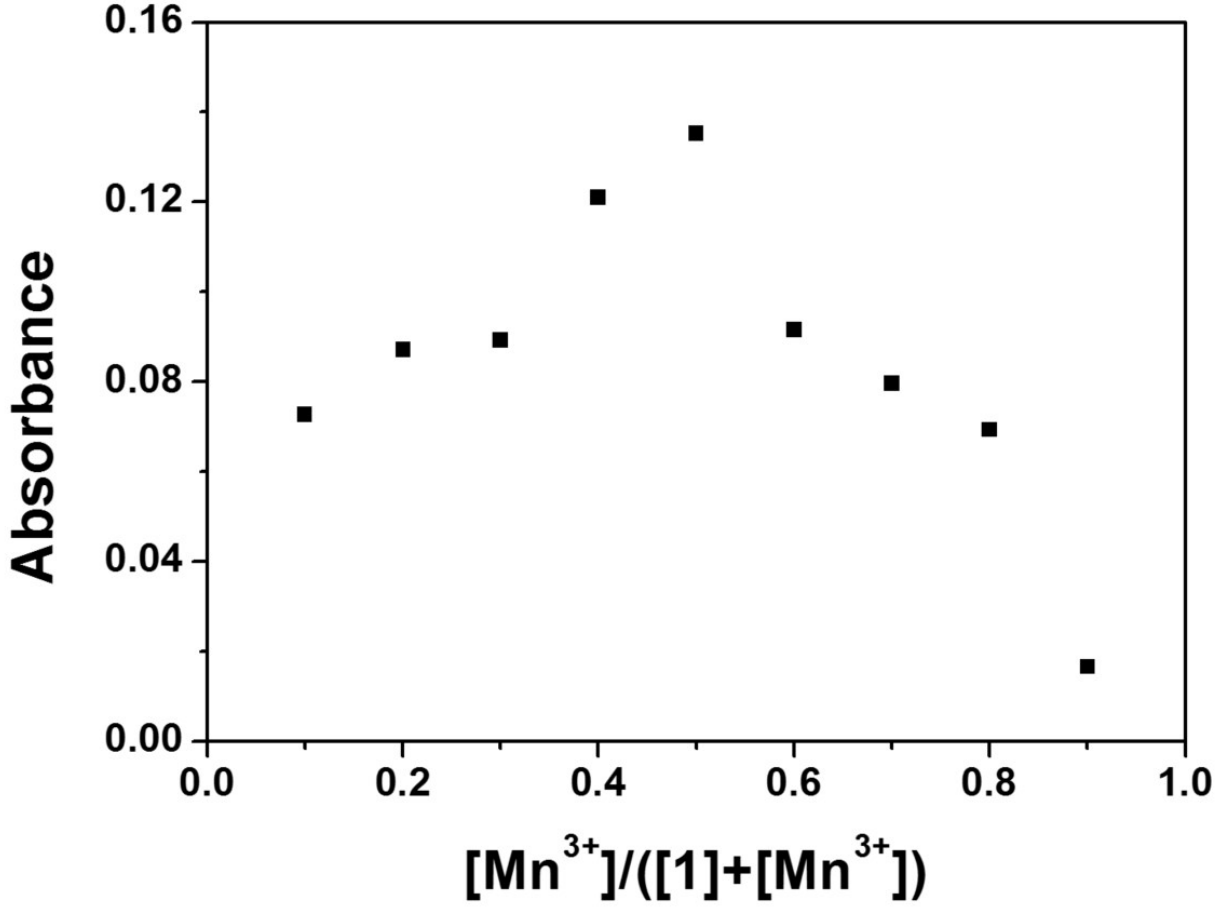


Fig. S1 Job plot for the binding of **1** with Mn^{3+}. Absorbance at 437 nm was plotted as a function of the molar ratio $[Mn^{3+}]/([\mathbf{1}] + [Mn^{3+}])$. The total concentrations of Mn^{3+} ions with receptor **1** were 1.0×10^{-5} M.

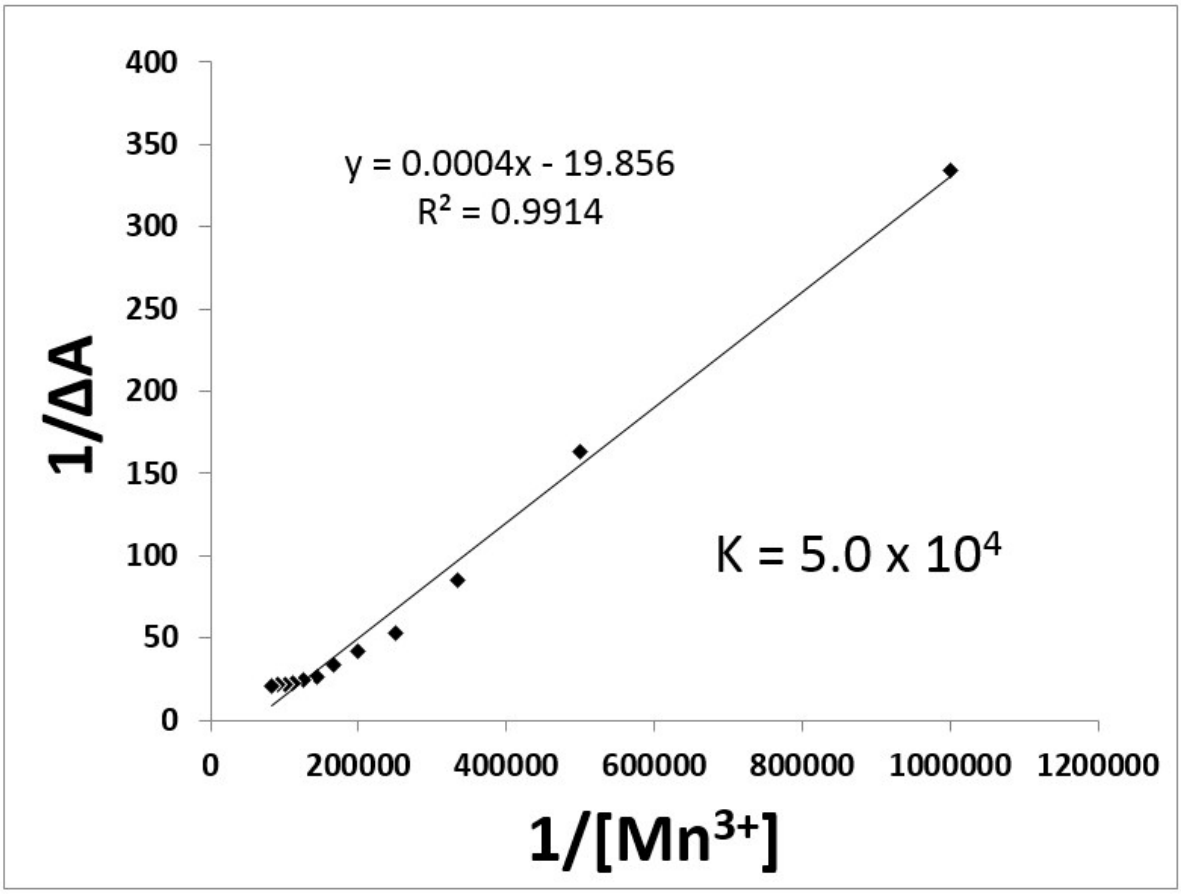


Fig. S2 Benesi-Hildebrand plot (absorbance at 500 nm) of **1**, assuming a 1:1 stoichiometry for association between **1** and Mn^{3+}.

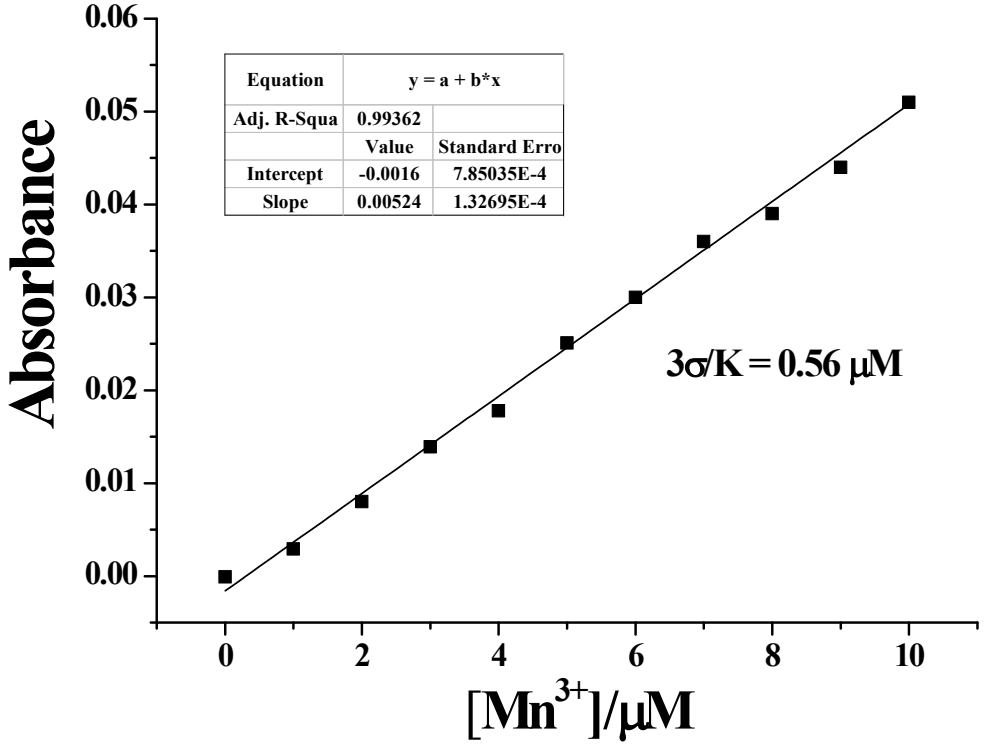
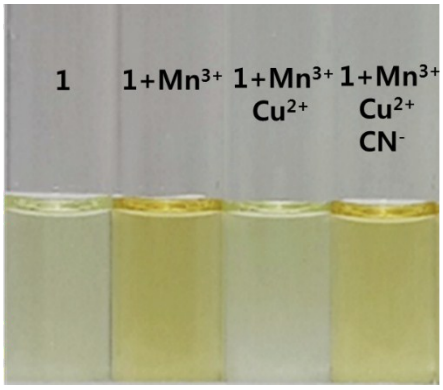
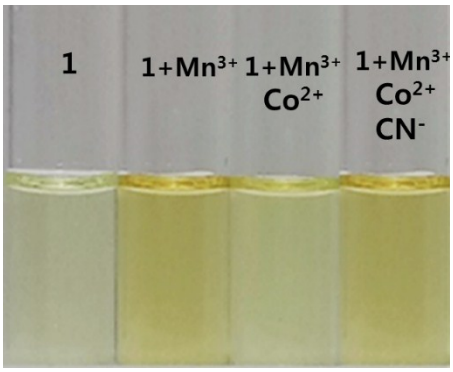


Fig. S3 Determination of the detection limit based on change in the ratio (absorbance at 500 nm) of **1** (10 μM) with Mn^{3+}.

(a)





(b)

Fig. S4 (a) Colorimetric changes of **1**-Mn^{3+} and 1-Mn^{3+}-Cu^{2+} (10 μM) in absence or presence of CN^- (150 equiv). (a) Colorimetric changes of **1**-Mn^{3+} and 1-Mn^{3+}-Co^{2+} (10 μM) in absence or presence of CN^- (150 equiv).

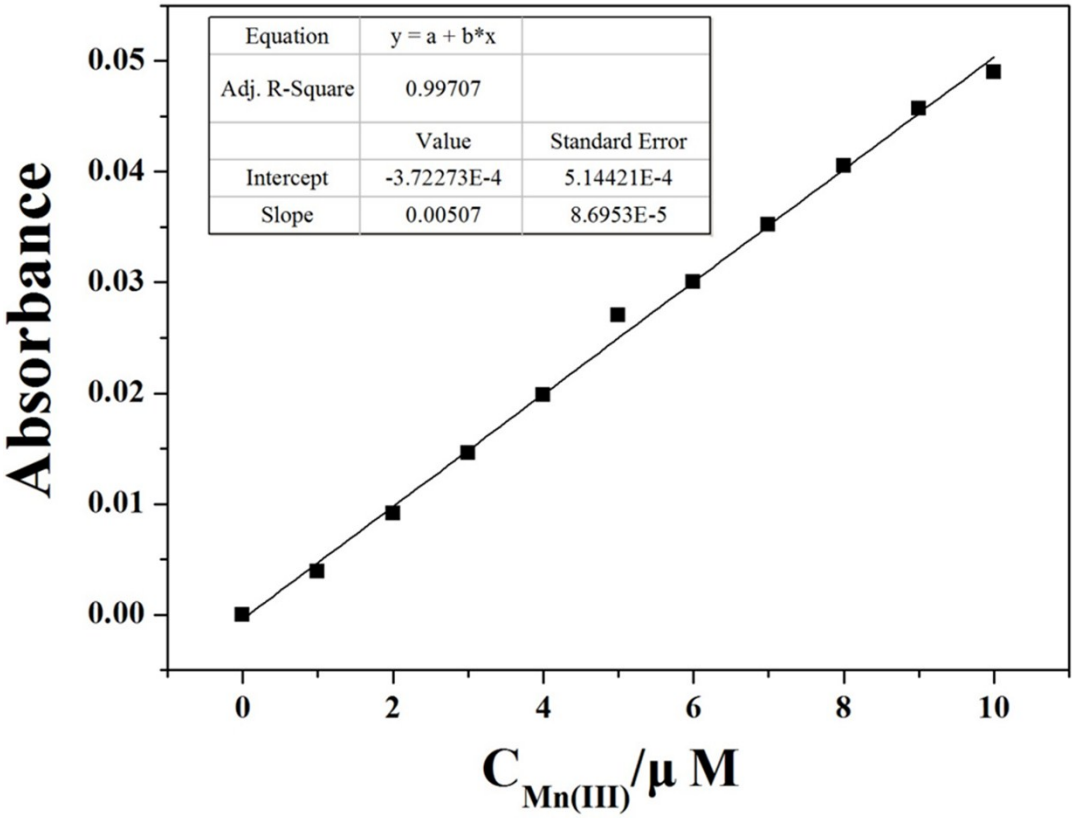


Fig. S5 UV-vis absorbance (at 500 nm) of **1** as a function of Mn (III) concentration ([**1**] = 30 μmol/L and [Mn(III)] = 0.00-10.00 μmol/L). Conditions: all samples were conducted in buffer-CH_3CN solution (7:3, v/v, 10 mM bis-tris, pH 7.0).

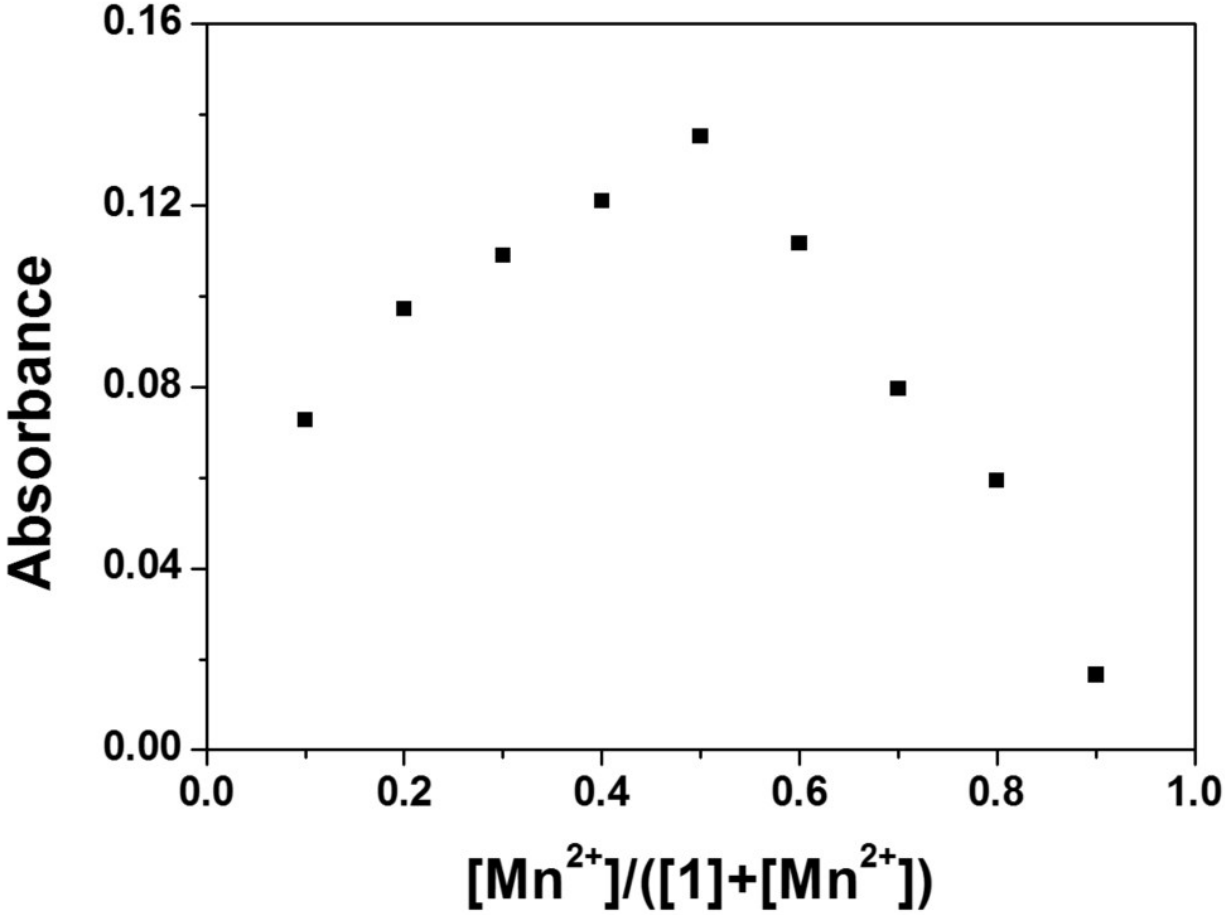


Fig. S6 Job plot for the binding of **1** with Mn^{2+}. Absorbance at 437 nm was plotted as a function of the molar ratio $[Mn^{2+}]/([\mathbf{1}] + [Mn^{2+}])$. The total concentrations of Mn^{2+} ions with receptor **1** were 1.0 x 10^{-5} M.

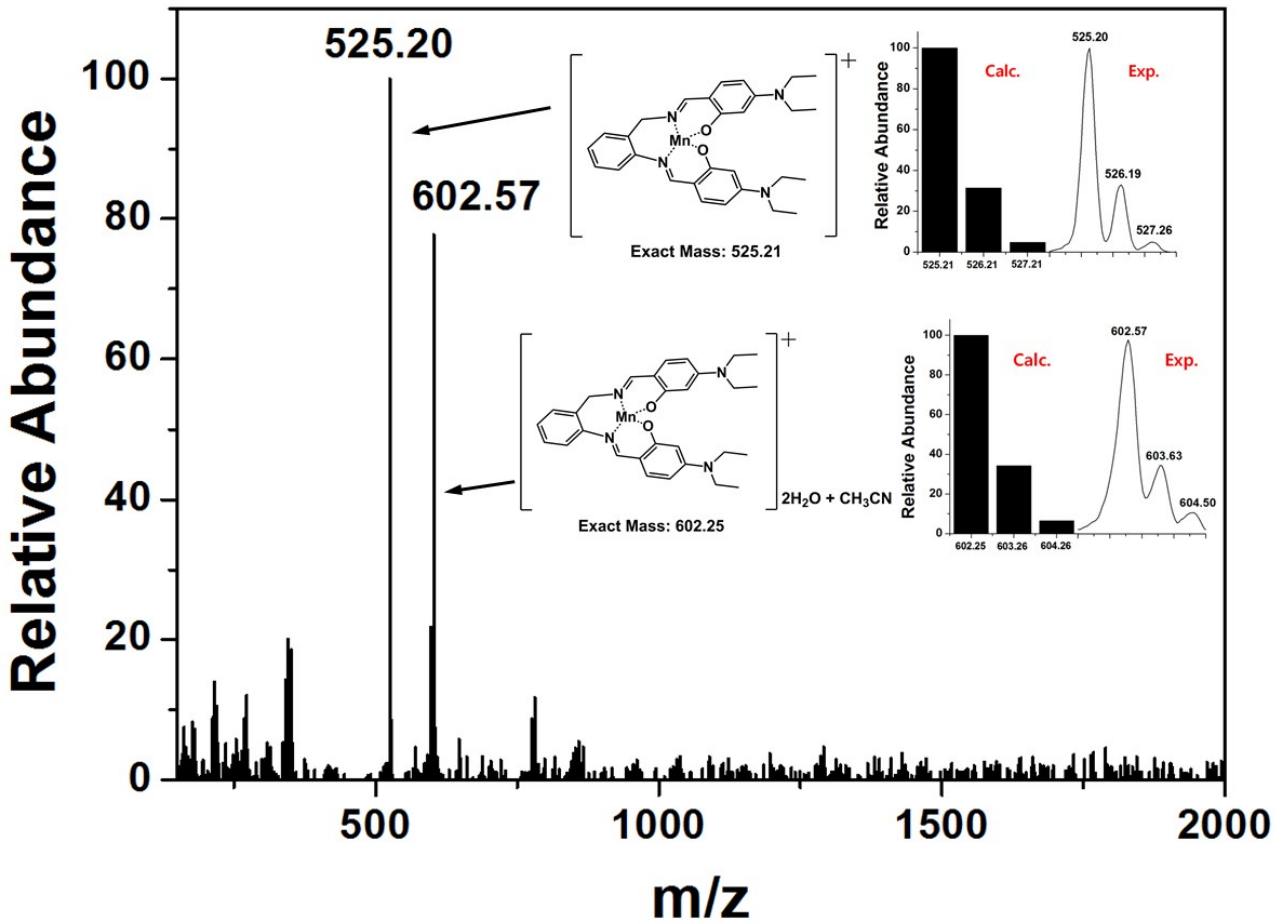


Fig. S7 Positive-ion electrospray ionization mass spectrum of **1** (100 μM) upon addition of 1 equiv of Mn^{2+}.

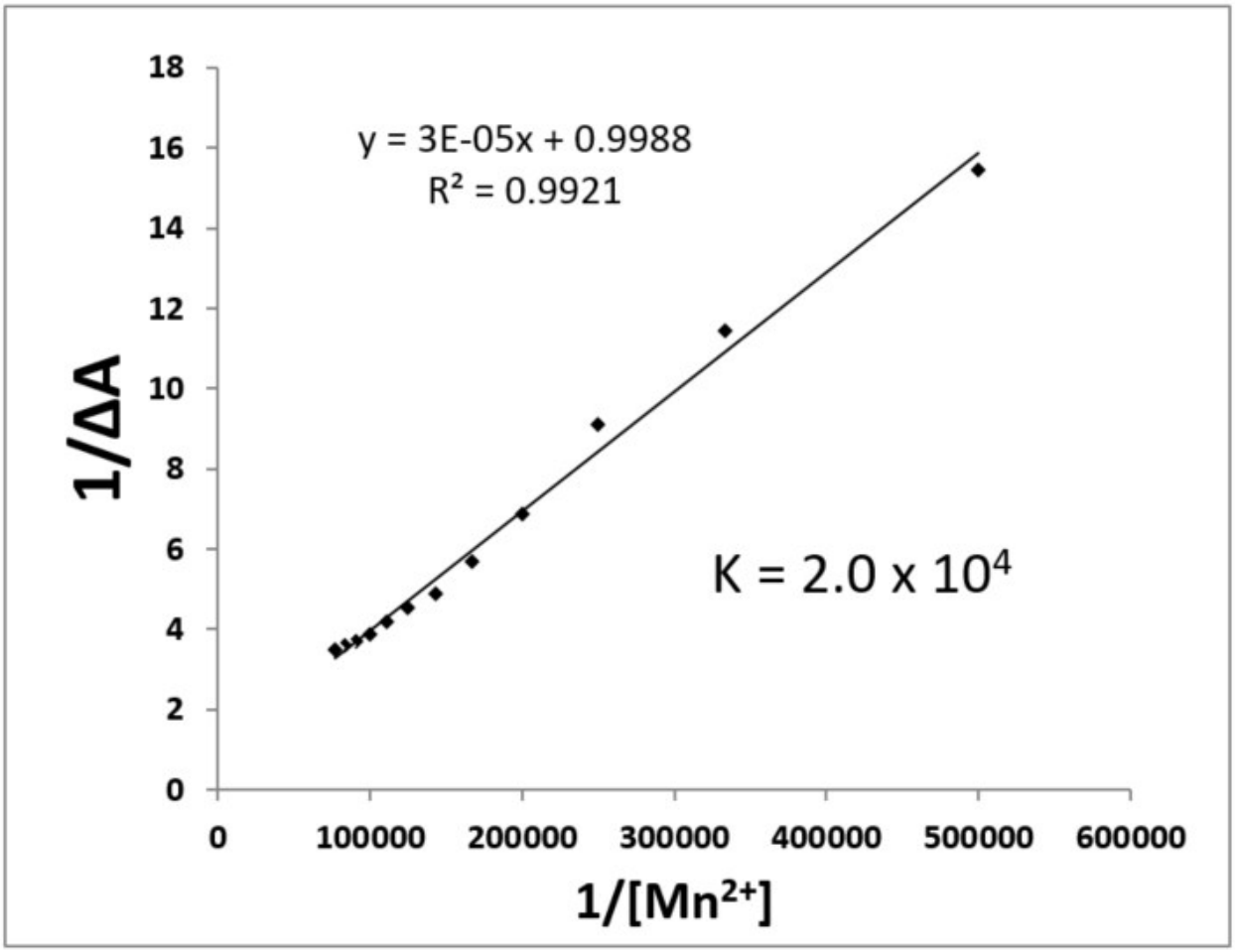


Fig. S8 Benesi-Hildebrand plot (absorbance at 375 nm) of **1**, assuming a 1:1 stoichiometry for association between **1** and Mn^{2+}.

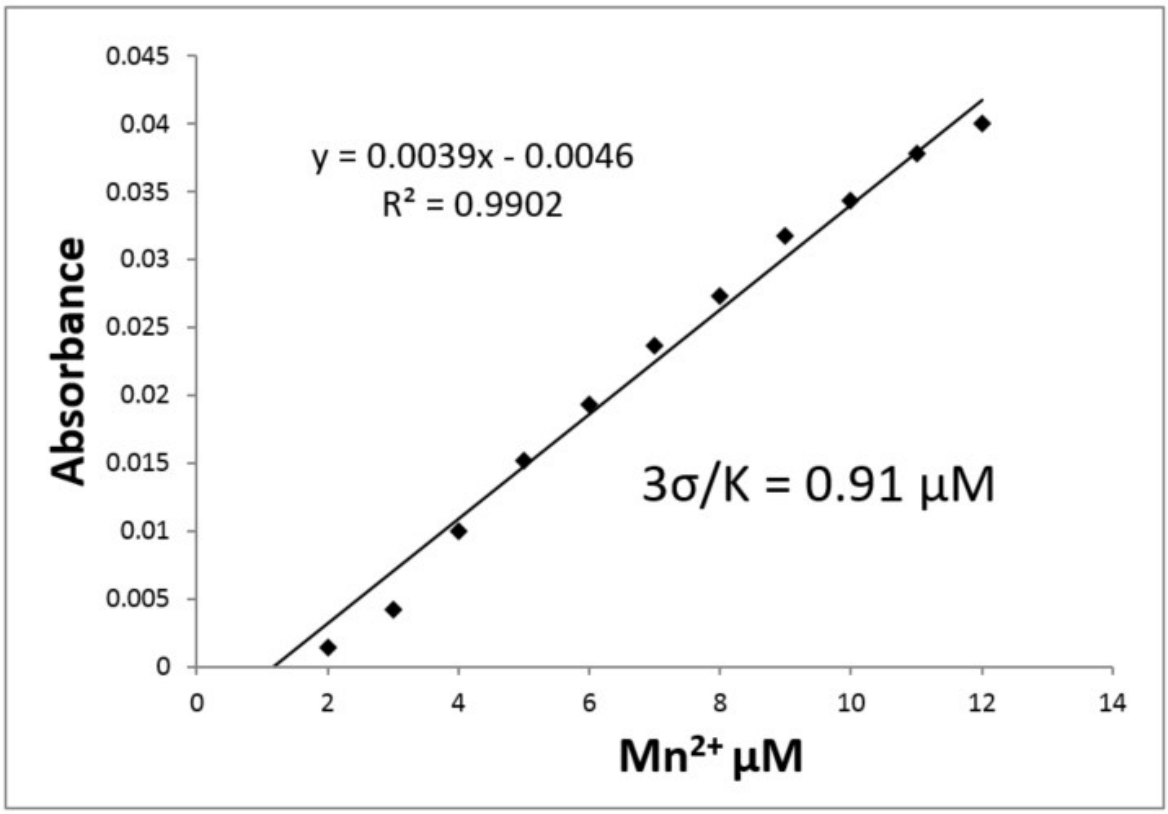
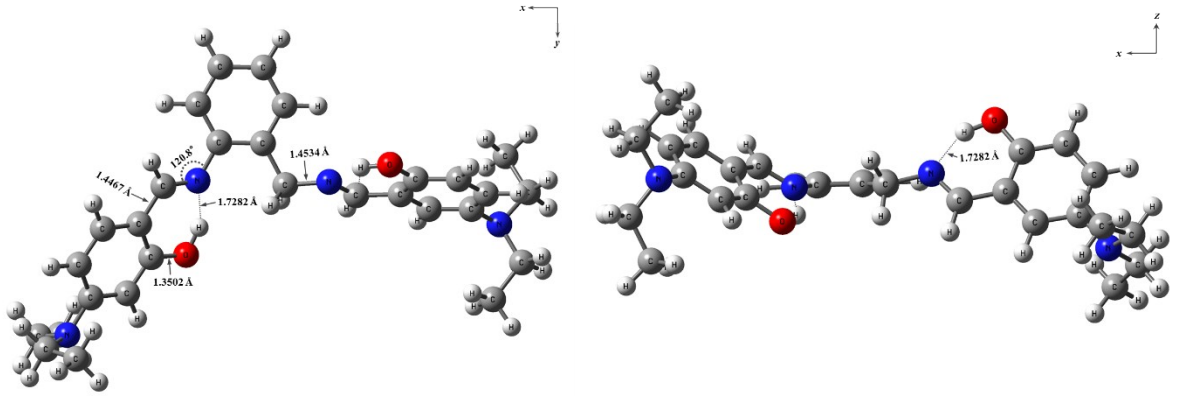


Fig. S9 Determination of the detection limit based on change in the ratio (absorbance at 500 nm) of **1** (10 μM) with Mn^{2+}.

(a)



(b)

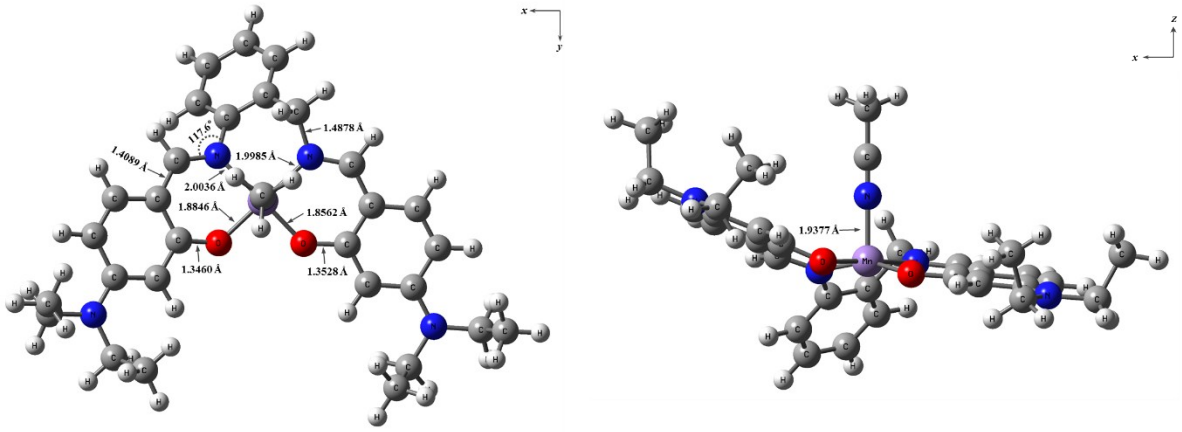


Fig. S10 The energy-minimized structures of (a) **1** and (b) **1**-Mn^{3+} complex.

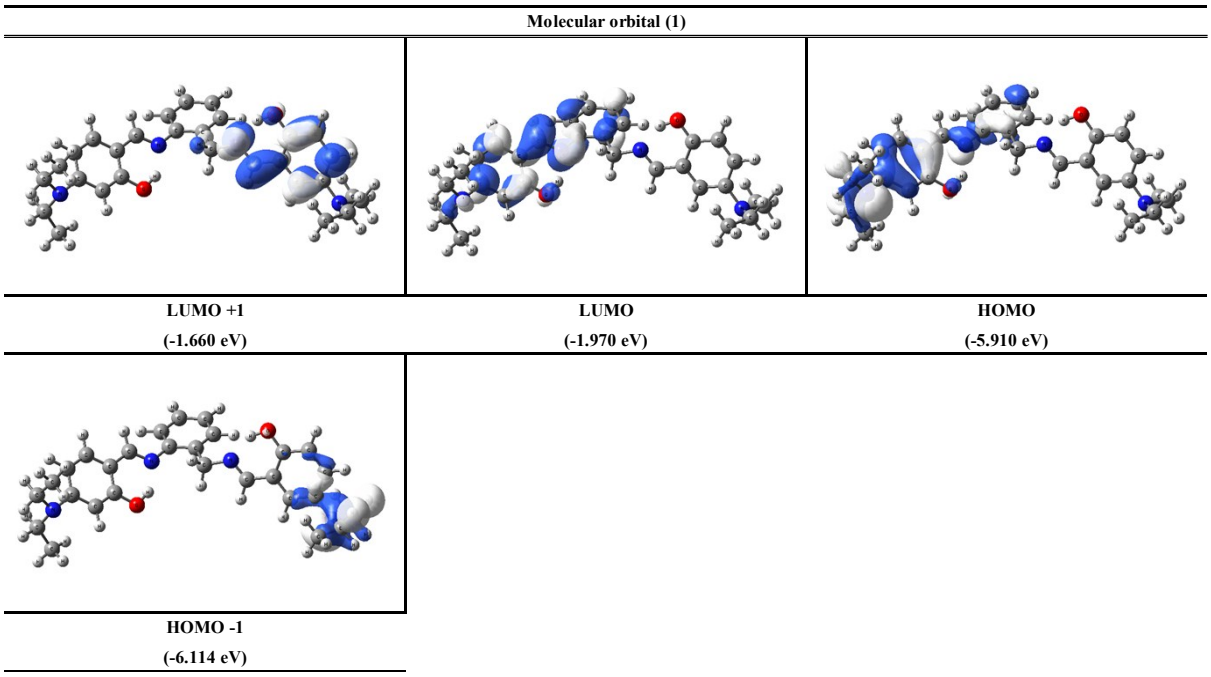


Fig. S11 Isosurface (0.030 electron bohr^{-3}) of molecular orbitals participating in the major singlet excited states of **1**.

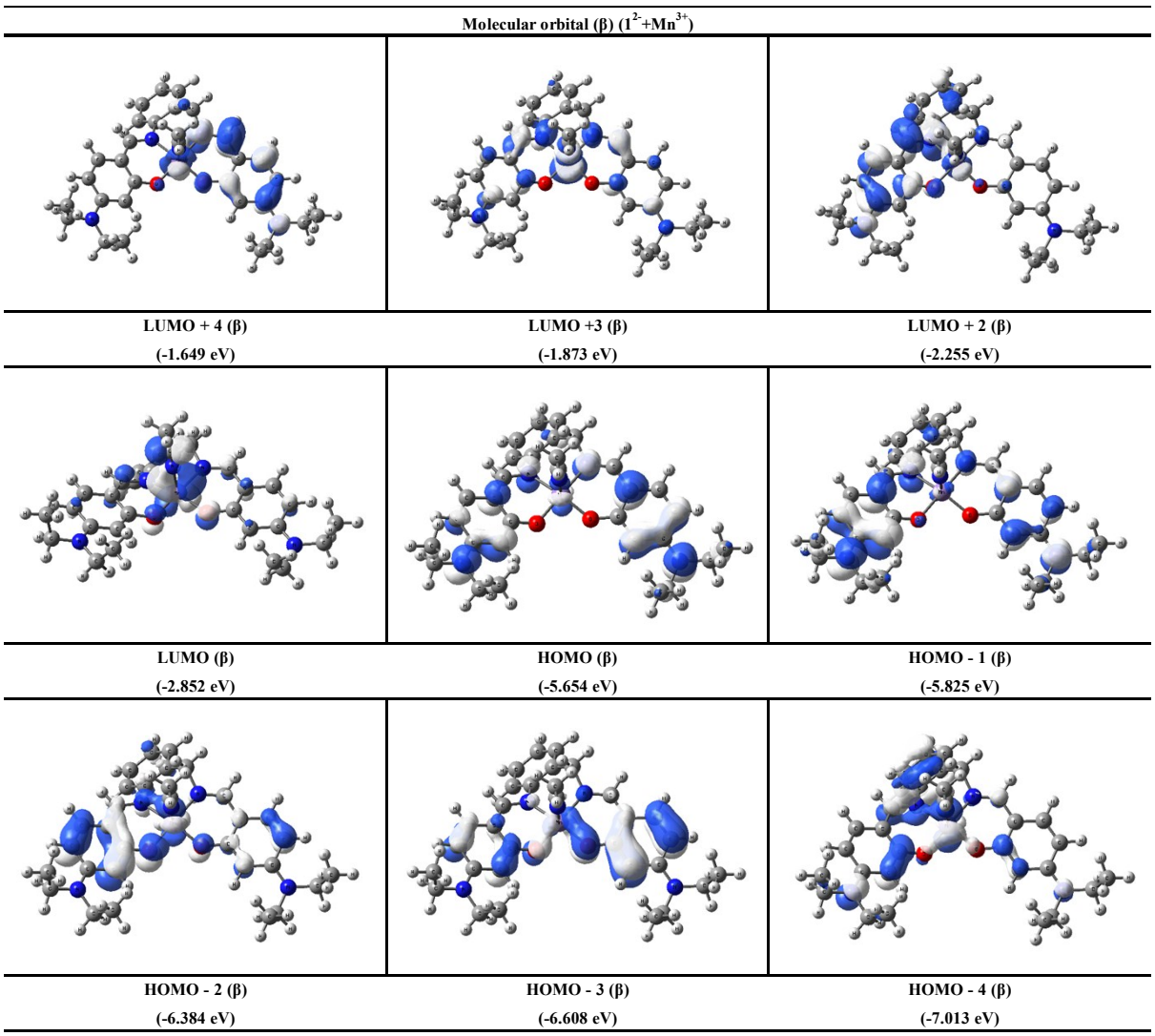


Fig. S12 Isosurface (0.030 electron $bohr^{-3}$) of molecular orbitals (α spin) participating in the major singlet excited states of **1**-Mn^{3+} complex.

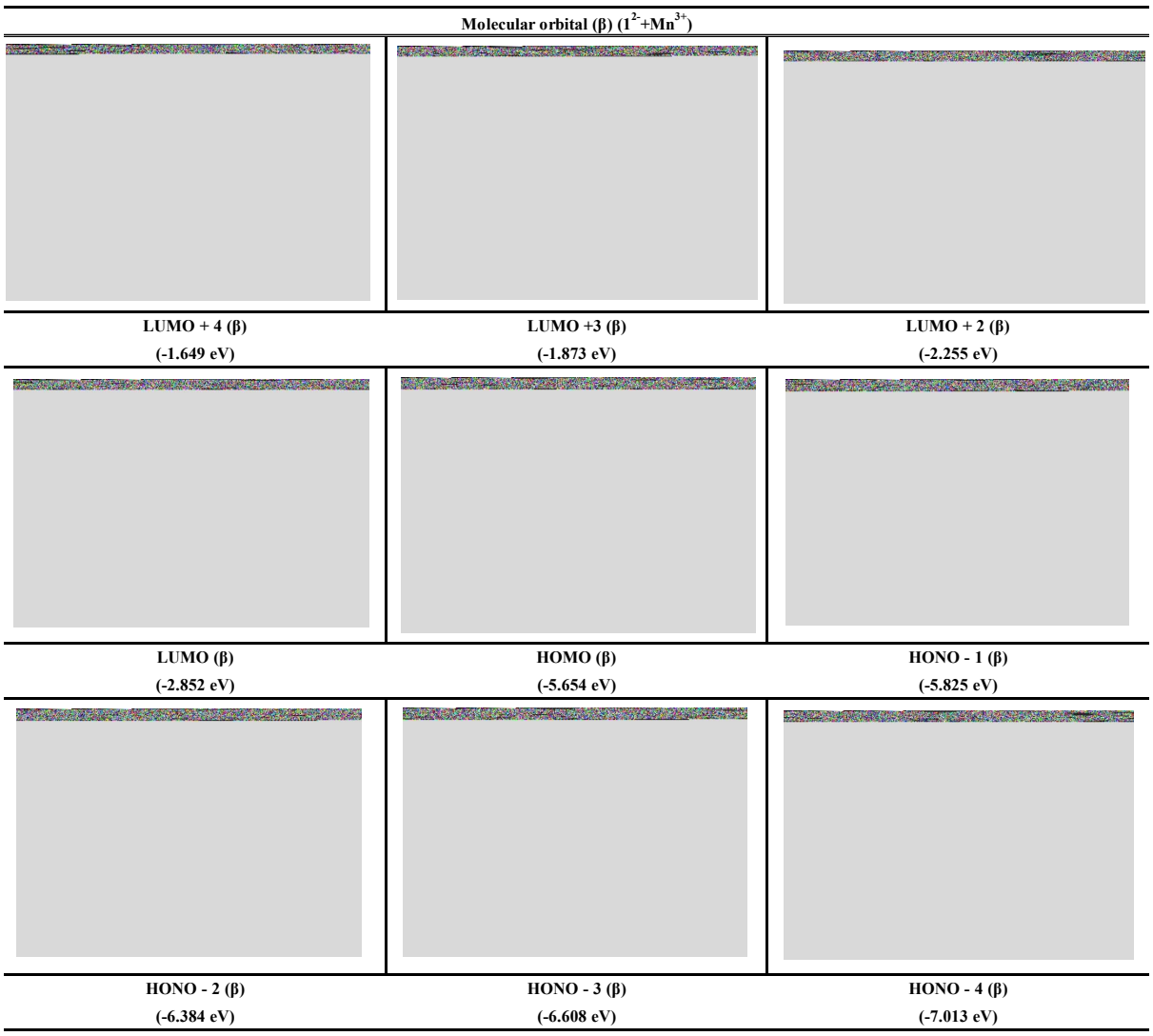


Fig. S13 Isosurface (0.030 electron $bohr^{-3}$) of molecular orbitals (β spin) participating in the major singlet excited states of **1**-Mn^{3+} complex.