Electronic Supplementary Material (ESI) for Dalton Transactions.

Light harvesting indolyl-substituted phosphoramide ligand for the enhancement of Mn(II) luminescence

Electronic supporting Information

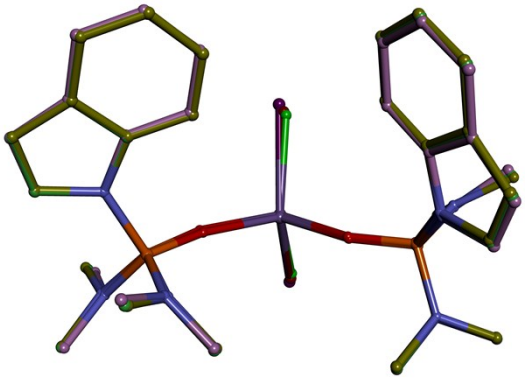

Fig. S1. Superimposition of the three $[MnX_2L_2]$ compounds (carbon atoms in green, magenta and yellow for the chloro-, bromo- and iodo-complexes, respectively).

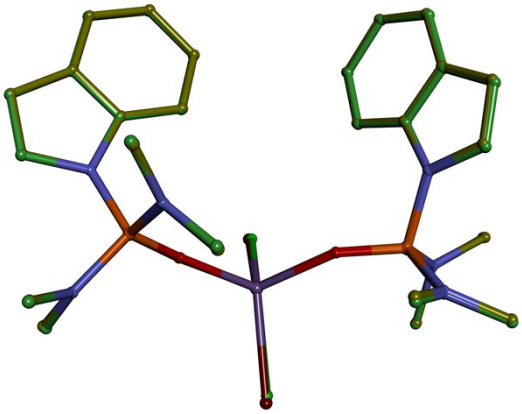

Fig. S2. Superimposition of $[MnCl_2L_2]$ and $[MnBr_2L_2]$ (carbon atoms in green for the chloro-complex and in magenta for the bromo-complex).

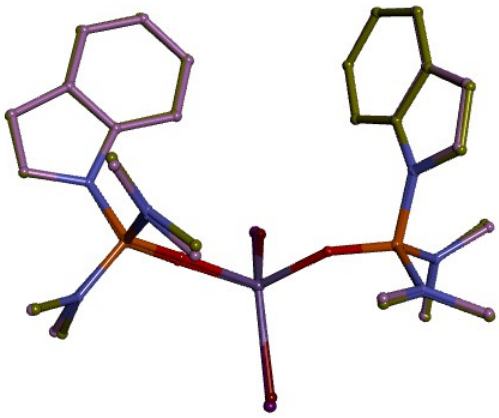

Fig. S3. Superimposition of $[MnBr_2L_2]$ and $[MnI_2L_2]$ (carbon atoms in magenta for the bromo-complex and in yellow for the iodo-complex).

Table S1. Parameter of some planes [Å].

Atoms used to generated the Plane	Root-mean-square deviation from ideal best plane	Total Puckering Amplitude (Q)	Distance of the phosphorus atom to the plane
Chloro compound			
N11 C12 to C19	0.0099	0.030(3)	0.354(3)
P1 N12 C121 C122	0.0649		0.037(1)
P1 N13 C131 C132	0.0568		0.032(1)
N21 C22 to C29	0.0109	0.033(3)	0.198(3)
P2 N22 C221 C222	0.0302		0.017(1)
P2 N23 C231 C232	0.0647		0.037(1)
Bromo compound			
N11 C12 to C19	0.0088	0.027(2)	0.376(2)
P1 N12 C121 C122	0.0538		0.030(1)
P1 N13 C131 C132	0.0607		0.034(1)
N21 C22 to C29	0.0103	0.031(1)	0.202(2)
P2 N22 C221 C222	0.0546		0.031(1)
P2 N23 C231 C232	0.0352		0.020(1)
Iodo compound			
N11 C12 to C19	0.0063	0.019(2)	0.434(2)
P1 N12 C121 C122	0.0466		0.026(1)
P1 N13 C131 C132	0.0503		0.028(1)
N21 C21 to C28	0.0117	0.035(2)	0.2092(2)
P2 N22 C221 C222	0.0391		0.022(1)
P2 N23 C231 C232	0.0277		0.015(1)

Table S2. Crystal data and structure refinement.

Identification code	$[MnCl_2L_2]$	$[MnBr_2L_2]$	$[MnI_2L_2]$
Empirical formula	$C_{24}H_{36}Cl_2MnN_6O_2P_2$	$C_{24}H_{36}Br_2MnN_6O_2P_2$	$C_{24}H_{36}I_2MnN_6O_2P_2$
Formula weight	628.37	717.29	811.27
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions	a = 10.3500(8) Å	a = 10.4594(5) Å	a = 10.6662(7) Å
	b = 15.7450(13) Å	b = 15.7962(8) Å	b = 15.8451(12) Å
	c = 18.6481(14) Å	c = 19.0025(9) Å	c = 19.6427(15) Å
	β = 99.437(2)°	β = 99.319(2)°	β = 100.640(2)°
Volume	2997.8(4) Å^3	3098.1(3) Å^3	3262.7(4) Å^3
Z	4	4	4
Density (calculated)	1.392 Mg/m^3	1.538 Mg/m^3	1.652 Mg/m^3
Absorption coefficient	0.758 mm^{-1}	3.140 mm^{-1}	2.425 mm^{-1}
F(000)	1308	1452	1596
Crystal size	0.172 x 0.109 x 0.047 mm	0.263 x 0.259 x 0.121 mm	0.235 x 0.226 x 0.169 mm
Θ range for data collection	2.214 to 26.456°	2.357 to 28.368°	2.330 to 28.377°
Index ranges	$-12 \le h \le 12$	$-13 \le h \le 13$	$-14 \le h \le 12$
	$-19 \le k \le 19$	$-21 \le k \le 20$	$-20 \le k \le 21$
	$-19 \le l \le 23$	$-24 \le l \le 25$	$-25 \le l \le 26$
Reflections collected	25091	69466	56685
Independent reflections	6164 [R_{int} = 0.0908]	7731 [R_{int} = 0.0606]	8153 [R_{int} = 0.0373]
Reflections observed (>2σ)	4240	6776	7437
Data Completeness	0.995	0.999	0.998
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7425 and 0.6431	0.7457 and 0.3403	0.7457 and 0.5669
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6164 / 0 / 342	7731 / 0 / 342	8153 / 0 / 342
Goodness-of-fit on F^2	1.010	1.055	1.090
Final R indices [I>2σ(I)]	R_1 = 0.0514	R_1 = 0.0302	R_1 = 0.0234
	wR_2 = 0.0840	wR_2 = 0.0655	wR_2 = 0.0509
R indices (all data)	R_1 = 0.0974	R_1 = 0.0380	R_1 = 0.0280
	wR_2 = 0.0959	wR_2 = 0.0680	wR_2 = 0.0522
Largest diff. peak and hole	0.390 and -0.425 e.Å-3	0.448 and -0.747 e.Å-3	0.742 and -1.000 e.Å-3

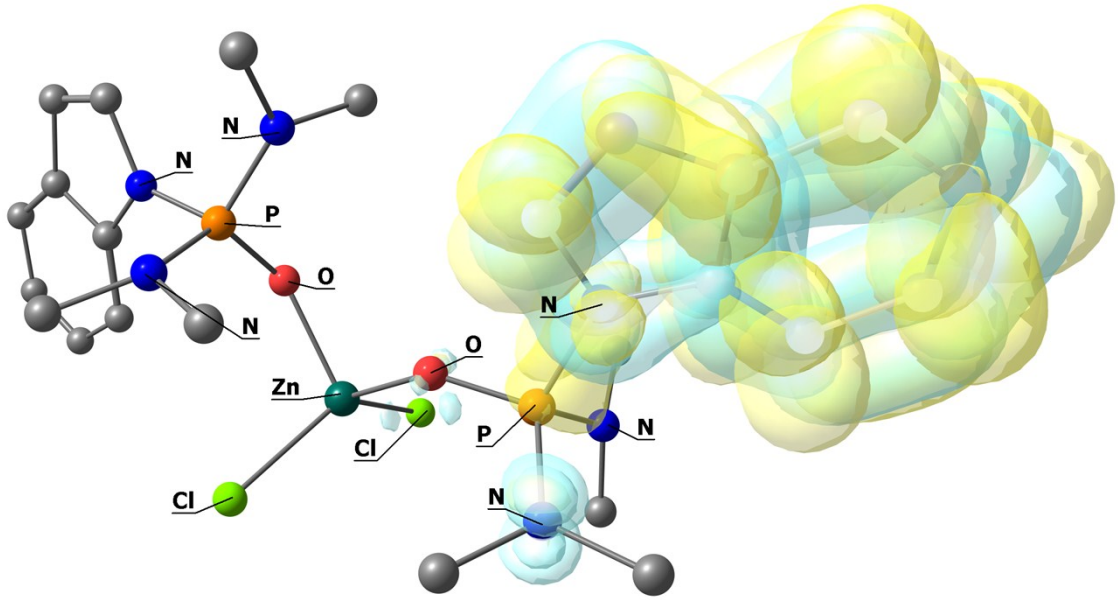

Fig. S4. Superposition of HOMO-1 and HOMO-3 orbitals (light blue tones) with LUMO and LUMO+2 orbitals (light yellow tones) of $[ZnCl_2L_2]$. Surface isovalue = 0.04 a.u. Carbon atoms in grey, hydrogen atoms omitted for clarity.

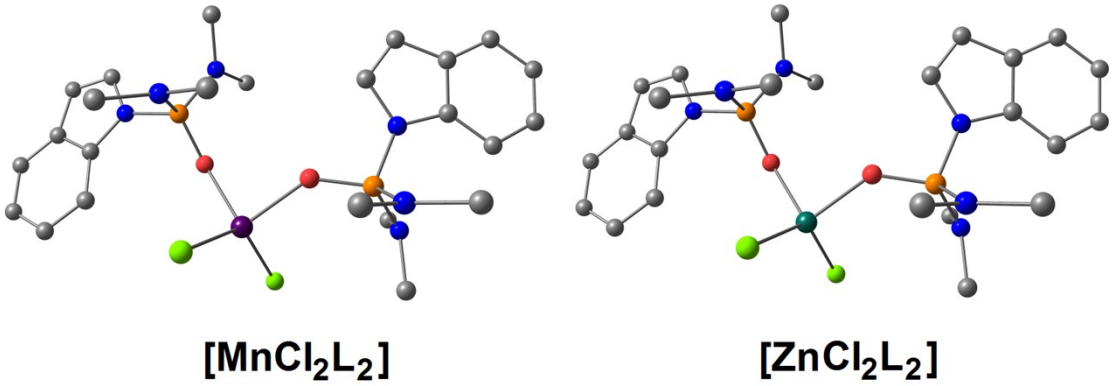

Fig. S5. DFT-optimized structures of $[MnCl_2L_2]$ (sextet state) and $[ZnCl_2L_2]$ (singlet state) (ωB97X/def2-SVP calculations). Colour map: Mn, violet; Zn, dark green; Cl, green; O, red; P, orange; N, blue; C, grey. Hydrogen atoms are omitted for clarity. RMSD = 0.075 Å.

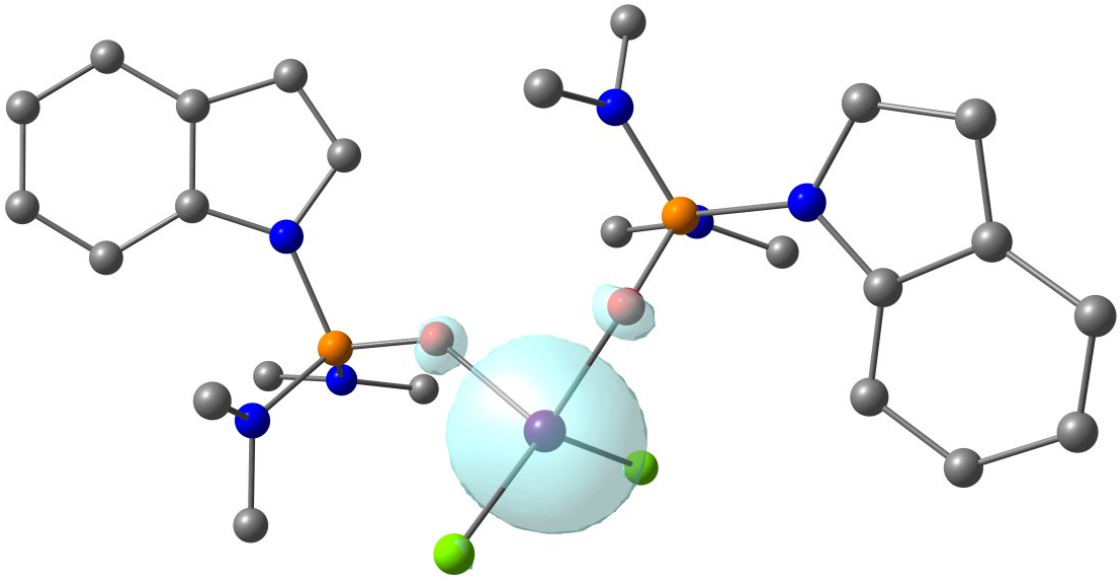

Fig. S6. Spin density of [$MnCl_2L_2$], sextet state. Surface isovalue = 0.005 a.u. Colour map: Mn, violet; Cl, green; O, red; P, orange; N, blue; C, grey. Hydrogen atoms are omitted for clarity.

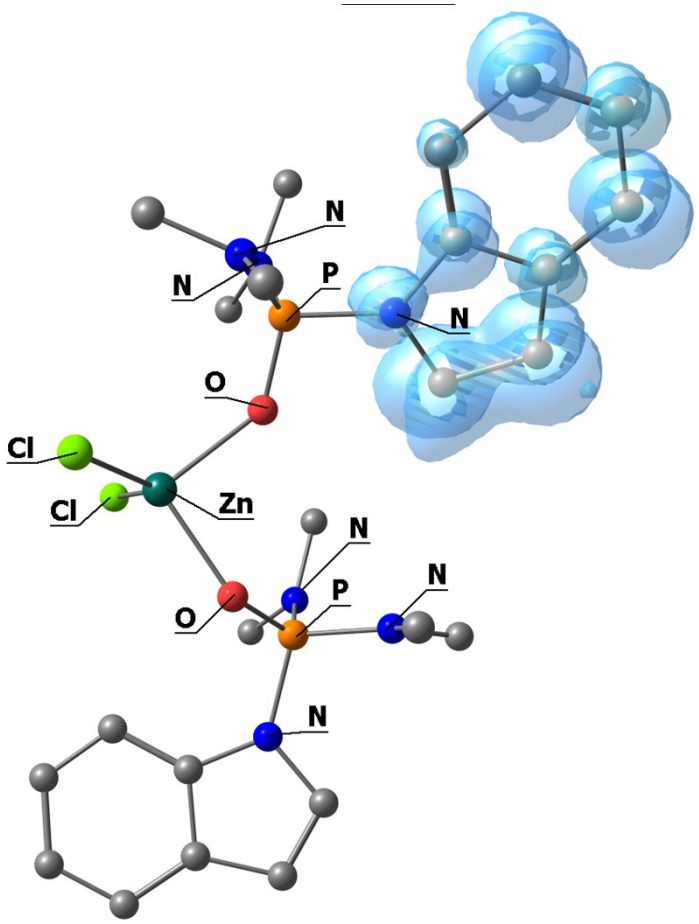

Fig. S7. Spin density of [$ZnCl_2L_2$], triplet state. Surface isovalue = 0.005 a.u. Colour map: Zn, dark green; Cl, green; O, red; P, orange; N, blue; C, grey. Hydrogen atoms are omitted for clarity.