

Supporting Information

1. UV-visible

Orbitals	Symmetry	Metal or Porphyrin
— $d_{x^2-y^2}$	b_{1g}	Metal
— π^*	e_g^*	Porphyrin (LUMO)
— d_{z^2}	a_{1g}	Metal
— d_{xz}, d_{yz}	e_g	Metal
— d_{xy}	b_{2g}	Metal
— π	a_{2u}	Porphyrin } (HOMO)
— π	a_{1u}	

Figure SI-1. Energy levels of the frontier orbitals of manganese(III) metalloporphyrins.

2. Crystallography

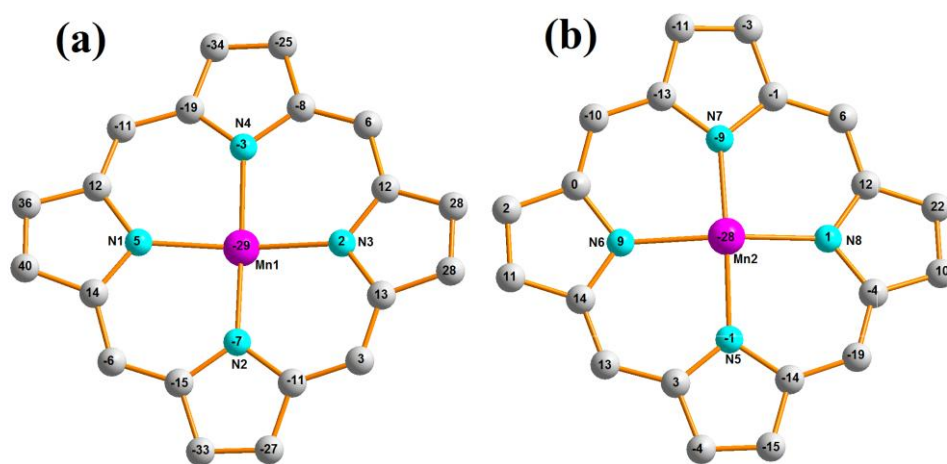


Figure SI-2. Formal diagrams of the porphyrinato cores of $[\text{Mn}^{\text{III}}(\text{TPP})(\text{OAc})]$ (a): first molecule in the asymmetric unit and (b): second molecule in the asymmetric unit. The displacement of each atom from the mean plane of the 24-atom porphyrin macrocycle is given in unit of 0.01 Å.

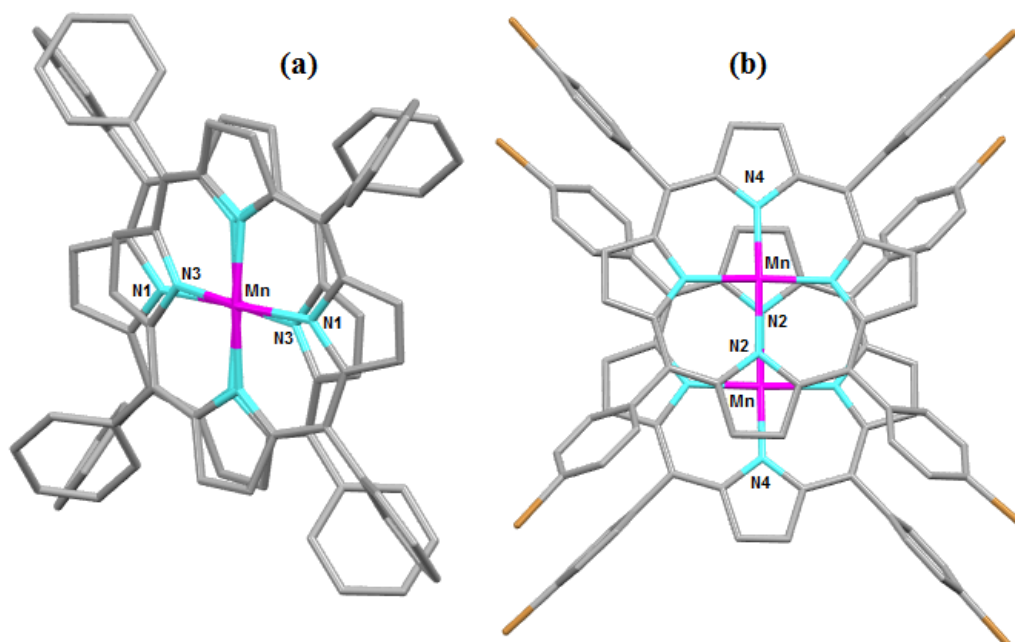


Figure SI-3. Projection showing the parallel superposition of the vectors joining opposite nitrogen atoms of the two macrocycles of one dimer, (a): complex 1 and (b): complex 2.

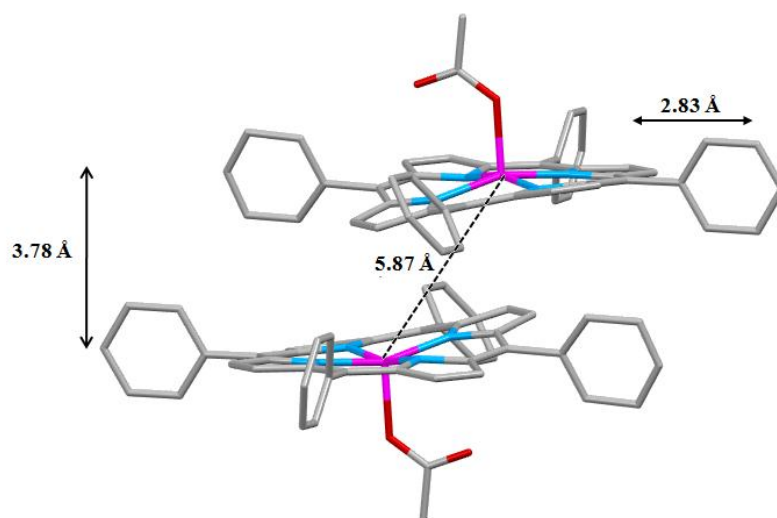


Figure SI-4. Schematic representations of one dimer of the $[\text{Mn}^{\text{III}}(\text{TPP})(\text{OAc})]$ complex.

Table SI-1. Hydrogen bonds and Selected C–H...Cg intermolecular interactions for **1-2**.

Complex	D ^a ...A ^b [Å]	D–H...A
Complex 1		
C23–H23...O2 ^[i]	3.308 (6)	155
C35–H35...O1 ^[ii]	3.301 (5)	135
C41–H41...Cl3A ^[iii]	3.614 (5)	146
C41–H41...O2 ^[iii]	3.252 (6)	144
C22–H22...Cg3 ^[iv]	3.402 (4)	119
C24–H24...Cg4 ^[i]	3.437 (5)	139
C31–H31...Cg12 ^[vi]	3.600 (5)	155
C35–H35...Cg1 ^[ii]	3.692 (6)	141
C38–H38...Cg9 ^[v]	3.828 (5)	155
C44–H44...Cg10 ^[iv]	3.737 (4)	151
Complex 2		
C7–H7...Cl4A ^[i]	3.290 (13)	156
C29–H29...O1 ^[ii]	3.190 (8)	128
C34–H34...Cl4A ^[iii]	3.497 (14)	144
C22–H22...Cg10 ^[iii]	3.742(8)	144
C29–H29...Cg6 ^[iii]	3.617(7)	126
C32–H32...Cg1 ^[iv]	3.562(7)	140

^a D = donor atom, ^b A = acceptor atom.

Complex 1:

Cg1 is the centroid of the N1/C1–C4 five-member ring, Cg3 is the centroid of the N3/C8–C11 five-member ring. Cg4 is the centroid of the N4/C13–C16 five-member ring, Cg9 is the centroid of the C21–C26 six-member ring. Cg10 is the centroid of the C27–C32 six-member ring, Cg12 is the centroid of the C39–C44 six-member ring. Symmetry codes : (i) -1+x,y,z; (ii) -x,1-y,1-z ; (iii) -1/2+x,1/2-y,1/2+z ;(iv) -x,-y,-z ; (v) 1/2-x,1/2+y,1/2-z ; (vi) x,y,-1+z.

Complex 2:

Cg1 is the centroid of the N1/C1–C4 five-member ring, Cg10 is the centroid of the C27–C32 six-member ring. Cg11 is the centroid of the C21–C26 six-member ring.

Symmetry codes: (i) -x,1-y,1-z; (ii) x,y,z; (iii) 2-x,1-y,1-z ;(iv) 1-x,1-y,1-z.

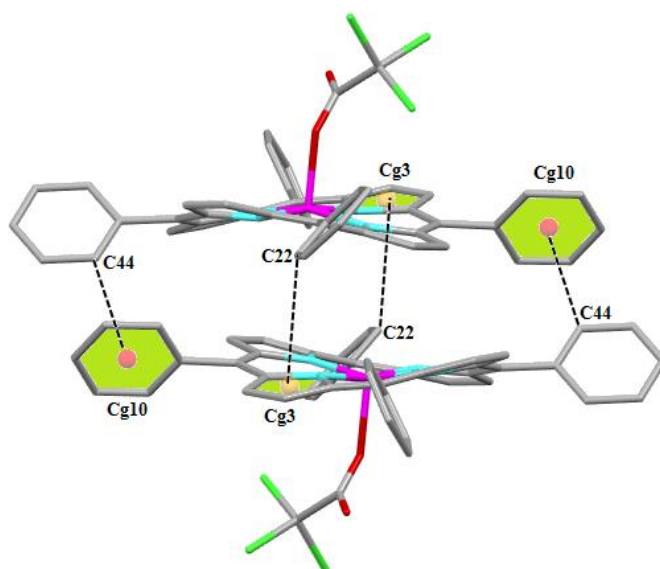


Figure SI-5. Schematic representation of the C–H \cdots Cg intermolecular interactions in complex **1** where Cg is the centroid of a phenyl ring of the TPP porphyrinate.

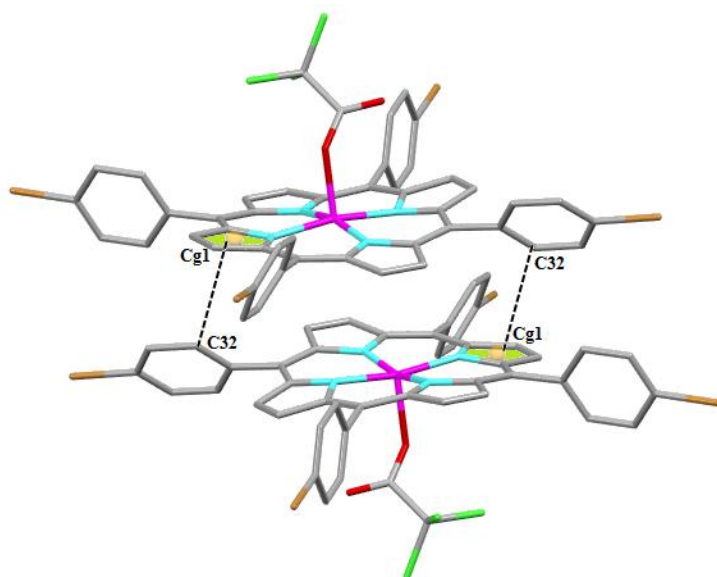


Figure SI-6. Schematic representation of the C–H \cdots Cg intermolecular interactions in complex **1** where Cg is the centroid of a pyrrole ring of the TBrPP porphyrinate.