**Supporting Information**

**1. UV-visible**



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 [MnIII(TPP)(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 in 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 [MnIII(TPP)(OAc)] complex.

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

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Complex Da···Ab [Å] D–H···A

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*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

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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, Cg10is 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…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…Cg intermolecular interactions in complex **1** where Cg is the centroid of apyrrole ring of the TBrPP porphyrinate.