**DMAP and HMTA Manganese(III) *meso*-Tetraphenylporphyrin-based coordination complexes: Syntheses, Physicochemical Properties, Structural and Biological activities**

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**Contents**

1. IR spectroscopy……………………………………………………………….2

2. X-ray Molecular structure ………...……………………………………….....4

3. Hirshfeld surface analysis ………………...………………..………………....8

4. Cyclic voltammetry …....……………...…………………………………….11

**1. IR spectroscopy**

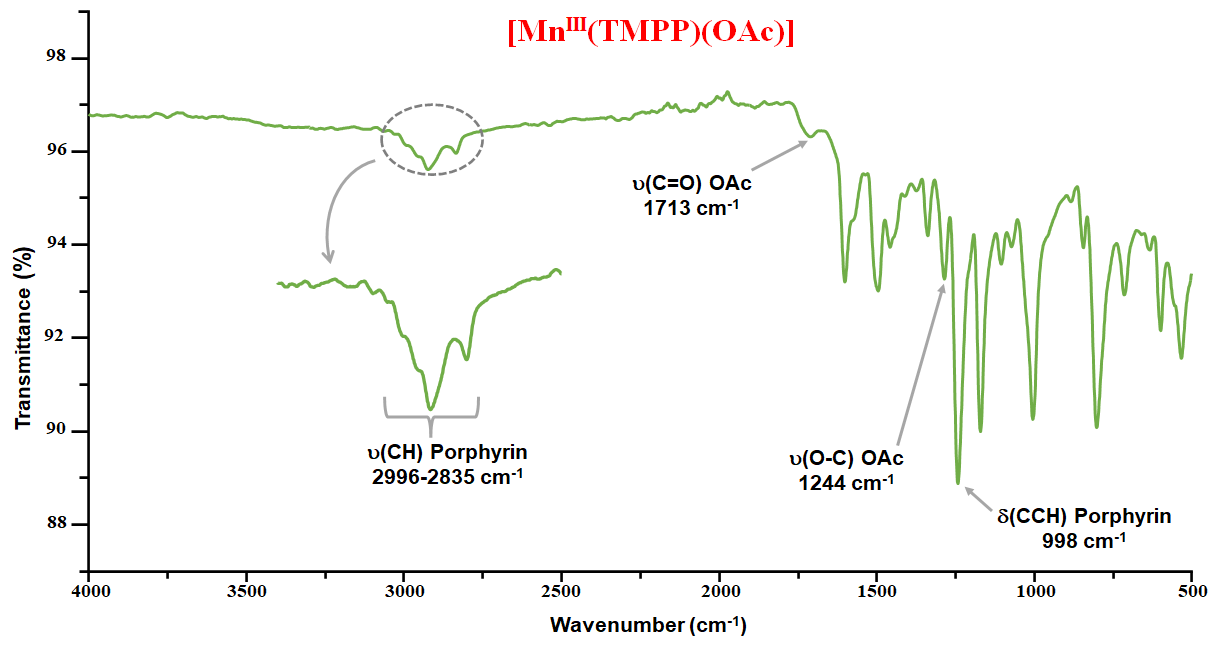
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Fig.S1. Neat IR spectrum of [MnIII(TMPP)(OAc)].

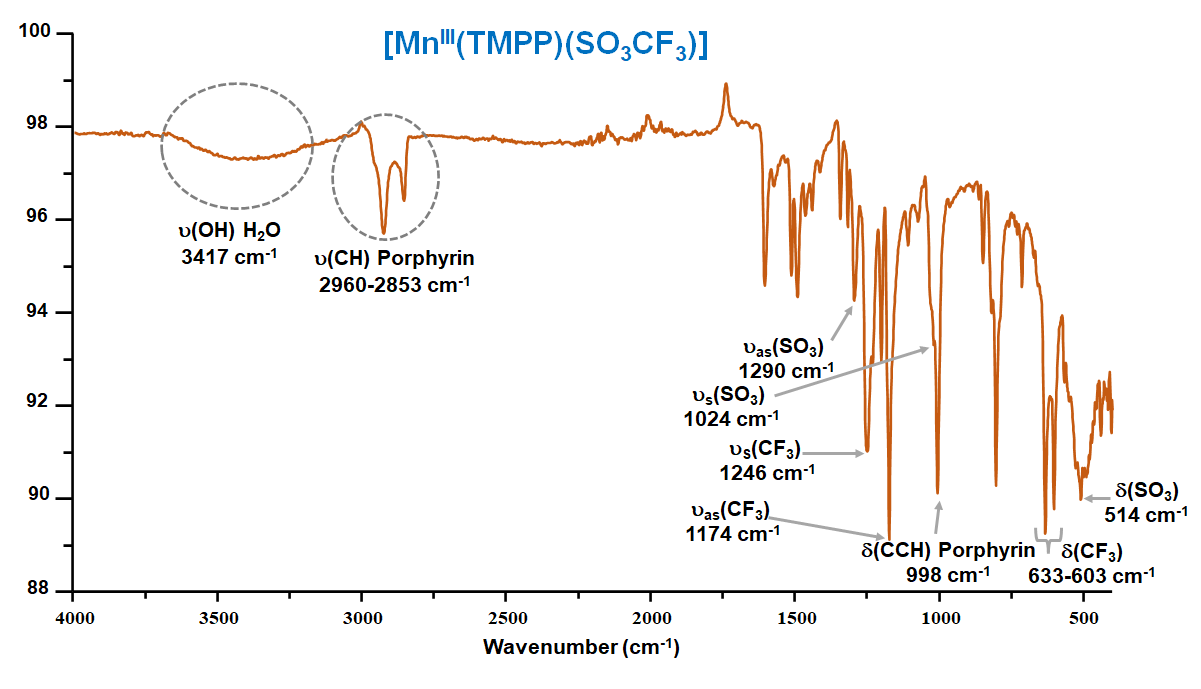
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Fig.S2. Neat IR spectrum of [MnIII(TMPP)SO3CF3)].

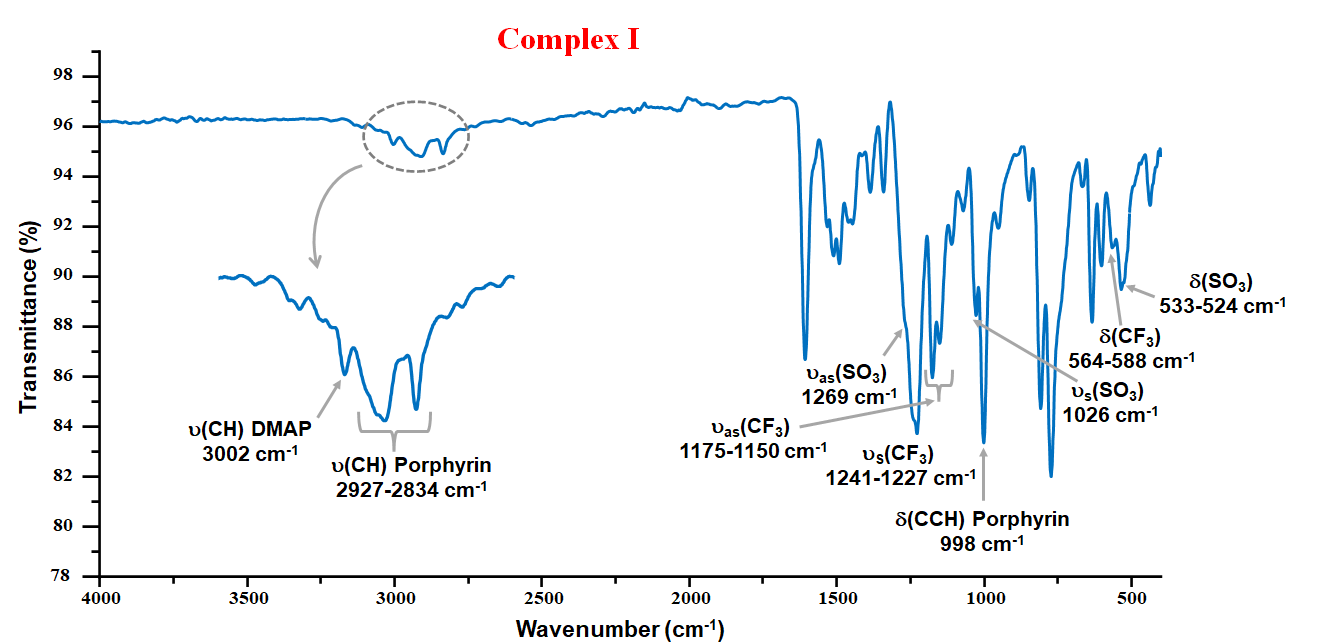
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Fig. S3. Neat IR spectrum of Complex **I**.

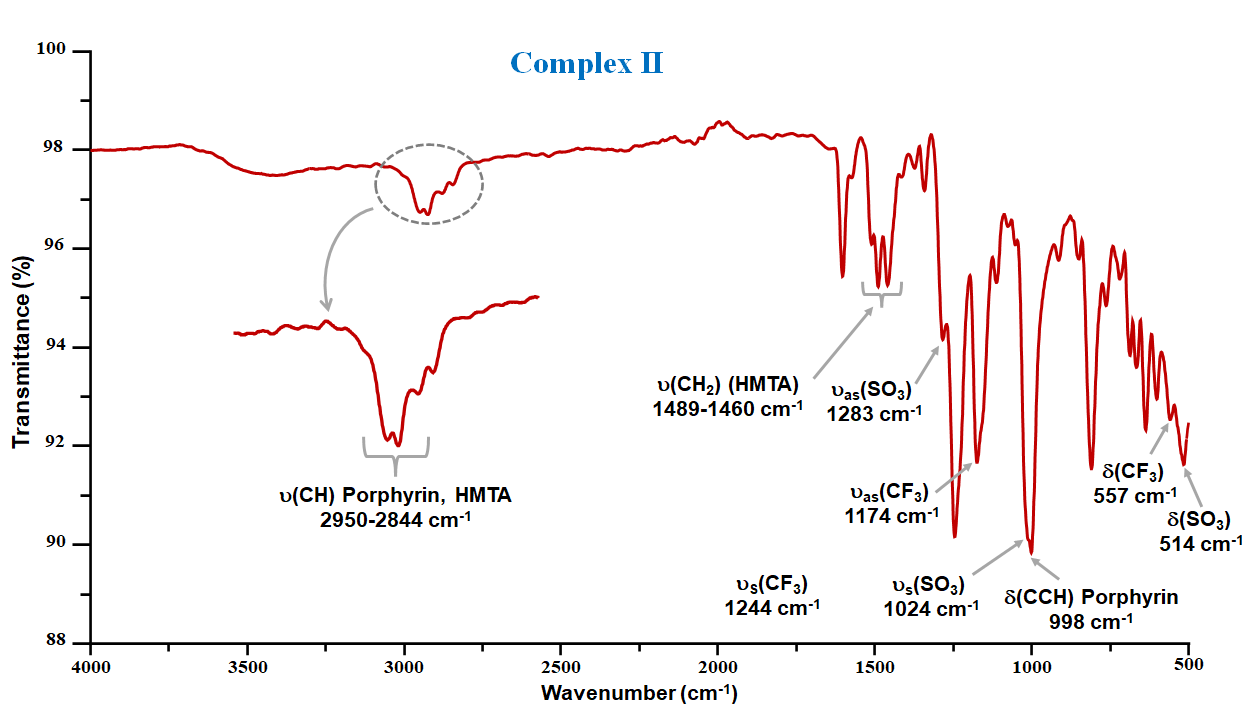
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Fig.S4. Neat IR spectrum of Complex **II**.

**2. X-ray Molecular structure**

Table S1. Inter- and intra-molecular interactions for **I**.

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*Hydrogen bond*

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Da-H…Ab Symmetry D…A [Å] D-H…A [°]

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C8-H8…O31+x,y,z 3.391(4) 164

C18-H18…O1-1+x,y,z3.426(4) 163

C25-H25…O61-x,1-y,2-z 3.327(4)143

C29-H29…F21-x,-y,2-z3.443(4)168

C44-H44…O6x,y,z3.235(4)133

C57-H57…O51-x,1-y,2-z 3.208(5)151

C64-H64…O6 -x,1-y,2-z 3.053(6)162

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*Interactions C-H…Cg*

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C–H⋅⋅⋅Cg (π) Symmetry code C⋅⋅⋅Cg (π) C–H⋅⋅⋅Cg

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C34-H34…Cg10 1-x,-1/2+y,3/2-z 3.470(5) 113

C46-H46…Cg4 -x,-y,2-z 3.676(4) 163

C54-H54B…Cg10 x,-1+y,z 3.461(4) 134

C61-H61C…Cg9 x,1+y,z 3.569(4) 143

C65-H65…Cg13 -x,1/2+y,3/2-z 3.550(5) 168

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*Inter- and Intra-molecular interactions C-X…Cg*

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C–X⋅⋅⋅Cg (π) Symmetry code C⋅⋅⋅Cg X…Cg C–H⋅⋅⋅Cg

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C64-Cl2…Cg13x,y,z4.536(5)3.768(2)104.69

C63-F1…Cg14x,y,z4.577(4)3.419(4)146.6

C63-F2…Cg21-x,-y,2-z4.458(5)3.489(3)129.6

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**a**: D = donor, **b**: A = acceptor, X =heteroatom, Cg =centroid.

Cg2: is the centroid of the N2/C6-C9 pyrrole five-membered ring.

Cg4: is the centroid of the N4/C16-C19 pyrrole five-membered ring.

Cg9: is the centroid of the N5/C49-C53 phenyl six-membered ring.

Cg10: N7/C56-C60 phenyl six-membered ring.

Cg13: C35-C40 a phenyl ix-membered ring.

Cg14: C42-C47 a phenyl six-membered ring.

Table S2. Inter and intra-molecular interactions for **II**.

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*Hydrogen bond*

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Da-H…Ab Symmetry D…A [Å] D-H…A [°]

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C2-H2…O3 x,y-z-1 3.188(3) 121

C8-H8-Cl1 1+x,1+y,z 3.695(2) 171

C17-H17B-F3 1-x,-y,1-z 3.499(4) 166

C24-H24B-O3 1-x,1-y,1-z 3.563(4) 170

C27-H27B-O3 2-x,2-y,1-z, 3.392(3) 151

C32-H32A-F2 x,y,z 2.917(3) 109

C32-H32A-N4 x,y,z 3.183(3) 124

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*C-H…Cg Interactions*

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C–H⋅⋅⋅Cg (π) Symmetry code C⋅⋅⋅Cg (π) C–H⋅⋅⋅Cg

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

C25-H25B…Cg2 2-x,1-y,1-z 3.485(3) 122

C29-H29A…Cg1 2-x,1-y,1-z 3.559(3) 120

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**a**: D = donor, **b**: A = acceptor, X =heteroatom, Cg =centroid.

Cg1: is the centroid of the N1/C2-C4 pyrrole five-membered ring.

Cg2: is the centroid of the N2/C6-C9 pyrrole five-membered ring.

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Fig. S5. Inter-and intra-molecular interactions C–H⋅⋅⋅Cgand hydrogen bonds in the crystal lattice of **I** view along the [010] direction.

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Fig. S6. Inter-and intra-molecular interactions C–H⋅⋅⋅Cgand hydrogen bonds in the crystal structure of the complex **I** view along the [100] direction.

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Fig. S7. Inter-and intramolecular interactions C–X⋅⋅⋅Cgin the crystal structure of **I** view along the [100] direction.



Fig. S8. Inter-and intra-molecular interactions C–H⋅⋅⋅Cg in the crystal structure of **II** view along the [010] direction.

**3.** **Hirshfeld Analysis**

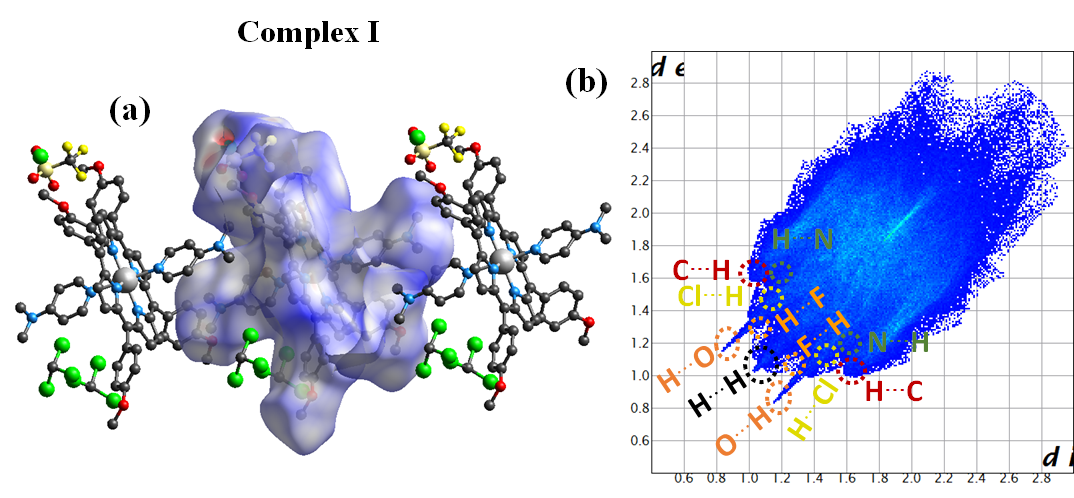


Fig. S9. **(a):** Hirshfeld surface mapped with *dnorm* for **I**. **(b):** Full fingerprint plot for **I**.

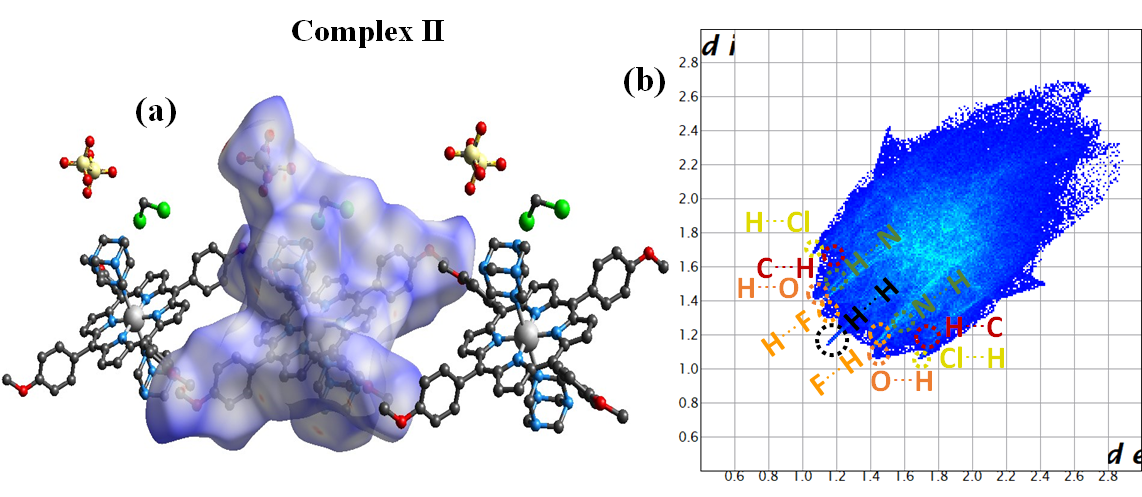


Fig. S10. **(a):** Hirshfeld surface mapped with *dnorm* for **II**. **(b):** Full fingerprint plot for **II**.

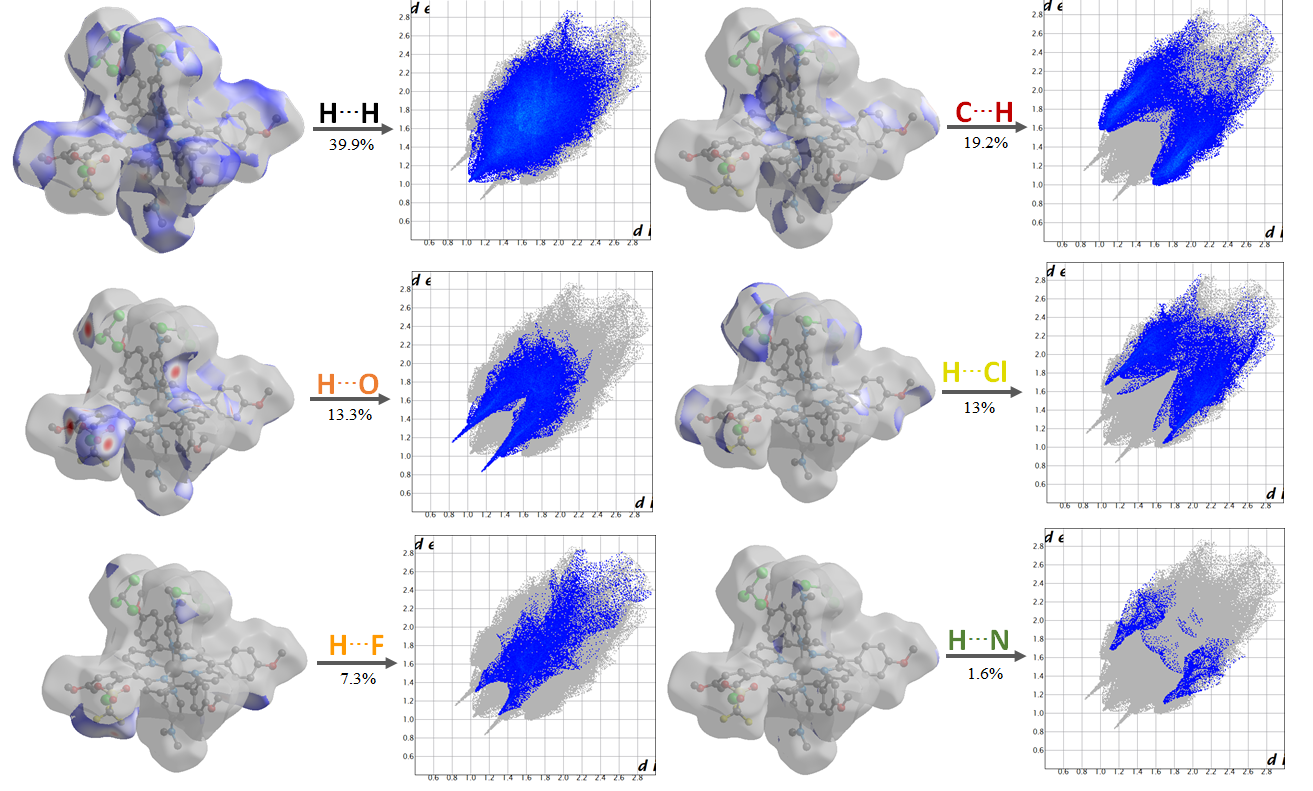


Fig. S11. Hirshfeld surface mapped over dnorm and decomposed fingerprint plots for the dominant interactions for **I**.

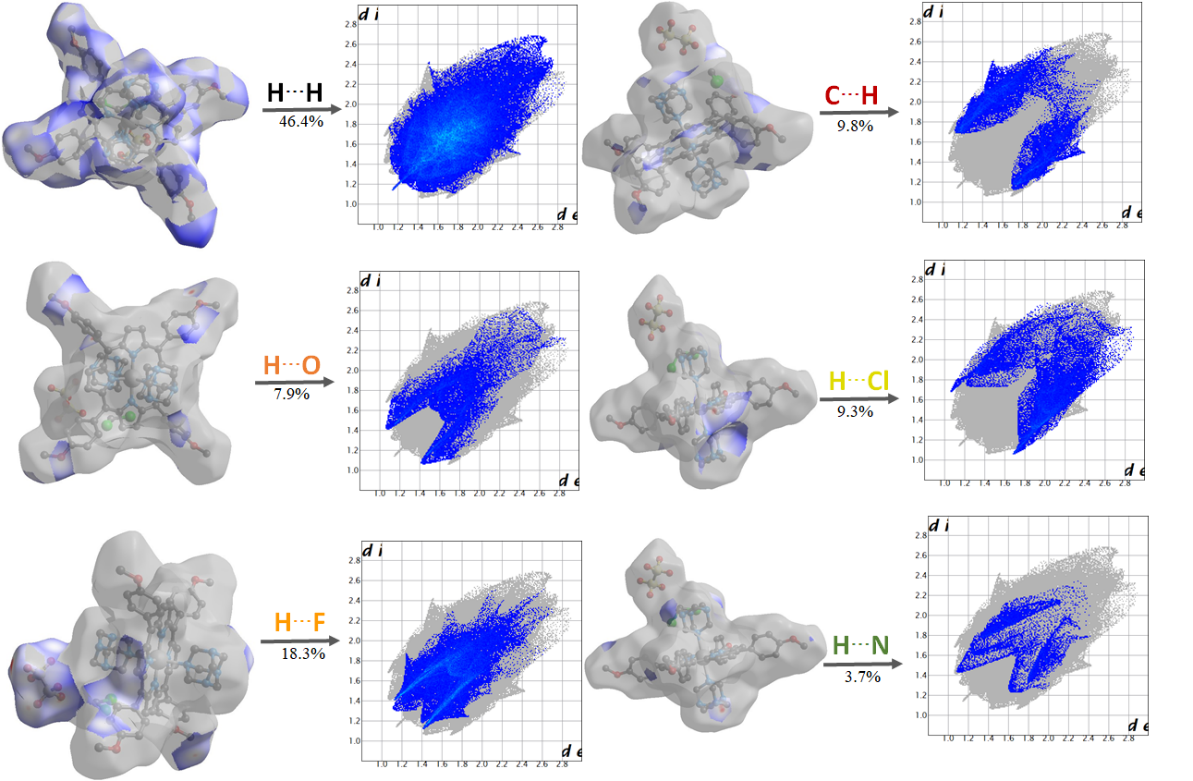


Fig. S12. Hirshfeld surface mapped over dnorm and decomposed fingerprint plots for the dominant interactions for **II**.

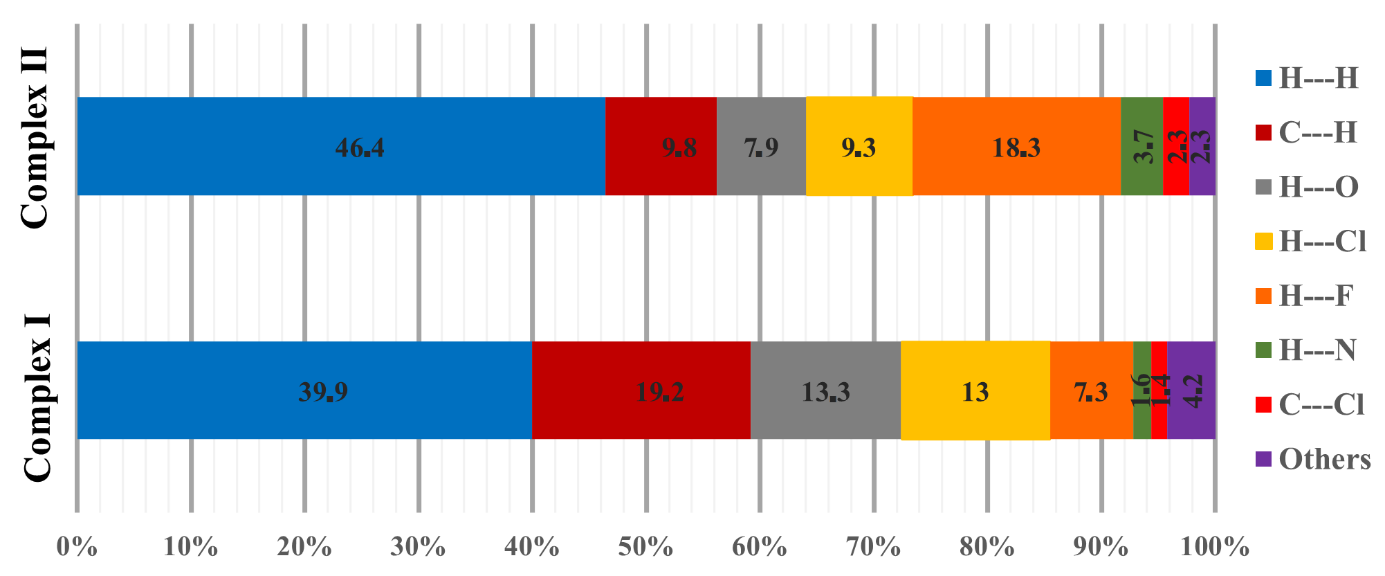
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Fig. S13. Summary of percentage contributions of the diverse noncovalent interactions to the Hirshfeld surface in the crystal structures of complexes **I-II**.

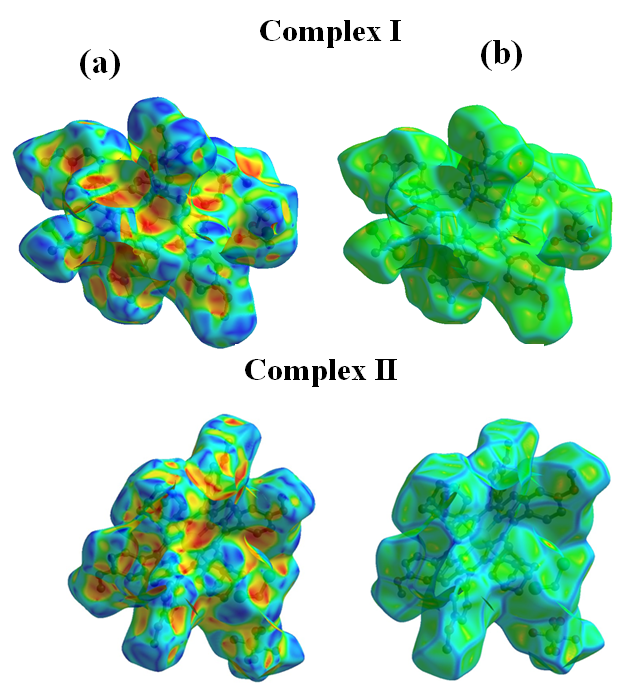


Fig. S14. **(a):** Shape index and **(b):** Curvedness of complexes **I-II**

**4. Cyclic voltammetry**

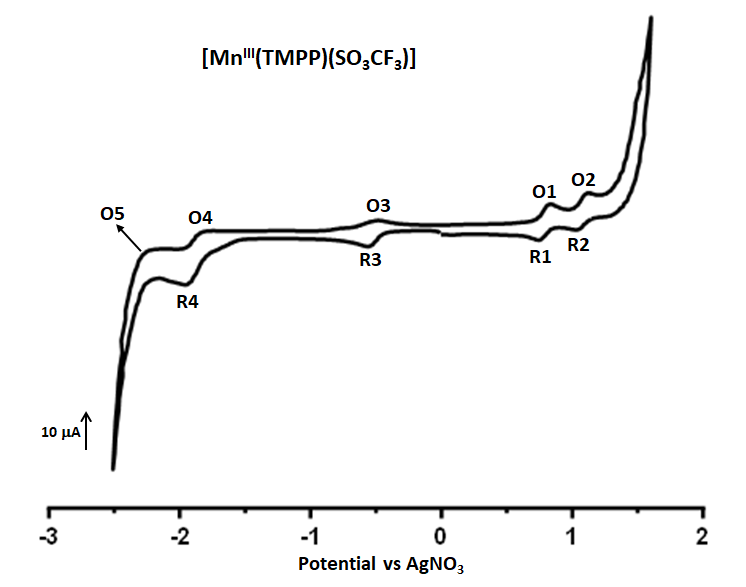


Fig. S15. Cyclic voltammograms of [MnIII(TMPP)(SO3CF3)]. The solvent is dichloromethane, and the concentration is ca. 10–3 M in 0.2 M TBAP, 50 mV/s, vitreous carbon working electrode (Ø = 3 mm).