# **Supporting Information**

# Dimanganese(III) porphyrin dication diradical and its transformation to a $\mu$ -hydroxo porphyrin-oxophlorin heterodimer

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#### Instrumentation

UV-vis-NIR spectra were recorded on a PerkinElmer Lambda 950 UV-vis-NIR spectrometer. High resolution mass spectra (ESI) were recorded using a Waters Micromass QuattroMicro triple quadrupole mass spectrometer.

# X-ray Structure Solution and Refinement.

Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low temperature apparatus and intensity data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ = 0.71073 Å). The data integration and reduction were processed with SAINT software.<sup>1</sup> An absorption correction was applied.<sup>2</sup> The structure was solved by the direct method using SHELXS-97 and was refined on F2 by full-matrix least-squares technique using the SHELXL-2014 program package.<sup>3</sup> Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogen was treated as riding atoms using SHELXL default parameters.

# Magnetic measurements.

Magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer over the temperature range 5 to 300 K. The magnetic data were fitted, using the software PHI,<sup>4</sup> to a model considering antiferromagnetic coupling between the unpaired spin (S = 1/2) of the porphyrin  $\pi$ -cation radicals with the high-spin (S = 2) manganese(III) centers, antiferromagnetic interaction between the radical spins (S = 1/2) on the two porphyrin units of *trans*-2•ClO<sub>4</sub> and interaction between two high-spin manganese centers in *trans*-2•ClO<sub>4</sub>.

Presence of small amount of mononuclear Mn(III) impurity and temperature-independent paramagnetism have also been taken into account. Intermolecular interactions in *trans*-2•ClO<sub>4</sub>, have been excluded to keep the fitting model simple. In case of *cis*-3, the antiferromagnetic interactions between the two high-spin Mn(III) centers were considered for data fitting. Two set of data were collected over the temperature range of 5 to 300 K, by using applied magnetic fields of 0.1 T and corrected for diamagnetism using Pascal's constant.<sup>5</sup> The plots are shown in Figure 3 (see text). The value of g has been kept fixed at 2.00. The parameters obtained after fitting the magnetic data for *trans*-2•ClO<sub>4</sub> are:  $J_{Mn-r} = -49.12$ cm<sup>-1</sup>,  $J_{Mn-Mn} = 1.83$  cm<sup>-1</sup>,  $J_{Mn-r} = -71.99$  cm<sup>-1</sup>, D = -0.55 cm<sup>-1</sup>, while the values for *cis*-3 are: J = -30 cm<sup>-1</sup>, D = -9 cm<sup>-1</sup>. The D values are similar to those observed for other manganese complexes reported in the literature.<sup>6</sup>

#### **Computational Details.**

All geometry optimizations were initiated from the crystal structure coordinates of the U form of trans-2•ClO<sub>4</sub> and cis-3. All structures were optimized using the Gaussian 09, revision B.01, package.<sup>7</sup> Geometry optimizations were carried out without any constraints and frequency calculations were also carried out on all optimized structures. Free energies were taken from the Gaussian frequencies and contain, zero-point, thermal and entropic corrections to the energy. Geometry optimizations have been carried out using the unrestricted hybrid density functional method B3LYP,<sup>8</sup> along with unrestricted density functional method B97D,<sup>9</sup> which incorporates a force-field-like pairwise dispersion correction developed by Grimme. The basis set was LANL2DZ for manganese atom and 6-31G\*\* for carbon, nitrogen, chlorine, oxygen and hydrogen atoms, basis set combination labeled as BS1. U form of trans-2•ClO<sub>4</sub> was optimized as charge neutral species for three different spin multiplicities: (a) undectet (11) state (considering the radical centers of the two porphyrin units ferromagnetically coupled to the respective manganese center), (b) nonet (9) state (where the two radical spins are antiferromagnetically coupled to each other) and (c) septet (7) state (where the radical spins are antiferromagnetically coupled to the respective manganese center). Self-consistent reaction field (SCRF) method was applied in all the optimizations to consider solvent effect (chloroform was used as solvent) and frequency corrections ensured that there are no imaginary frequencies. Visualization of the molecular orbitals and the corresponding diagrams were done using the Chemcraft software.<sup>10</sup>

#### Calculation and visualization of Fukui indices

The electron density was calculated at the B3LYP/BS1 level of theory for the neutral and anionic species. For the neutral and anionic species, the single point calculations were performed on the geometry taken from single crystal X-ray coordinates. The program "Multiwfn -- A Multifunctional Wavefunction Analyzer" (version 3.5)<sup>11</sup> was used to subtract the electron densities and plot the corresponding isosurfaces using Chemcraft software. It is known that when the Fukui function,  $f^{+}$ , has a positive isosurface the nucleophilic attack is favored on that intramolecular region. In our case, the positive surface of  $f^{+}$  function is distributed on the *meso* carbon of the dimanganese dication diradical dimer, *trans*-2•ClO<sub>4</sub>, as compared to the corresponding *meso* carbon of its diiron analog<sup>12</sup> where it is missing (*vide infra*). Furthermore, for the quantification of the  $f^{+}$  values in atomic level, condensed Fukui function values were calculated using the atomic charges determined by the post-SCF Hirshfeld population analysis.<sup>13</sup> The greater condensed Fukui function  $f^{+}$  values indicate greater nucleophilicity of that particular atom, which is in good agreement with our experimental findings. The Hirshfeld atomic charges were used because of their little dependence on the basis set used. Hirshfeld charges q and  $f^{+}$  values are also summarized (*vide infra*).<sup>14</sup>

# **Experimental Section:**

#### Materials

The free ligands *trans*-1,2-bis(*meso*-octaethylporphyrinyl)ethene and *cis*-1,2-bis(*meso*-octaethylporphyrinyl)ethene was synthesized by modifying the literature method.<sup>15</sup> Reagents and solvents were purchased from commercial sources and were purified by standard procedures before use.

#### Synthesis of *trans*-1:

100 mg of *trans*-1,2-bis(*meso*-octaethylporphyrinyl)ethene (0.091 mmol) was dissolved in 60 mL of chloroform. 300 mg of  $MnCl_2 \cdot 4H_2O$  (1.56 mmol) dissolved in 10 mL of dry methanol was added to the above solution. The solution thus obtained was refluxed for 3 hours and then washed with 10% HCl (aq.) solution. The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then evaporated to complete dryness. The solid product was purified by column chromatography on silica gel using chloroform:methanol (98:2) as eluent. Yield: 74 mg (63%).

UV-vis (dichloromethane)  $[\lambda_{max}, nm (\epsilon, M^{-1} cm^{-1})]$ : 362 (3 × 10<sup>4</sup>), 475(2 × 10<sup>4</sup>), 580 (7 × 10<sup>3</sup>), 628 (3.6 × 10<sup>3</sup>).

#### Synthesis of *cis*-1:

100 mg of *cis*-1,2-bis(*meso*-octaethylporphyrinyl)ethene (0.091 mmol) was dissolved in 40 mL of chloroform. 300 mg of MnCl<sub>2</sub>·4H<sub>2</sub>O (1.56 mmol) dissolved in 8 mL of dry methanol was added to the above solution. The solution thus obtained was refluxed for 3 hours and then washed with 10% HCl (aq.) solution. The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then evaporated to complete dryness. The solid product was purified by column chromatography on silica gel using chloroform:methanol (96:4) as eluent. Yield: 70 mg (62%). UV–vis (dichloromethane) [ $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 360 (3 × 10<sup>4</sup>), 475(2 × 10<sup>4</sup>), 574 (6 × 10<sup>3</sup>), 620 (2.8 × 10<sup>3</sup>).

# Synthesis of *trans*-2•ClO<sub>4</sub>:

To a dichloromethane (20 mL) solution of *trans/cis*-1 (100 mg, 0.079 mmol), a solution of 59 mg (0.167 mmol) Fe(ClO<sub>4</sub>)<sub>3</sub> in 2 mL CH<sub>3</sub>CN was added and the resulting solution was stirred in air at room temperature for 40 minutes. During the progress of the reaction, the colour of the reaction mixture changed from bright red to brown. The solution was then evaporated to complete dryness. The resulting solid was then dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub>, filtered off to remove unreacted oxidant and then carefully layered with hexane. On standing for 8-10 days in air at room temperature, dark brown needle shaped crystals were obtained, which were then isolated by filtration, washed with hexane, and dried in vacuum. Yield 92 mg (70%). UV-vis [ $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 358 (1.2 × 10<sup>4</sup>), 530 (1.0 × 10<sup>4</sup>), 691 (0.6 × 10<sup>4</sup>), 1150 (3.0 × 10<sup>3</sup>).

#### Synthesis of *cis*-3:

To a dichloromethane (60 mL) solution of *trans*-2•ClO<sub>4</sub> (100 mg, 0.061 mmol), a solution of 1.5 ml of tetrabutylammonium hydroxide (25% in methanol) was added and the resulting solution was stirred in air at room temperature for 10 minutes. During the progress of the reaction, the colour of the reaction mixture changed from dark brown to dark green. The solution was then evaporated to complete dryness. The resulting solid was then dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub>, and carefully layered with hexane. On standing for 6-8 days in air at room temperature,

dark green crystals were obtained, which were then isolated by filtration, washed with hexane, and dried in vacuum. Yield 48 mg (62%). UV-vis [ $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 367 (2.3 × 10<sup>4</sup>), 417 (1.8 × 10<sup>4</sup>), 471 (2.08 × 10<sup>4</sup>), 569 (6.6 × 10<sup>3</sup>).

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**Figure S1**. Absorption spectra (curved line, left axis) in  $CH_2Cl_2$  and oscillator strengths (vertical line, right axis) of *trans*-**2**• $ClO_4$  obtained from TD-DFT calculations at the B3LYP/BS1 level.



**Figure S2**. IR spectra (selected portion only) of solid polycrystalline samples of (A) *trans*-1 and (B) *trans*-2•ClO<sub>4</sub>. The  $\pi$ -cation radical marker bands in *trans*-2•ClO<sub>4</sub> have been labeled.



**Figure S3.** A perspective view (at 100 K) of *trans*-1 showing 50 % thermal contours (H-atoms have been omitted for clarity).



Figure S4. Diagram illustrating the molecular packing of *trans*-1 in the unit cell (H-atoms have been omitted for clarity).



**Figure S5**. Diagram illustrating the molecular packing of *trans*- $2 \cdot \text{ClO}_4$  in the unit cell (H-atoms have been omitted for clarity).



**Figure S6**. (A) Selected bond distances (in Å) between oxidized and unoxidized complexes have been compared. H-atoms, axial ligands and counter ions have been omitted for clarity. (B) Diagram showing the angle between the least-squares plane of  $C_{20}N_4$  porphyrinato core (red) and the calculated  $C_4$  plane of the bridging ethylene group (green) of *trans*-**2**•ClO<sub>4</sub>.



**Figure S7**. Diagram illustrating the molecular packing of *cis*-**3** in the unit cell (H-atoms have been omitted for clarity).



**Figure S8**. Spin coupling model of (A) *trans*-**2**•ClO<sub>4</sub>, and (B) diiron(III) porphyrin dication diradical dimer.



**Figure S9.** B3LYP/BS1 optimized structure of *trans*-1. Parentheses contain the experimental value obtained from the X-ray structure (H-atoms have been omitted for clarity). All bond lengths are given in Å.



**Figure S10.** B3LYP/BS1 optimized structures of *cis-3* in the (A) *keto* and (B) *enol* form. Parentheses contain the experimental value obtained from the X-ray structure. All bond lengths are given in Å and angles are in degree.



**Figure S11**. Relative spin-state energies of septet (7), nonet (9), and undectet (11) states of *trans*-**2**•ClO<sub>4</sub> as calculated using B3LYP/BS1 and B97D/BS1 level of theory. All the  $\Delta E$  and  $\Delta E$ +ZPE value are relative to nonet (9) state.



**Figure S12**. Energy diagrams and selected Kohn-Sham orbitals of (A) *trans*-1 and (B) *trans*-2•ClO<sub>4</sub> at B3LYP/BS1 level of theory.



**Figure S13.** Calculated Mulliken spin densities for (A) *trans*-**2**•ClO<sub>4</sub>, and (B) diiron(III) dication diradical dimer<sup>13</sup> at the B97D/BS1 level of theory.



**Figure S14.** Isosurface of the Fukui function,  $f^+$ : (A) diiron(III) dication diradical dimer, and (B) *trans*-**2**•ClO<sub>4</sub>, calculated at an isovalue of 0.002 by Multiwfn; (blue corresponds to positive and red corresponds to negative values). *Meso* carbons showing the  $f^+$  in both the complexes are encircled.



**Figure S15**. Values of condensed Fukui function on *meso* carbons of (A) diiron(III) dication diradical dimer, and (B) *trans*-2•ClO<sub>4</sub>.



**Figure S16.** Comparison between selected bond distances from (A) single crystal X-ray structure of *cis*-**3**, B3LYP/BS1 optimized structures in both possible forms of *cis*-**3**: (B) keto form, and (C) enol form.



**Scheme S1.** Two possible forms of (A) meso-hydroxylated porphyrins (oxophlorins) and (B) *cis*-**3**.

State	Energy	Wavelength	Oscillator	Excitation of the main transition	Weight (%)
	(eV)	(nm)	Strength		
	0.0500	1250.05	0.1.000		
3	0.8593	1370.25	0.1680	HOMO-6 → LUMO	56
4	0 9101	1300.12	0.0998	НОМО→ ЦИМО	64
	0.9101	1200.12	0.0770		
9	1.394	889.14	0.0362	HOMO -3→ LUMO	79
10	1.4121	878.01	0.0371	HOMO-7 → LUMO	72
16	1.7261	718.31	0.1363	HOMO-3→ LUMO	50
19	1.8773	660.45	0.0489	HOMO-4 → LUMO	62
22	1.9170	640.77	0.1986	HOMO-1 → LUMO+1	46
24	1.9443	637.70	0.0356	HOMO-2 → LUMO+3	32
27	1.9894	623.23	0.1068	HOMO-1 → LUMO+3	32
28	1.9938	621.85	0.0617	HOMO-2 → LUMO+3	25
36	2.1120	587.03	0.0323	HOMO → LUMO+8	23
41	2.1699	571.38	0.1113	HOMO-3→ LUMO+3	79
50	2.3809	520.74	0.0763	HOMO → LUMO+5	42
56	2.4699	501.98	0.0499	HOMO-1 → LUMO+4	30
64	2.5275	490.54	0.0414	HOMO-2→ LUMO+6	33
70	2.5760	470.31	0.1531	HOMO → LUMO+8	62
78	2.6838	461.97	0.323	HOMO-4 →LUMO+1	56
118	2.9387	419.19	0.0974	HOMO-2 → LUMO	32
120	2.9577	390.12	0.1124	HOMO → LUMO+11	74

 Table S1. TD-DFT calculated Excited States for trans-2•ClO<sub>4</sub>.\*

\*The states whose oscillator strengths are less than 0.03 are not included.

	trans-1	trans-2•ClO <sub>4</sub>	cis-3
Formula	C <sub>74</sub> H <sub>88</sub> Cl <sub>2</sub> Mn <sub>2</sub> N <sub>8</sub>	C <sub>74</sub> H <sub>92</sub> Cl <sub>4</sub> Mn <sub>2</sub> N <sub>8</sub> O <sub>1</sub>	C <sub>75</sub> H <sub>90</sub> Cl <sub>2</sub> Mn <sub>2</sub> N <sub>8</sub> O
		8	2
T (K)	100(2)	100(2)	100(2)
Formula weight	1270.30	1633.23	1316.32
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P -1	<i>P</i> 2/n	<i>P</i> 21/n
<i>a</i> , Å	12.2256(19)	19.481(5)	14.777(5)
<i>b</i> , Å	13.0137(19)	9.679(5)	20.110(5)
<i>c</i> , Å	13.2500(19)	22.850(5)	22.102(5)
$\alpha$ , deg	97.286(4)	90	90
$\beta$ , deg	101.380(4)	95.489(5)	93.147(5)
γ, deg	106.260(4)	90	90
$V, Å^3$	1946.5(5)	4289(3)	6558(3)
Ζ	1	2	4
dcalcd, g•cm <sup>-3</sup>	1.084	1.265	1.333
$\mu$ , mm <sup>-1</sup>	0.435	0.485	0.521
F(000)	672	1708	2784
No. of unique data	7219	7999	12183
Completeness to theta =	99.7 %	99.9 %	99.8 %
25.242°			
No of parameters	398	498	818
refined			
GOF on F <sup>2</sup>	1.038	1.025	1.035
$R1^{a} [I > 2\sigma(I)]$	0.0650	0.0528	0.0764
R1 <sup>a</sup> (all data)	0.0988	0.0878	0.1705
wR2 <sup>b</sup> (all data)	0.1792	0.1216	0.1387
Largest diff. peak and	0.926 and -0.592	0.510 and -0.351	0.468 and -0.453
hole	e.Å <sup>-3</sup>	e.Å- <sup>3</sup>	e.Å-3

 Table S2. Crystallographic data and data collection parameters.

$$\mathbf{a}_{R1} = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}; \qquad \mathbf{b}_{wR2} = \sqrt{\frac{\sum \left[w(Fo^2 - Fc^2)^2\right]}{\sum \left[w(Fo^2)^2\right]}}$$

	trans-1	trans-2•ClO <sub>4</sub>	cis-3
Mn(1)-N(4)	1.988(3)	2.000(2)	1.995(4)
Mn(1)-N(1)	1.990(3)	2.014(3)	1.982(4)
Mn(1)-N(2)	1.996(3)	1.987(3)	1.989(4)
Mn(1)-N(3)	2.003(3)	1.988(3)	2.003(4)
Mn(1)-Cl(1)	2.4471(13)		
Mn(1)-O(1)		2.188(2)	2.011(3)
Mn(1)-O(2)		2.316(2)	
C20–C37	1.498(5)	1.364(4)	1.493(6)
C37–C37A	1.327(8)	1.420(6)	1.322(6)
Mn(2)-N(101)			1.987(4)
Mn(2)-N(104)			1.995(4)
Mn(2)-N(102)			1.996(4)
Mn(2)-N(103)			1.999(4)
Mn(2)-O(1)			2.040(3)
O(1)-H(1)			0.9706
N(4)-Mn(1)-N(1)	88.63(13)	89.44(11)	87.66(15)
N(4)-Mn(1)-N(2)	165.73(13)	177.74(11)	167.56(15)
N(1)-Mn(1)-N(2)	89.85(13)	90.06(11)	90.48(15)
N(4)-Mn(1)-N(3)	89.60(13)	89.86(11)	89.79(15)
N(1)-Mn(1)-N(3)	165.44(13)	175.98(10)	163.73(15)
N(2)-Mn(1)-N(3)	88.31(13)	90.48(11)	88.56(15)
N(2)-Mn(1)-O(1)		91.06(10)	96.78(14)
N(3)-Mn(1)-O(1)		94.84(10)	
N(4)-Mn(1)-O(1)		91.14(10)	
N(1)-Mn(1)-O(1)		89.13(10)	94.95(13)
N(2)-Mn(1)-O(2)		88.40(9)	
N(3)-Mn(1)-O(2)		89.97(10)	
N(4)-Mn(1)-O(2)		89.37(9)	
N(1)-Mn(1)-O(2)		86.07(10)	
O(1)-Mn(1)-O(2)		175.17(9)	
N(4)-Mn(1)-Cl(1)	93.80(10)		
N(1)-Mn(1)-Cl(1)	91.69(10)		

 Table S3. Selected bond distances (Å) and angles (°).

N(2)-Mn(1)-Cl(1)	100.42(10)	
N(3)-Mn(1)-Cl(1)	102.84(10)	
N(101)-Mn(2)-O(1)		91.05(14)
N(104)-Mn(2)-O(1)		104.41(14)
N(102)-Mn(2)-O(1)		93.02(14)
N(103)-Mn(2)-O(1)		105.85(14)
Mn(1)-O(1)-Mn(2)		144.36(16)
Mn(1)-O(1)-H(1)		102.6
Mn(2)-O(1)-H(1)		112.1

**Table S4**. Comparison between selected structural and geometrical parameters of *trans*-**2**•ClO<sub>4</sub> obtained from its molecular structure and from B3LYP/BS1optimized geometries with different spin state combinations.

	<i>trans</i> -2•ClO <sub>4</sub> (from molecular structure)	S = 9 (from optimized structure )	S = 7 (from optimized structure)	S = 11 (from optimized structure)
Mn-N <sub>p</sub> (Å)	1.997(3)	1.998	1.996	2.006
C20–C37 (Å)	1.364(4)	1.380	1.405	1.374
C37–C37A (Å)	1.420(6)	1.411	1.403	1.435
$\frac{\Delta G^a}{(\text{kcal/mol})}$		0.00	13.55	3.16

<sup>*a*</sup> Free energies (expressed in units of kcal/mol) of *trans*-2•ClO<sub>4</sub> are relative to the nonet state and include solvent, entropical and thermal corrections.

diiron(III) dication diradical dimer			trans-2•ClO <sub>4</sub> ,				
Atoms	Neutral (q <sub>N</sub> <sup>Hirsh</sup> )	Anion (q <sub>N+1</sub> <sup>Hirsh</sup> )	ſ	Atoms	Neutral (q <sub>N</sub> <sup>Hirsh</sup> )	Anion (q <sub>N+1</sub> <sup>Hirsh</sup> )	$f^+$
C-16	-1.977334	-1.981945	0.004611	C-30	-2.548183	-2.536753	-0.01143
C-22	-0.829377	-0.831773	0.002396	C-24	-0.743501	-0.751183	0.007682
C-28	-1.659482	-1.660476	0.000994	C-18	-1.372927	-1.375496	0.002569
C-101	-1.800551	-1.802292	0.001741	C-115	-2.544347	-2.537608	-0.006739
C-107	-0.887870	-0.883669	-0.004201	C-109	-0.741771	-0.754753	0.012982
C-113	-1.607797	-1.611628	0.003831	C-103	-1.370564	-1.376063	0.005499

**Table S5.** Values of condensed Fukui function at the B3LYP/BS1 level of theory by Hirshfeld population analysis.\*

\*The Hirshfeld charges reported above were estimated based on build-in sphericalized atomic densities.

**Table S6.** Comparison between selected structural and geometrical parameters of *cis*-**3** obtained from its molecular structure and from B3LYP/BSI optimized geometry (values shown within the parentheses are obtained from X-ray structure).

	Core-I	Core-II	
$Mn-N_p(Å)$	2.023 [1.992(4)]	2.001 [1.994(4)]	
Mn-OH (Å)	2.046 [2.011(3)]	2.116 [2.040(3)]	
C-O (Å)		1.255 [1.255(5)]	
Mn…Mn (Å)	4.040 [3.856]		
C20–C37 (Å)	1.497 [1.493(6)]		
C37–C37A (Å)	1.345 [1.322(6)]		
Mn-OH-Mn (°)	151.995 [143.61(16)]		