# Supporting Information for

# Nitrosyl isomerism in amorphous Mn(TPP)(NO) solid

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#### **Experimental Methods**

### Procedures for preparing Mn(TPP) amorphous solid and studying its reaction with NO.

As a source of Mn(TPP) (TPP = tetraphenylporphyrinato dianion) the relatively stable parent complexes Mn(TPP)(L) (L = pyridine or piperidine), were synthesized according to a published method.<sup>1</sup> Then, as done previously,<sup>2</sup> the parent complex was introduced into the Knudsen cell of the high vacuum system and heated at 490 K for ~3 h until the vacuum gauge indicated complete dissociation of the axial ligand. The resulting Mn(TPP) was sublimed from the Knudsen cell at ~520 K and deposited on a CsI (IR spectra measurements) or CaF<sub>2</sub> (electronic spectra measurements) substrate of the optical cryostat cooled to 10 K by a Helium closed cycle refrigeration system (ARS Inc., USA, Model 8200) equipped with temperature controller (LakeShore, USA, Model 331S). The layer was warmed to room temperature under dynamic vacuum, the pumping was then interrupted, and a slight excess of purified NO was introduced into the cryostat containing Mn(TPP). After a time delay of 30 minutes, the unreacted NO was pumped out, and the FTIR or UV-Vis spectra were measured at different temperatures of the substrate. Before recording the spectra, the sample was maintained at given temperature for a minimum of 10 minutes.

NO was purified by the freeze pumping method and then passed through a column of KOH pellets to free it of higher nitrogen oxides. The purity was checked by IR measurements of the layer obtained by slow deposition of NO on the cooled substrate of the optical cryostat (80 K). The IR spectra did not show the presence of any  $N_2O$ ,  $N_2O_3$ , or water. The isotopically labelled nitric oxide <sup>15</sup>NO (96.5% enrichment) was purchased from the Institute of Isotopes, Republic of Georgia, and purified in the same way.

The FTIR spectra were recorded using "Nexus" spectrophotometer of the Thermo Nicolet Corporation (USA) and UV-visible spectra were measured on a "Specord M-40" (Carl Zeiss, Jena) spectrophotometer.

### **Procedures for DFT calculations**

DFT calculations were performed at UCSB for the nitrosyl Mn(P)(NO) ( $P^{2-}$  = porphinato dianion) systems in the singlet, triplet and quintet spin states at spin unrestricted BP86/TZVP, TPSS/DGDZVP and PBE/DGDZVP levels of theory without symmetry constraints using the Gaussian 03 software package. The geometries of various spin states with linear and bent *O*- or *N*- nitrosyl ligands were optimized and vibrational frequencies calculated.

DFT calculations at Leuven were performed using the Turbomole 6.3 program package.<sup>3</sup> Geometries were optimized for the lowest-lying spin states using the BP86 functional,<sup>4,5</sup> with an ecp-10-mdf basis set (including one f primitive with exponent 1.8) on Mn and 6-31G(d) basis sets on ligand atoms (Basis I). Proper symmetries,  $C_s$  and  $C_{4v}$ , were applied during these optimizations, and all calculations were followed with a frequency analysis to ensure that the calculated structures are indeed structural minima. All relative DFT electronic energies reported in the tables below were obtained with more extended basis sets, i.e. def2-TZVP

for all atoms. Four different functional were used: two GGA, BP86<sup>4,5</sup> and B97D,<sup>6</sup> one meta-GGA TPSS,<sup>7,8</sup> and the B3LYP hybrid functional.<sup>4,8,10</sup> The B97D functional has been parametrized for dispersion interaction, which has been shown to give an important contribution to metal-ligand bonding.<sup>11,12</sup> For the other three functionals, an empirical dispersion correction<sup>6</sup> (denoted as –D) was included in all DFT energies. The unrestricted DFT formalism as used in all cases. For the (S=0) state, only B3LYP gives an unrestricted solution which is slightly lower (0.1 kcal/mol) than the RB3LYP energy. For the three other functionals the unrestricted calculation converges to a restricted solution.

The CASSCF/CASPT2 calculations were performed with the Molcas 7.6 package.<sup>13</sup> Extended ANO-rcc basis sets<sup>14,15</sup> were used, with the following contractions: [7s6p5d3f2g1h] for Mn, [4s3p2d1f] for C, N, O, and [3s1p] for H. The Cholesky decomposition technique was used to approximate the two-electron integrals, using a threshold of 10<sup>-6</sup> au.<sup>16</sup> Scalar relativistic effects were included using the standard second- order Douglas–Kroll–Hess Hamiltonian.<sup>17-19</sup> In the perturbation step, an imaginary level shift<sup>20</sup> of 0.1 au was used to prevent intruder states, while the default IPEA shift for the zeroth-order Hamiltonian<sup>21</sup> (0.25 au) was used. All valence electrons, including the metal (3s,3p) semicore electrons, were included in the CASPT2/RASPT2 calculations.

The active space was constructed according to the standard rules for transition metal systems.<sup>22-24</sup> For all three states considered, all five Mn 3d orbitals, the NO ( $\pi$ ,  $\pi^*$ ) orbital, and the porphyrinate N lone pair combination involved in  $\sigma$ -donation with Mn 3d<sub>xy</sub> are included. Only for those structures containing a linear Mn–NO bond (the (S=0) and the (S=1) (d<sub>x</sub>2-y2)<sup>1</sup>(d<sub>xy</sub>)<sup>1</sup> state) strong  $\sigma$ -donation from NO into the 3d<sub>z</sub>2 orbital is observed, and the NO  $\sigma$  orbital was included in the active space. In the (S=1) (d<sub>x</sub>2-y2)<sup>1</sup> (d<sub>z</sub>2)<sup>1</sup>state the M–NO bond is bent, and the d<sub>z</sub>2 orbital becomes non-bonding Figure S1).

#### More details on the DFT calculations:

The results of the DFT calculations at UCSB are summarized in Table S1. The results of calculations carried out at Leuven are summarized in Tables S2 and S3. As shown in Figure 1, the Mn–NO bond involves a strongly covalent  $\pi$ -interaction between the Mn  $(3d_{xz}, 3d_{yz})$  and NO  $\pi^*$  orbitals, giving rise to a strongly delocalized bonding and antibonding MOs  $(d_{xz,yz}, \pi_{x,y}^*)_b$  and  $(d_{xz,yz}, \pi_{x,y}^*)_a$  respectively, the former being doubly occupied, the latter unoccupied in all low-lying configurations. With a linear M–NO bond ( $C_{4v}$  structures),  $\sigma$ -donation from NO into the Mn  $3d_{z2}$  orbital is also observed, leading to a destabilization (and mixing with NO  $\sigma$  character) of  $3d_{z2}$ , which is unoccupied. Similarly, the  $3d_{xy}$  orbital is destabilized by  $\sigma$ -antibonding interactions with the four porphyrin nitrogens. In the (S=0) state, the non-bonding  $3d_{x2-y2}$  orbital is doubly occupied. Two (S=1) states are reached by transferring an electron from this orbital into one of the  $\sigma$ -antibonding orbitals  $3d_{z2}$  or  $3d_{xy}$ . In the latter case, this involves electron redistribution in the equatorial plane,

leaving the M–NO bond linear. However, when  $3d_{22}$  is populated, the antibonding character is removed by a bending of the Mn–NO bond and concomitant decrease of the overlap with NO  $\sigma$  orbital, and a C<sub>s</sub> structure is obtained with Mn–NO bent in either the xz or yz plane (i.e. in between the porphyrin N ligands). The most important structural parameters of the singlet and two triplet states are given in Table S2, whereas Table S3 reports the relative energies of the three states, as obtained from different DFT functionals and from CASPT2. The linear (S=1) structures is predicted at a considerably higher energy than both other states. However the linear (S=0) and bent (S=1) structures are rather close-lying at all levels of theory, although as noted previously<sup>25-28</sup> the results obtained from DFT are strongly functional dependent. As usual, the pure GGA functionals BP86 and TPSS tend to overstabilize the (S=0) with respect to the (S=1) state. BP97D performs better, predicting the (S=0) and (S=1) states very close in energy. On the other hand, the hybrid functional B3LYP seems to significantly overstabilize the triplet state. CASPT2 also predicts the (S=1) state to be most stable, although the difference is smaller. Previous CASPT2 calculations on heme model systems<sup>27,28</sup> indicated that this method has a slight tendency to favor high spin with respect to low spin states. However, it should also be noted that any interaction, any axial ligation, caused, for example, by the crystal environment, would destabilize the 3d<sub>z2</sub>, thus favouring singlet with respect to the triplet state. As an example, CASPT2 calculations on Mn(P)(Im)(NO) (with Im = and axial imidazole ligand) firmly predict an (S=0) ground state for this complex, with the triplet  $C_s$  structure lying 13.5 kcal/mol higher in energy.



**Figure S1**: (A) Molecular orbitals diagram of Mn(P)(NO) in its (S=0) state. Electronic transitions leading to two possible (S=1) states are indicated. (B) Structure of the (S=0) state; (C) Structure of the (S=1) $(d_{x2-y2})^{1}(d_{z2})^{1}$  state; (D) Structure of the (S=1)  $(d_{x2-y2})^{1}(d_{xy})^{1}$  state.

 Table S1. Energy/Relative Energies of Mn(Porphine)(NO) complexes with respect to the lowest energy compound in the series

Configuration		Singlet			Triplet			Quintet	
		TPSS/DGDZVP	BP86/TZVP	PBE/DGDZVP	TPSS/DGDZVP	BP86/TZVP	PBE/DGDZVP	TPSS/DGDZVP	BP86/TZVP
	Energy (a.u.) Rel.energies, kcal/mol v(NO), cm <sup>-1</sup> Angle Mn-N-O,°	-2269.575 0 1800 179.98	-2269.994 0 1777 179.99	-2267.82836271 1808 179.99	-2269.555 13 1759	Converged into bent configuration		-2269.514 39 1682	NC
N Mn N	Energy (a.u.) Rel.energies, kcal/mol v(NO), cm <sup>-1</sup> Angle Mn-N-O,°	-2269.514 39 1305	Converged into linear configuration		-2269.562 9 1679 143.41	-2269.983 7 1660 145.47	-2267.81567399 8 1685 142.80	-2269.519 36 1629	-2269,936 36 1587
	Energy (a.u.) Rel.energies, kcal/mol v(NO), cm <sup>-1</sup>	-2269.507 43 1717	-2269.923 45 1696		-2269.520 35 1560	-2269.939 35 1569		NC	NC
N Mn N	Energy (a.u.) Rel.energies, kcal/mol v(NO), cm <sup>-1</sup>	Converged into bent configuration	NC		-2269,521 35 1535	-2269,939 34 1552		NC	NC

NC - Non converged

State	Point	Distances (Å)**			Angle ( <sup>0</sup> )	Frequency (cm <sup>-1</sup> )		
	group	r(N-O)	r(Mn-NO)	$\Delta$ Mn-N4	Mn-N-O	v(NO)* cal.	v(NO) exp.	
$^{1}A_{1}$	$C_{4v}$	1.191	1.602	0.313	180.0	1813.2	1735 <sup>29</sup> ,1760 <sup>30</sup>	
<sup>3</sup> A′	$C_s$	1.197	1.749	0.281	142.8	1681.2		
${}^{3}A_{2}$	$C_{4v}$	1.196	1.642	0.526	180.0	1782.2		

Table S2: Selected parameters of Mn(P)(NO) complexes from the BP86 structure optimization.

\* frequencies without scaling.

\*\* r(N-O) is the distance between N and O in the NO fragment. r(Mn-NO) is the distance between Mn and N.  $\Delta$ Mn-N4 is the Mn out-of-plane (defined by the 4 N) displacement.

**Table S3:** Relative electronic energy\* (kcal/mol) of the lowest-lying electronic states of Mn(P)(NO) with respect to the (S=0) state. The occupation of the main configuration is indicated for each state.

State	Configuration	BP86-D	B3LYP-D	TPSS-D	B97D	CASPT2
${}^{1}A_{1}$	$\left(d_{x2-y2}\right)^2$	0.0	0.0	0.0	0.0	0.0
<sup>3</sup> A′	$(\mathbf{d}_{x2-y2})^{\uparrow}(\mathbf{d}_{z2})^{\uparrow}$	6.2	-4.2	7.1	0.4	-1.5
${}^{3}A_{2}$	$\left(\mathbf{d}_{x2-y2}\right)^{\uparrow}\left(\mathbf{d}_{xy}\right)^{\uparrow}$	27.2	13.6	29.0	16.5	22.1

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