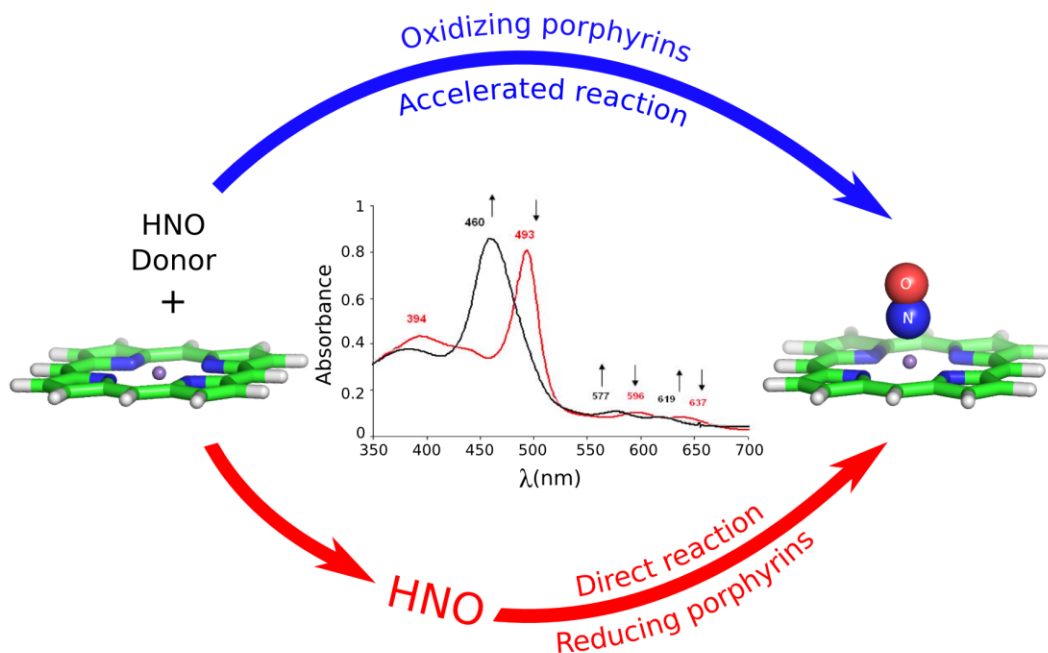# Supporting Information

Redox potential determines the reaction mechanism of HNO donors with Mn and Fe porphyrins: defining the better traps

Lucía Álvarez,[†] Sebastián A. Suarez,[†] Damian E. Bikiel,[†] Ines Batinić-Haberle,[‡] Julio S Reboucas,[#] Marcelo A. Martí,[†‡] Fabio Doctorovich[†*]

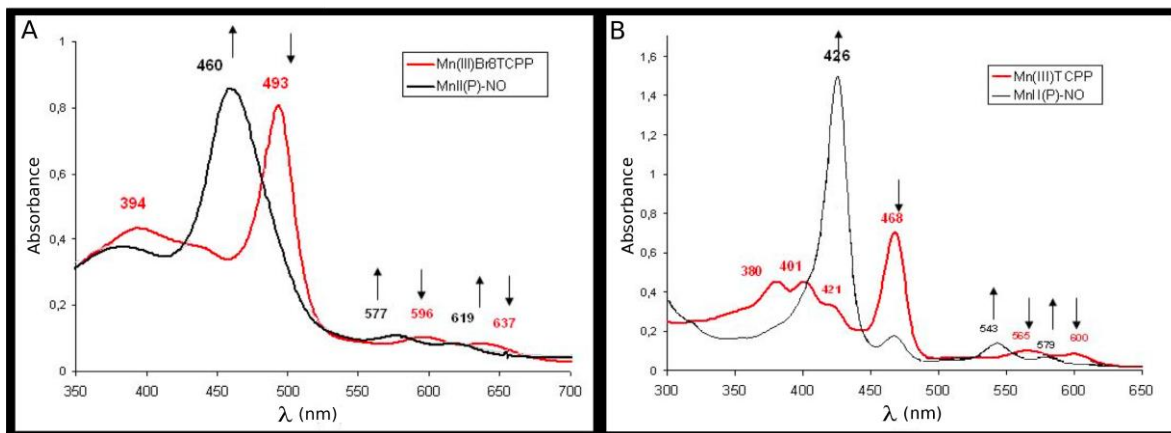**Figure SI 1**. A) Spectral changes for the reaction of $[Mn^{III}Br_8TCPP]^{3-}$ (a negative-reducing porphyrin) $1x10^{-5}$ M, (red line), $\lambda_{max}= 493$ nm) with AS in a 1:1 stoichiometric ratio, yielding $[Mn^{II}Br_8TCPP(NO)]^{4-}$. (black line, $\lambda_{max} = 460$ nm) in phosphate buffer 0.1 M at 25 °C. B) Spectral changes for the reaction of $[Mn^{III}TCPP]^{3-}$ (a negative-oxidizing porphyrin) $1x10^{-5}$ M, (red line), $\lambda_{max}= 468$ nm) with AS in a 1:100 ratio, that yields $[Mn^{II}TCPP(NO)]^{4-}$ (black line, $\lambda_{max} = 426$ nm) in phosphate buffer 0.1 M at 25 °C.

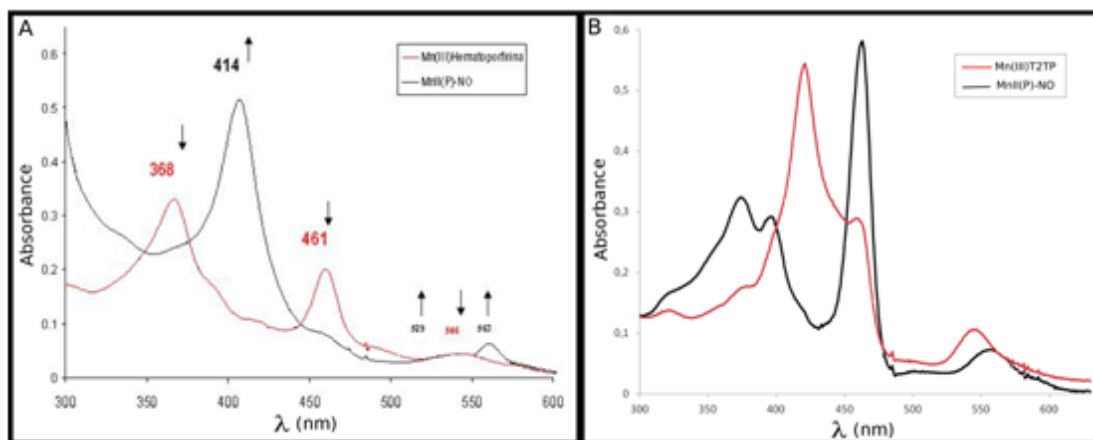**Figura SI 2.** A) Spectral changes for the reaction of $[Mn^{III}HematoP]^-$ (a negative reducing porphyrin) $5x10^{-6}$ M, (red line), $\lambda_{max}= 368$ nm) with AS in a 1:1 stoichiometric ratio, yielding $[Mn^{II}HematoP(NO)]$ (black line, $\lambda_{max} = 414$ nm) in phosphate buffer 0.1 M at 25 °C. B) Spectral changes for the reaction of $[Mn^{III}T-2-PyP]$ (a neutral reducing porphyrin) $1x10^{-5}$ M, (red line), $\lambda_{max}= 468$ nm) with AS in a 1:100 ratio, that yield $[Mn^{II}TSPPNO]^{4-}$ (black line, $\lambda_{max} = 426$ nm) in phosphate buffer 0.1 M at 25 °C.

Table 1 – The wavelengths of main absorption bands and molar absortivities for porphyrins and their NO-complexes.

Porphyrin / NO-Complex	λ Soret Absorption band (nm) (epsilon, cm^{-1}M^{-1})		Q Absorption band (nm) (epsilon, cm^{-1}M^{-1})	
[Mn^{III}HematoP]$^-$	368 (69300)	461 (30400)	546 (12000)	----
[Mn^{II}HematoP(NO)]$^{-2}$	----	414 (108000)	529 (15000)	563 (15000)
[Mn^{III}ProtoP]$^-$	371 (82500)	466 (34500)	553 (15000)	----
[Mn^{II}ProtoP(NO)]$^{-2}$	----	414 (100000)	535 (24000)	571 (25000)
[Mn^{III}TSPP]$^{3-}$	401 (40000)	468 (70000)	565 (10000)	600 (10000)
[Mn^{II}TSPP(NO)]$^{4-}$	----	426 (140000)	543 (14000)	579 (6000)
[Mn^{III}Br$_8$TCPP]$^{3-}$	394 (43000)	493 (78000)	596 (13000)	637 (10000)
[Mn^{II}Br$_8$TCPP(NO)]$^{4-}$	380 (38000)	460 (83000)	577 (13500)	619 (10000)
[Mn^{III} T-2-PyP]$^+$	374 (25000)	462 (70000)	550 (12000)	620 (11000)
[Mn^{II}T-2-PyP]NO	----	421 (95000)	544 (14600)	569 (5900)
[Mn^{III}T(TriMA)P]$^{5+}$,	379 (27000)	464 (68700)	570 (13700)	627 (12000)
[Mn^{II}T(TriMA)P(NO)]$^{4+}$,	----	423 (89000)	560 (12800)	609 (9000)

Comparison between AS at pH=7 and TSHA at pH=10 for two 'slow' porphyrins

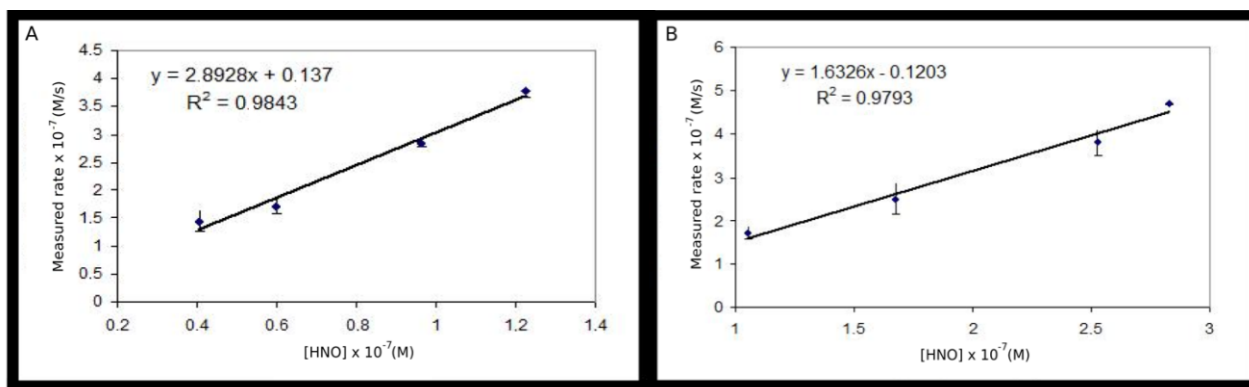**Figure SI 3.** Initial rate vs [HNO] estimated for the reaction for $[Mn^{III}TSPP]^{3-}$ (1×10^{-5} M) with A) AS (pH phosphate 7 buffer 0.1 M, 25°C). B) TSHA (pH 10 phosphate buffer 0.1 M, 25°C).
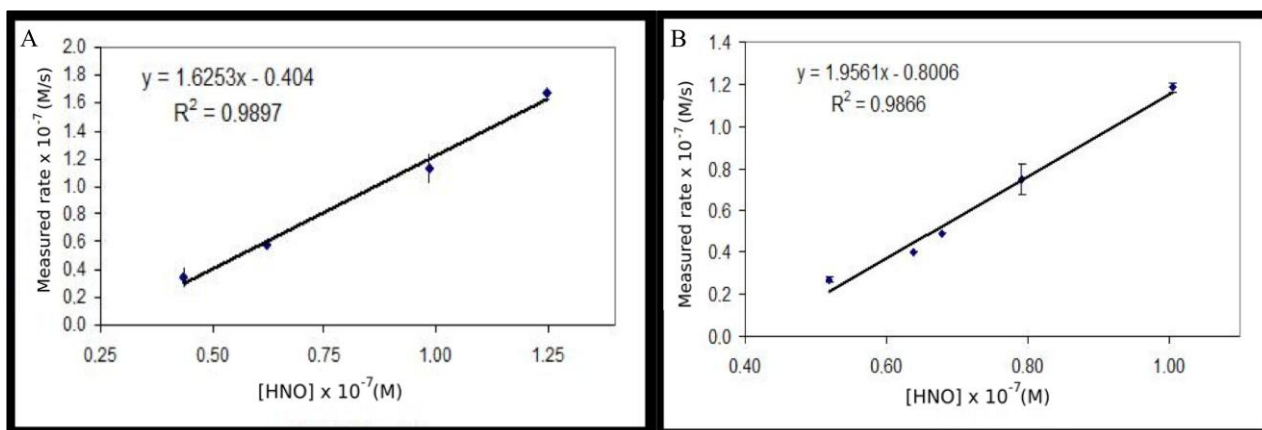

Figura SI 4. A) Initial rate vs [HNO] estimated for the reaction of the $[Mn^{III}HematoP]^{-}$ (1×10^{-5} M) with A) AS (pH 7 phosphate buffer 0.1 M, 25°C). B) TSHA (pH 10 phosphate buffer 0.1 M, 25 °C).

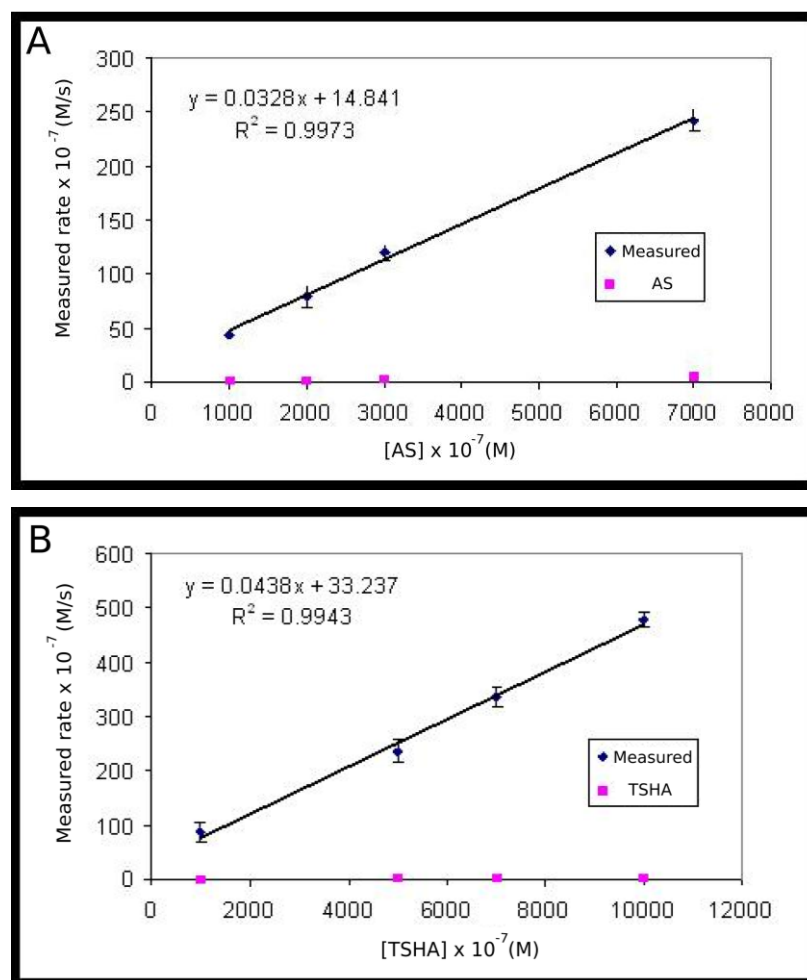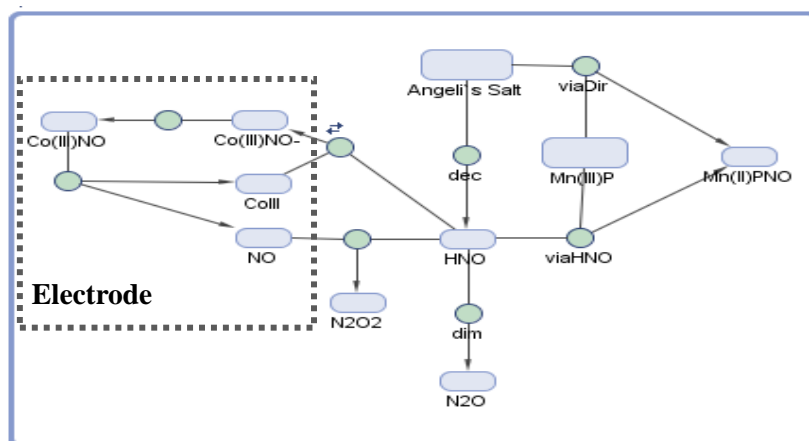Comparison between AS at pH=7 and TSHA at pH=10 for two 'fast' porphyrins

Figure SI 5. A) Initial rate vs [Donor] for the reaction with $[Mn^{III}Br_8TSPP]^{3-}$ ($1x10^{-5}$ M) con A) AS (pH 7 phosphate buffer 0.1 M, 25ºC). B) TSHA (pH 10 phosphate buffer 0.1 M, 25 ºC).
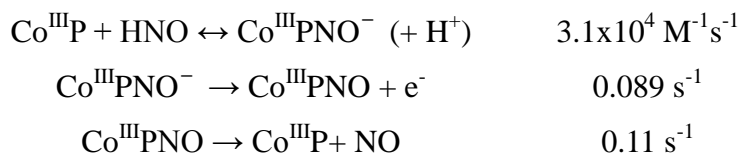
Kinetic simulations of HNO reactions in the presence of Mn^{III} porphyrins (and Co(P) modified electrode)

The minimal kinetic reaction model that can be used comprises the spontaneous decomposition of the donor in order to generate HNO:

#	Constant	Reaction	Value	Ref
1	k_{dec}	Angeli's salt $\rightarrow$ HNO	0.0023 s^{-1}	
2	viaDir	Mn^{III}P + AS $\rightarrow$ Mn^{II}PNO	(1 - 4000) M^{-1}s^{-1}	
3	viaHNO	Mn^{III}P + HNO $\rightarrow$ Mn^{II}PNO	(4x10^4 - 4x10^5) M^{-1}s^{-1}	
4	k_{dim}	2HNO $\rightarrow$ N$_2$O + H$_2$O	8x10^6 M^{-1}s^{-1}	
5	k_{NO_HNO}	HNO + NO $\rightarrow$ N$_2$O$_2^-$ +H$^+$	5.8x10^6 M^{-1}s^{-1}	

Electrode constant was preview described

$$Co^{III}P + HNO \leftrightarrow Co^{III}PNO^- \ (+ H^+) \qquad 3.1x10^4 \ M^{-1}s^{-1}$$
$$Co^{III}PNO^- \rightarrow Co^{III}PNO + e^- \qquad 0.089 \ s^{-1}$$
$$Co^{III}PNO \rightarrow Co^{III}P+ NO \qquad 0.11 \ s^{-1}$$

For the reactions 1, 4 and 5 the corresponding kinetic rate constants are known. For HNO and AS reaction with Mn^{III}P, these rate constants are not known for the present porphyrin, however, they can be reasonably approximated for the same reactions with other Mn porphyrins known in the literature. These two rate constants (2 and 3) were allowed to ride and obtained by the simulation (Matlab 2009b).The charges are omitted as they differ from porphyrin to porphyrin.