Supporting Information

Mechanistic studies on the nitrite-catalyzed reductive nitrosylation of highly charged anionic and cationic Fe^{III}-porphyrin complexes

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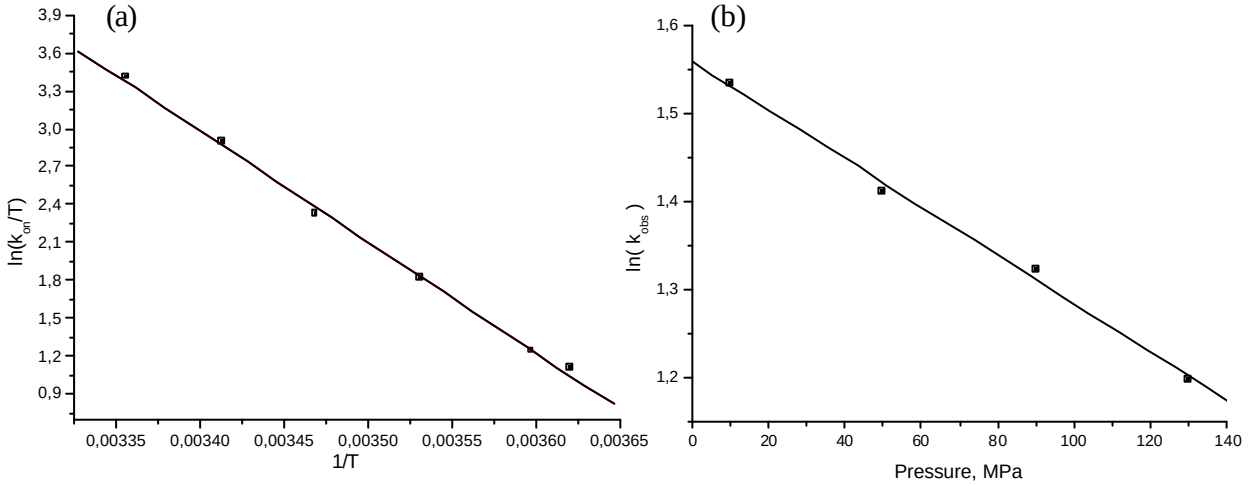

Figure S1. (a) Plot of ln(k_{obs}/T) versus 1/T in the temperature range 5 – 25 °C for the binding of nitrite to $(P^{8+})Fe^{III}(H_2O)_2$. Experimental conditions: $[(P^{8+})Fe^{III}]^{9+} = 7.5 \times 10^{-6}$ M, λ_{det} = 430 nm, I = 0.1 M (with KNO_3), pH 2.0. (b) Plot of ln(k_{obs}) versus pressure for the reaction of $(P^{8+})Fe^{III}(H_2O)_2$ with NO_2^- in the pressure range 10 – 130 MPa. Experimental conditions as in (a), $[NO_2^-]$ = 6 mM, λ_{det} = 430 nm, temp = 2.5 °C.

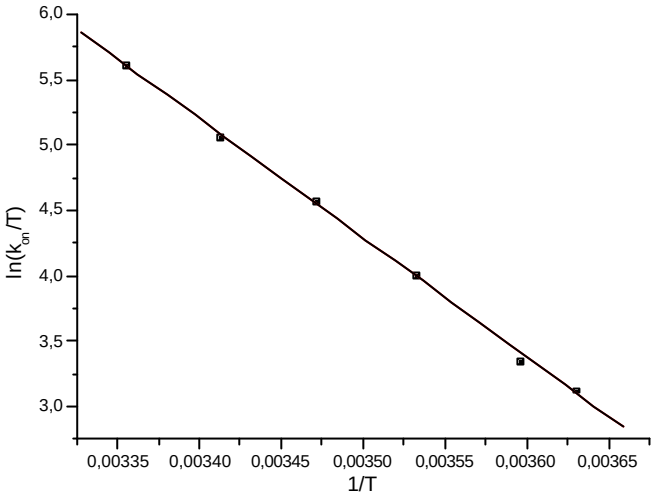

Figure S2. Plot of ln(k_{obs}/T) versus 1/T for nitrite binding to $(P^{8+})Fe^{III}(H_2O)_2$. Experimental conditions: $[(P^{8+})Fe^{III}]^{9+}$ = 7.5 $\times 10^{-6}$ M, $[NO_2^-]$ = 1 mM, λ_{det} = 430 nm, temp = 25 ^oC, I = 0.1 M (with KNO_3), pH 4.0

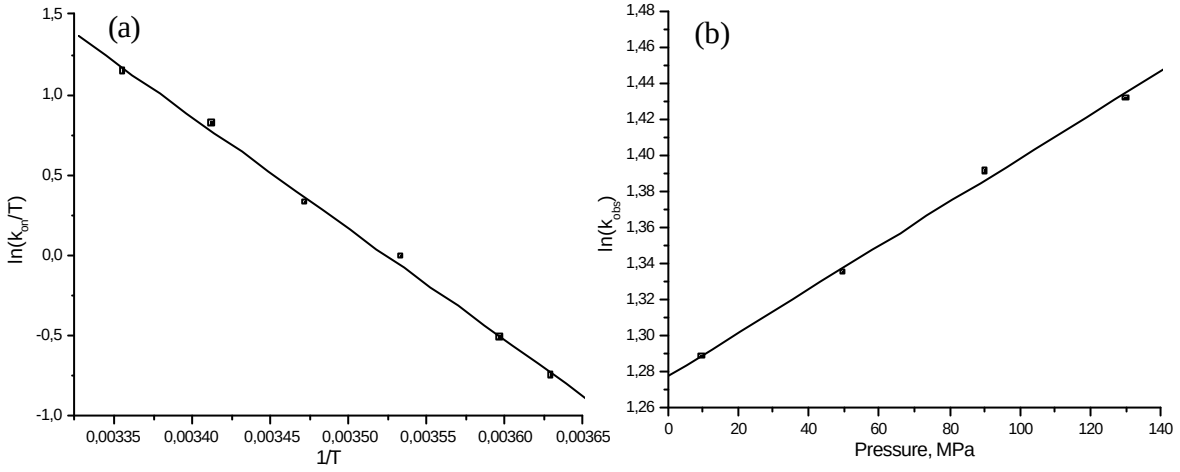

Figure S3. (a) Plot of ln(k_{obs}/T) versus 1/T in the temperature range 5 – 25 °C for the binding of NO_2^- to $(P^{8+})Fe^{III}(OH)$. Experimental conditions: $[(P^{8+})Fe^{III}]^{9+}$ = 8.5 × 10^{-6} M, $[NO_2^-]$ = 25 mM, λ_{det} = 435 nm, *I* = 0.1 M (with KNO_3), pH 8.0. (b) Plot of ln(k_{obs}) versus pressure for the reaction of $(P^{8+})Fe^{III}(OH)$ with NO_2^- in the pressure range 10 – 130 MPa. Experimental conditions as in (a), $[NO_2^-]$ = 10 mM.

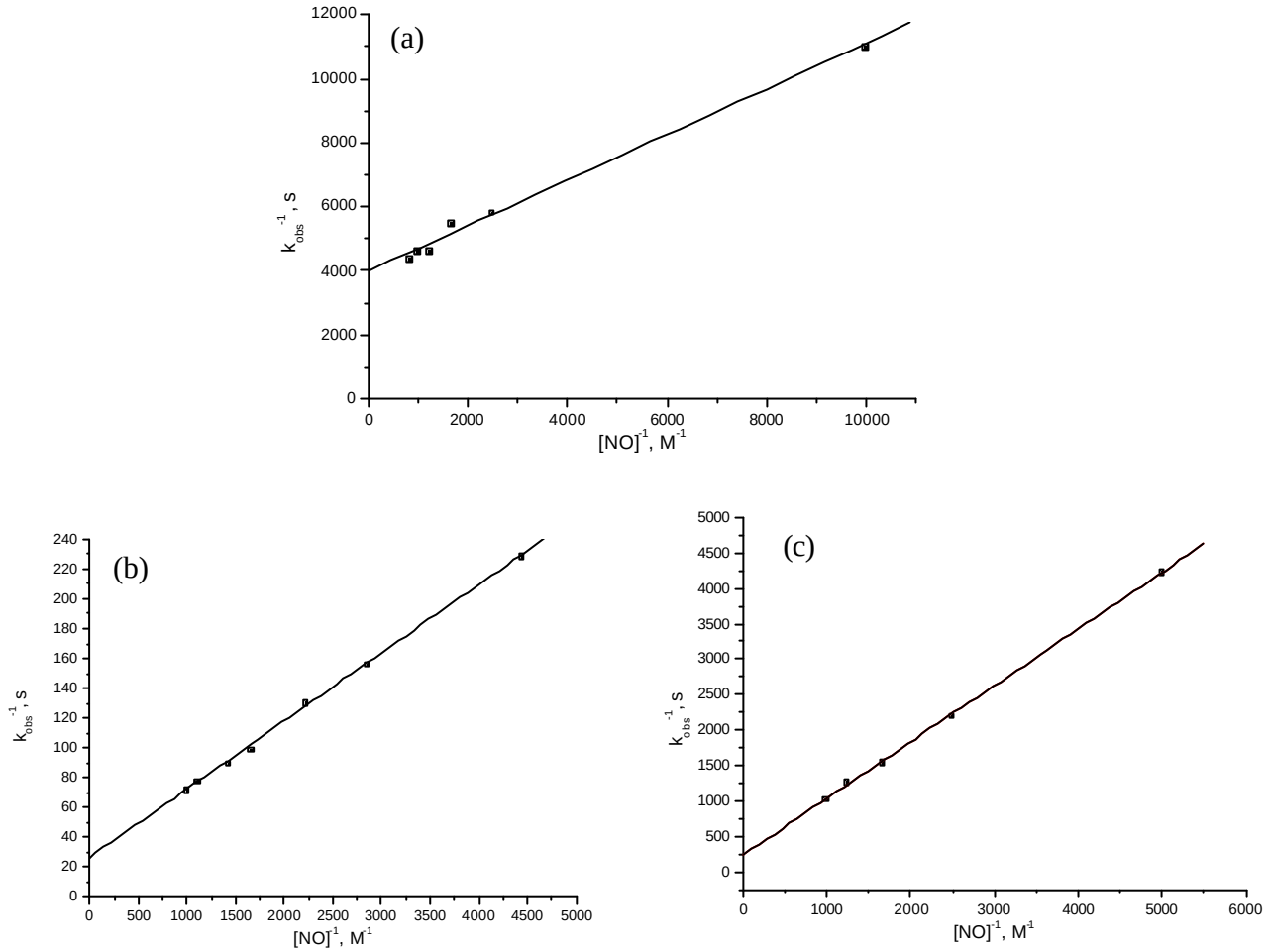

Figure S4. (a) Plot of $(k_{obs})^{-1}$ vs. $[NO]^{-1}$ for reductive nitrosylation of $(P^{8-})Fe^{II}(OH_2)(NO^+)$ at pH 7, (b) $(P^{8+})Fe^{II}(OH_2)(NO^+)$ at pH 2 and (c) $(P^{8+})Fe^{II}(OH)(NO^+)$ at pH 8. These plots are based on the kinetic data reported in Figures 7, 9 and 11. For experimental conditions see the mentioned figures.

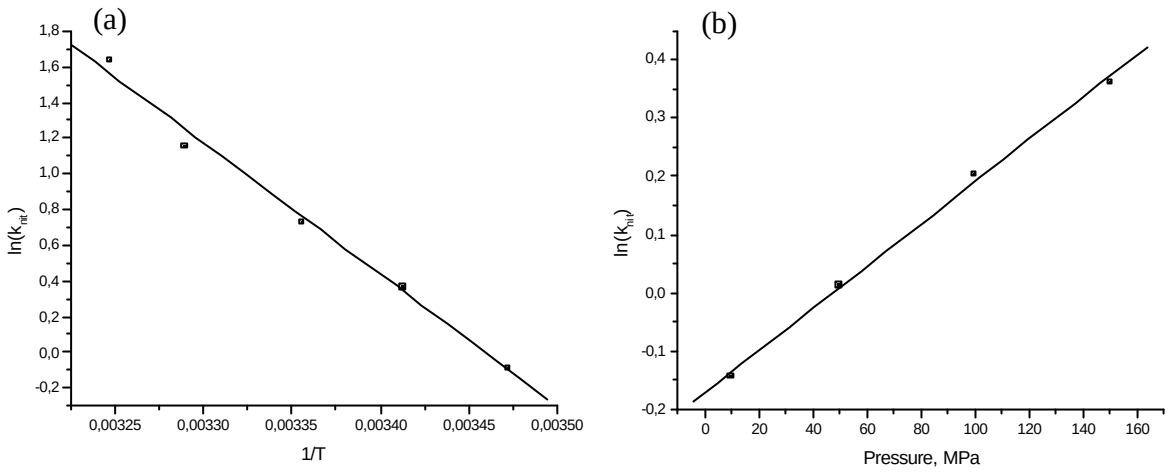

Figure S5. (a) Temperature dependence of reductive nitrosylation of $(P^{8-})Fe^{II}(H_2O)(NO^{+})$ by NO/nitrite. (b) Pressure dependence. Experimental conditions: (a) $[Fe^{III}(p^{8-})]^{7-} = 2.0 \times 10^{-5}$ M, [NO] = 1 mM, $[NO_2^{-}]$ = 1.5 mM, I = 0.1 M (with $NaClO_4$), pH 7.0 with Bis-tris buffer; (b) $[NO_2^{-}]$ = 0.5 mM, temp = 13.5 ^{o}C, λ_{det} = 426 nm.

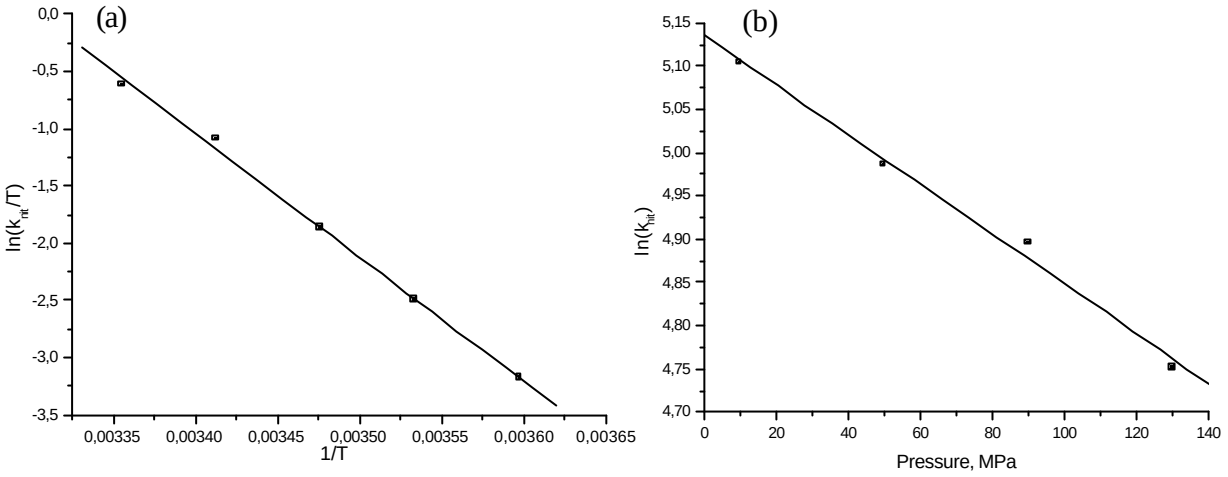

Figure S6. (a) Plot of ln(k_{nit}/T) versus 1/T for reductive nitroslyation of (P^{8+})Fe^{II}(H_2O)(NO^+) by NO/nitrite (where $k_{nit} = k_{obs}(1 + K_{NO})/K_{NO}$[NO] at constant [$NO_2^-$]) in the temperature range 5 – 25 ^oC, [NO_2^-] = 1 mM, λ_{det} = 431 nm. (b) Pressure dependence, Experimental conditions: [(P^{8+})Fe^{III}]$^{9+}$ = 1.0 $\times 10^{-5}$ M, [NO] = 1 mM, [NO_2^-] = 1 mM, temp = 25.0 ^oC, λ_{det} = 431 nm, I = 0.1 M (KNO_3), pH 2.0

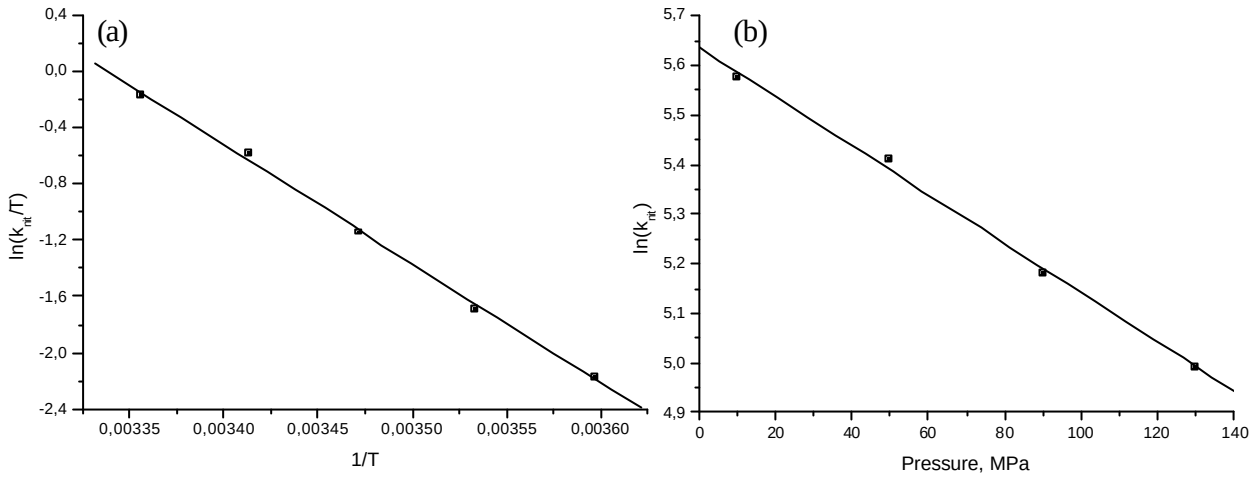

Figure S7. (a) Plot of $\ln(k_{nit}/T)$ versus 1/T for reductive nitroslyation of $(P^{8+})Fe^{II}(H_2O)(NO^{+})$ by NO/nitrite in the temperature range 5 – 25 ^{o}C, $[NO_2^{-}]$ = 1 mM, λ_{det} = 431 nm. (b) Pressure dependence, Experimental conditions: $[(P^{8+})Fe^{III}]^{9+}$ = 1.0 $\times 10^{-5}$ M, [NO] = 1 mM, $[NO_2^{-}]$ = 0.1 mM, λ_{det} = 431 nm, I = 0.1 M, pH 4.0

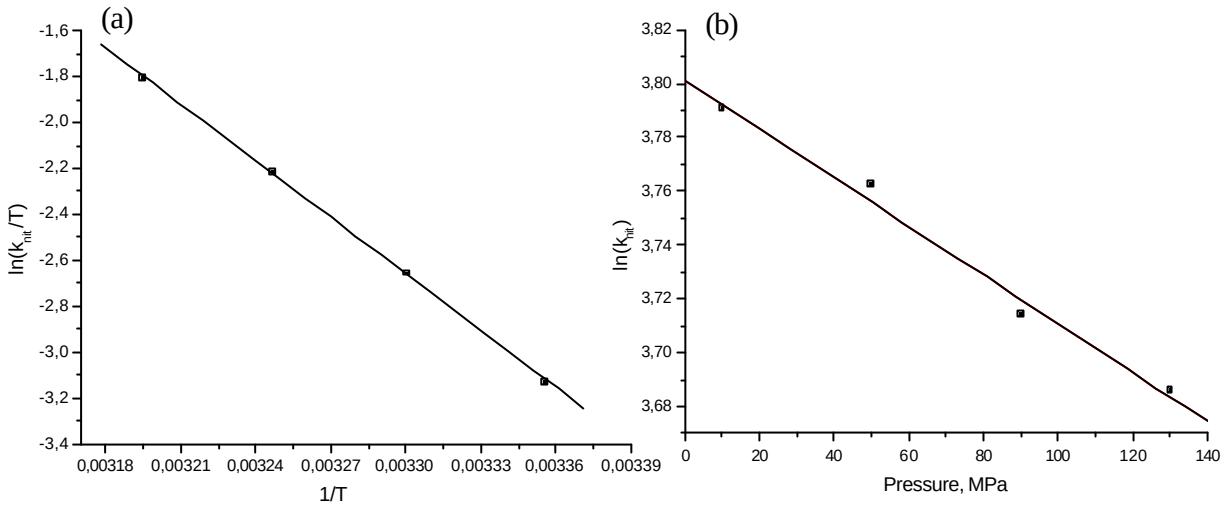

Figure S8. (a) Plot of $\ln(k_{nit}/T)$ versus 1/T in the temperature range 25 – 40 ^{o}C for reductive nitrosylation of $(P^{8+})Fe^{II}(OH)(NO^{+})$ by NO/nitrite. (b) Plot of $\ln(k_{nit})$ versus pressure in the range 10 – 130 MPa, [NO] = 0.5 mM, $[NO_2^{-}]$ = 0.5 mM. Experimental conditions: $[(P^{8+})Fe^{III}] = 8.5 \times 10^{-6}$ M, temp = 25 ^{o}C, λ_{det} = 435 nm, I = 0.1 M (with KNO_3), pH 8.0

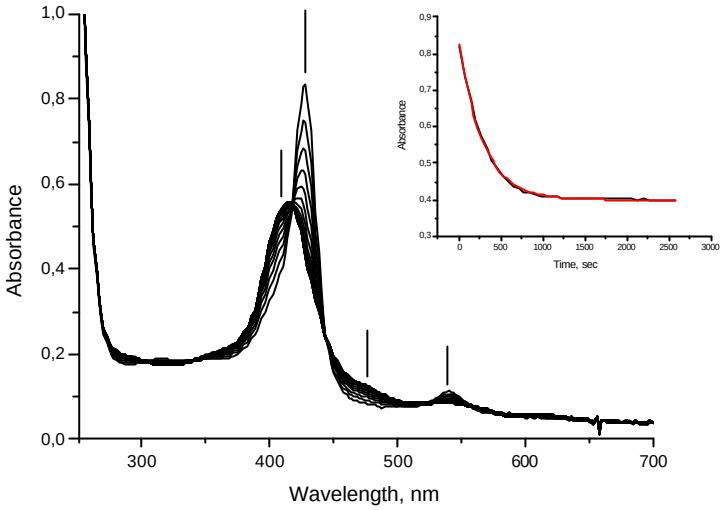

Figure S9. Spectral changes observed following the binding of NO to $(P^{8-})Fe^{III}(H_2O)_2$. Inset: kinetic trace of absorbance at 426 nm vs. time fitted to a single exponential function. Experimental conditions: $[(P^{8-})Fe^{III}]^{7-}$ = 1×10^{-5} M, [NO] = 1 mM, [added NO_2^-] = 2mM, temp = 25.0 ^{o}C, I = 0.1 M (with $NaClO_4$) pH = 7.0. The observed rate constant is $k_{obs} = 3.54 \times 10^{-3}$ s^{-1}.

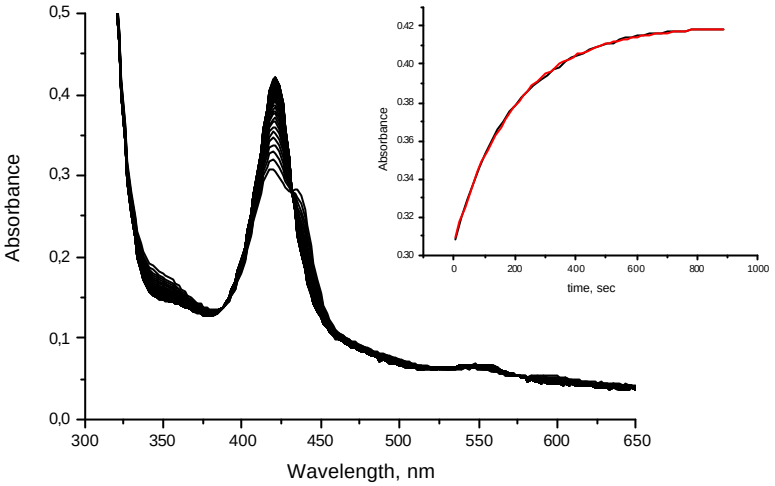

Figure S10. Spectral changes observed for the reaction of $(P^{8+})Fe^{II}(OH)(NO^{+})$ with NO/nitrite. Inset: kinetic trace of absorbance vs. time at 422 nm fitted with a single exponential function. Experimental conditions: $[(P^{8+})Fe^{III}]^{9+} = 7.5 \times 10^{-6}$ M, [NO] = 1 mM, $[NO_2^-]$ = 2 mM, temp = 25.0 ^{o}C, pH 8.0, I = 0.1 M (KNO_3). The spectra were recorded every 20 sec.