

Supporting Information

Mechanistic information on the nitrite-controlled reduction of aquacob(III)alamin by ascorbate at physiological pH

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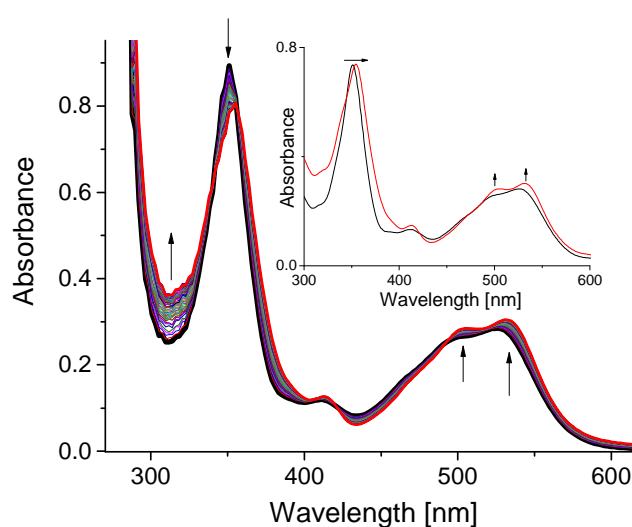


Figure S1. Spectral changes observed for the reaction of CblOH₂ (4.3×10^{-5} M) with NO₂⁻ (4.3×10^{-4} M) at pH = 7.2 (25 °C, 0.10 M Tris buffer). Spectra were recorded every 0.05 s. **Inset:** Initial spectrum of CblOH₂ (black line) and final spectrum of CblNO₂ (red line).

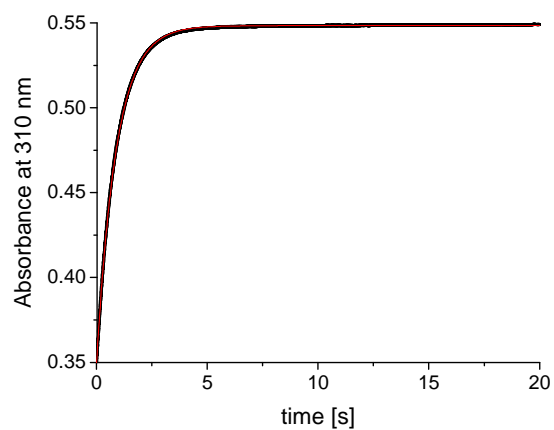


Figure S2. Typical kinetic trace recorded at 310 nm for the reaction between CblOH_2 and NO_2^- to form CblNO_2 . Experimental data – black trace; first-order fit – red trace.

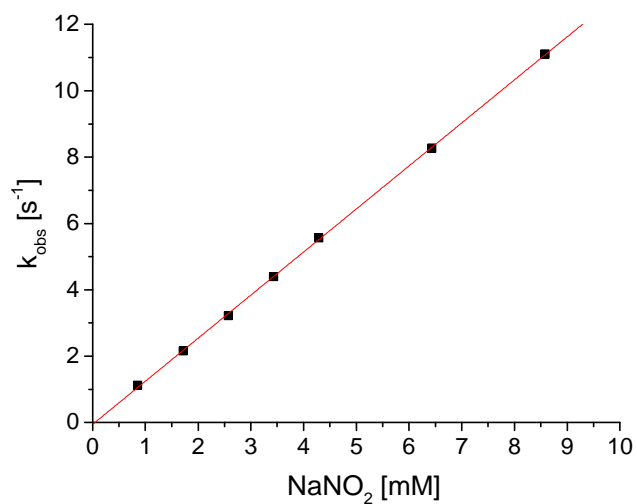


Figure S3. Plot of k_{obs} versus NO_2^- concentration for the reaction between $\text{CbI}(\text{OH})_2$ and NO_2^- . Experimental conditions: 8.6×10^{-5} M $\text{CbI}(\text{OH})_2$, 8.6×10^{-4} - 8.6×10^{-3} M NaNO_2 , pH = 7.2 (25 °C, 0.1 M Tris buffer).

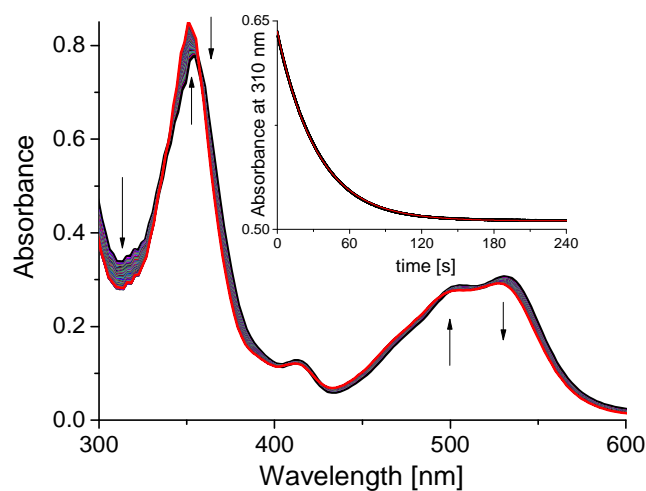


Figure S4. Spectral changes observed for the reaction of CblNO_2 ($4.3 \times 10^{-5} \text{ M}$; obtained by mixing equimolar solutions of CblOH_2 and NO_2^-) with HClO_4 (0.03 M) at 25 °C. Spectra were recorded every 0.375 s. **Inset:** Typical kinetic trace recorded at 310 nm under the same experimental conditions except for CblNO_2 concentration which is $8.6 \times 10^{-5} \text{ M}$.

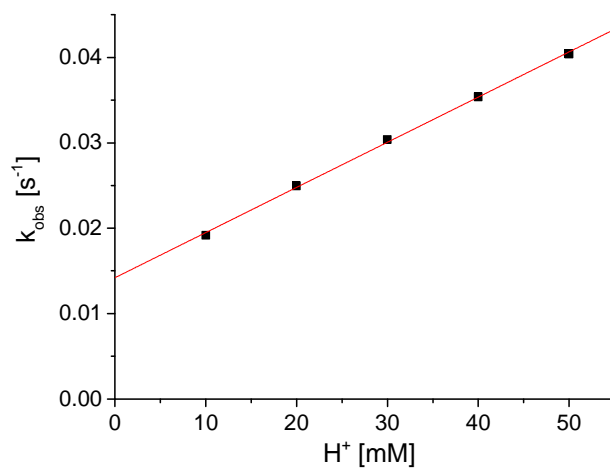


Figure S5. Plot of k_{obs} versus concentration of the acid for the reaction between CblNO_2 and HClO_4 . Experimental conditions: 8.6×10^{-5} M CblOH_2 , 8.6×10^{-5} M NO_2^- , 0.01 – 0.05 M H^+ , 25 °C.

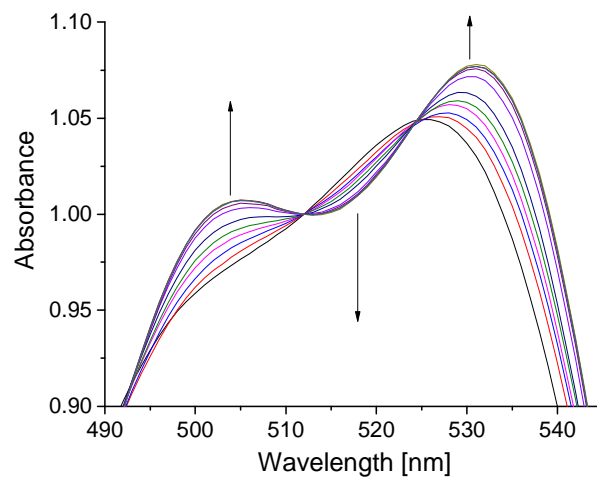


Figure S6. UV-Vis spectra recorded for the formation of CblNO₂ as a function of nitrite concentration, concentration ratio NaNO₂/CblOH₂ = 0.1 – 5.0, at pH = 7.2 and 25 °C.

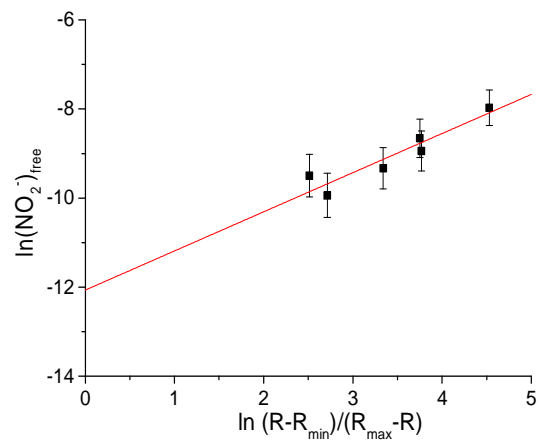


Figure S7. Plot of $\ln(\text{NO}_2^-)_{\text{free}}$ versus $\ln(R-R_{\text{min}})/(R_{\text{max}}-R)$ for the spectra in Figure S6 recorded in the concentration ratio of NaNO_2 and CblOH_2 ranging from 1.5 to 4.0.

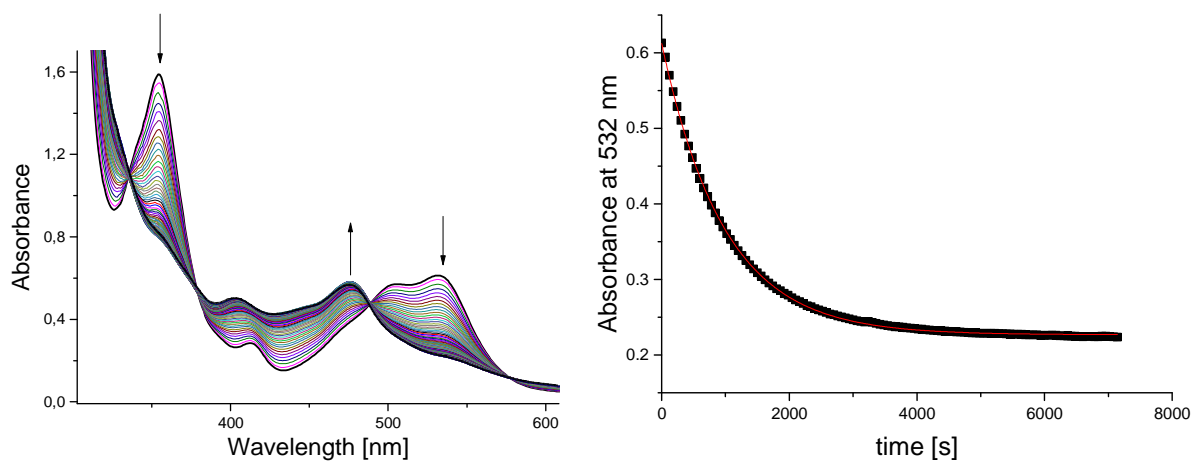


Figure S8. Spectral changes observed for the reaction between CblNO_2 ($7.6 \times 10^{-5} \text{ M}$, obtained by mixing CblOH_2 and NO_2^- , concentration ratio $\text{NO}_2^-/\text{CblOH}_2 = 40$) and Asc ($2.10 \times 10^{-2} \text{ M}$) at $\text{pH} = 7.2$ (25°C , 1.0 M Tris buffer, Ar atmosphere). Spectra were recorded every 2 min. Plot of absorbance at 532 nm versus time.