Electronic Supplementary Material (ESI) for Dalton Transactions.


# Reactions of persulfides with the heme cofactor of oxidized myoglobin and microperoxidase 11: reduction or coordination.

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**Figure S1.** UV-Vis spectra (top) and X-band EPR spectra (bottom) recorded at 10 K of (TMP)FeOH[1] (2 µM in toluene, field modulation amplitude of 0.1 mT, microwave power of 10 mW) before (red) and after (blue) addition of 5 equivalents of tBuSSH,[2] under anaerobic conditions.

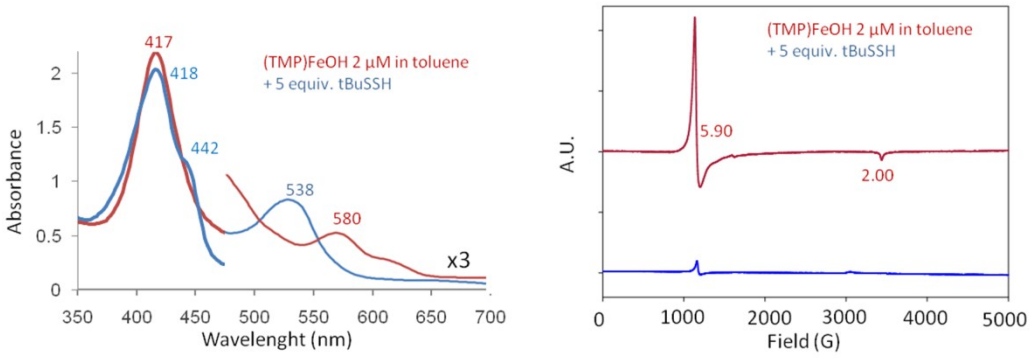



**Figure S2.** Variations of the current intensity recorded over time using the ISO-H2S-2 sensor upon the addition of P* (100 µM), then NAcMP11(III) (3 µM) then $Na_2S$ (2 µM) in HEPES buffer (50 mM, pH 7.4, DTPA 1mM) under anaerobic conditions.

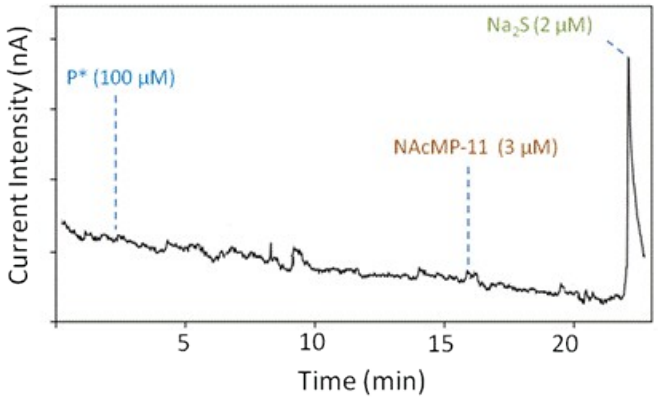


**Figure S3.** High Resolution mass spectrum of a mixture of NAcMP1(III) (20 µM) and P* (500 µM) in 10 mM Tris buffer (pH = 7.4) recorded in ESI+ mode. The deviation from the theoretical mass was calculated with Xcalibur 2.2.

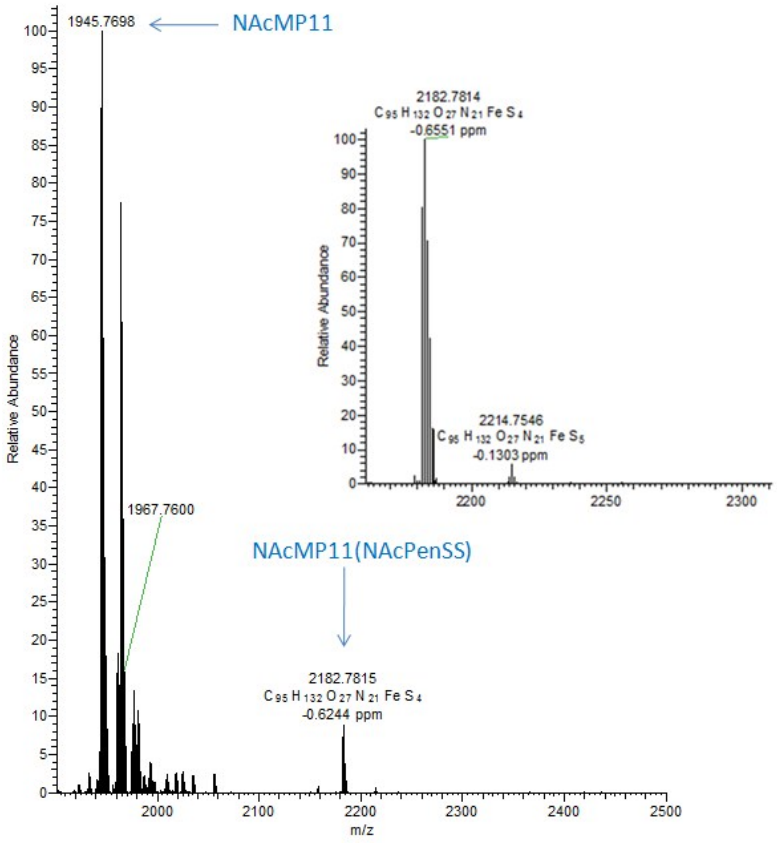



**Figure S4.** UV-Vis spectra recorded after the successive additions of 20 µM dithionite (green), 100 µM of P* (blue) and 10 mM NMI (cyan) to a solution of NAcMP11(III) (2 µM) (red) in HEPES buffer (50 mM, pH 7.4, DTPA 1mM) under anaerobic conditions.

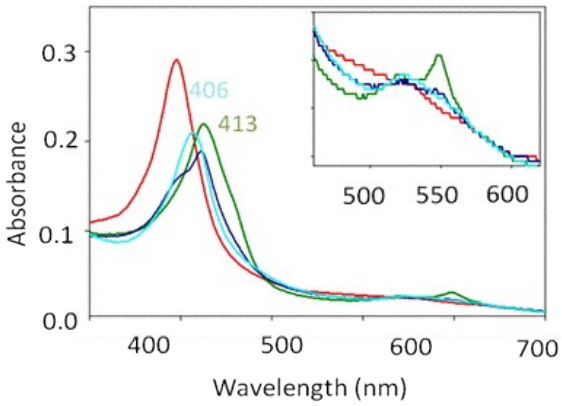


**Figure S5.** UV-vis spectra of metMb(III) (3.5 µM) before (red) and after (green) reactivity for 15 min with GSSH generated from 2.5 mM GSH and 0.5 mM $PhSO_2SNa$ in HEPES buffer (50 mM, pH 7.4, DTPA 1mM) under aerobic conditions.

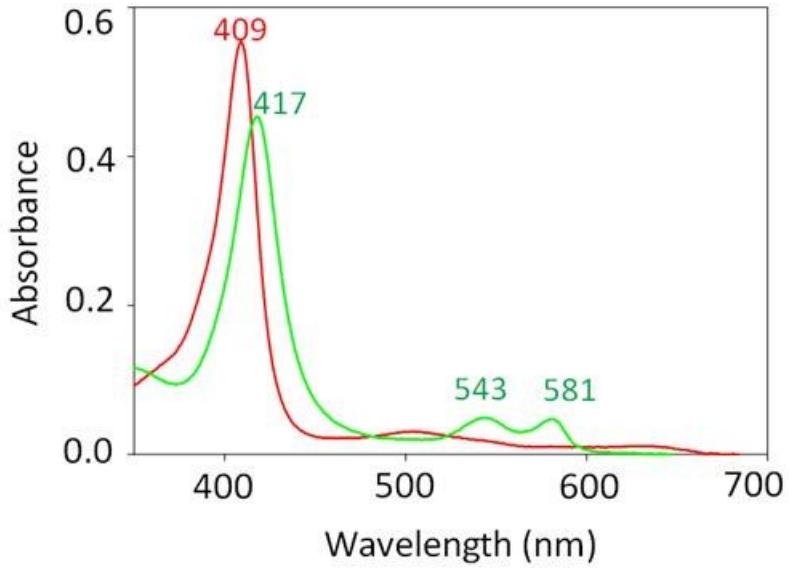



**Figure S6 .** Evolution of the UV-vis spectrum of the product initially formed by the reaction between metMb(III) (3.5 µM) and P* (100 µM) (red trace), and 15 minutes after addition of D-glucose (20 mM), glucose oxidase (100 U) and catalase (1000U) in HEPES buffer (50 mM, pH 7.4, DTPA 1mM) (green trace).

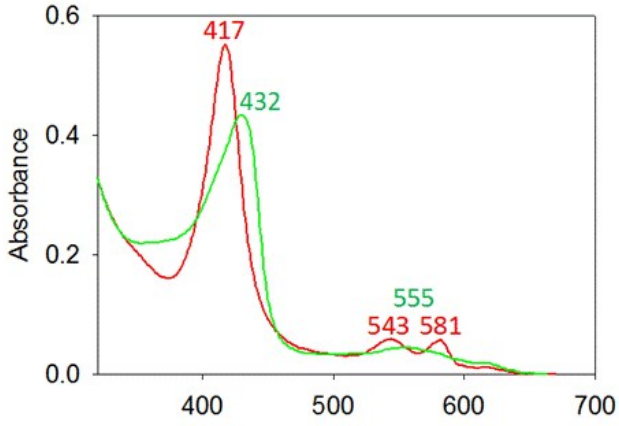


**Figure S7.** Representative experiments showing the variation of absorbance over time when metMb(III) (3.5 µM) is allowed to react with P* (50 µM) under anaerobic (A, formation of deoxyMb(II) recorded at 433 nm) or aerobic (B, formation of oxyMb(II) recorded at 581 nm) conditions. The data were fitted with an exponential function ($A(t) = y0 + a.(1-\exp^{(-k \times t)})$) and the resulting parameters are reported on the plots.

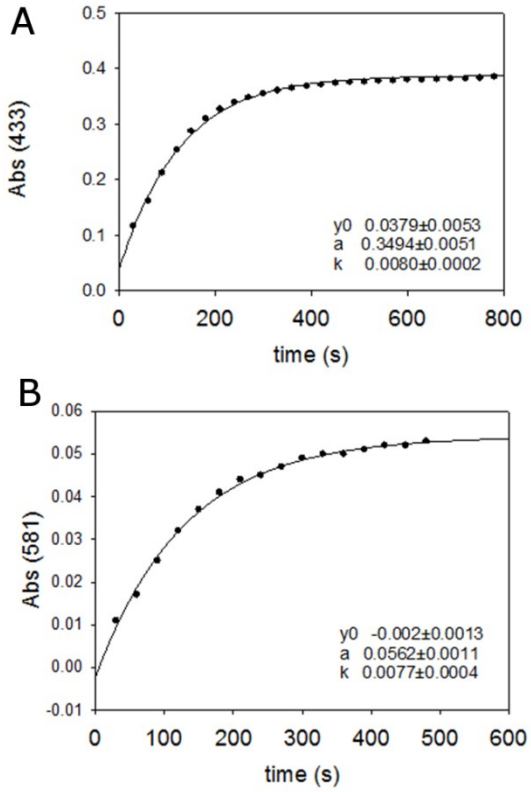


**Figure S8.** HPLC-MS spectra of the mixture obtained after the incubation of P* (100 µM) alone (left panel) or in the presence of 50 µM FerrylMb(IV) (right panel) in Tris buffer (10 mM, pH 7.4) for 30 minutes.

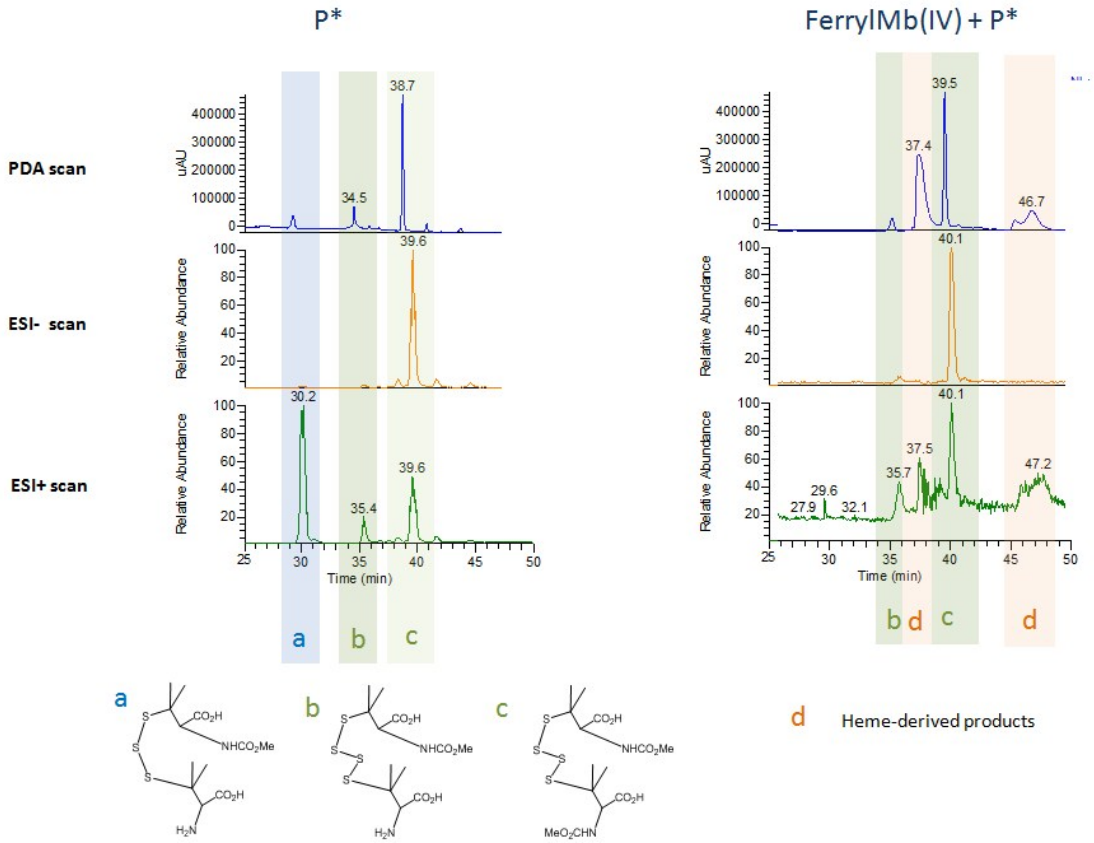



**Figure S9.** Zoom of the visible region (500-700 nm) of the UV-vis spectra obtained after the addition of 200 µM of P* to ferrylMb(IV) (2 µM) in the presence (red trace) or absence (blue trace) of catalase.

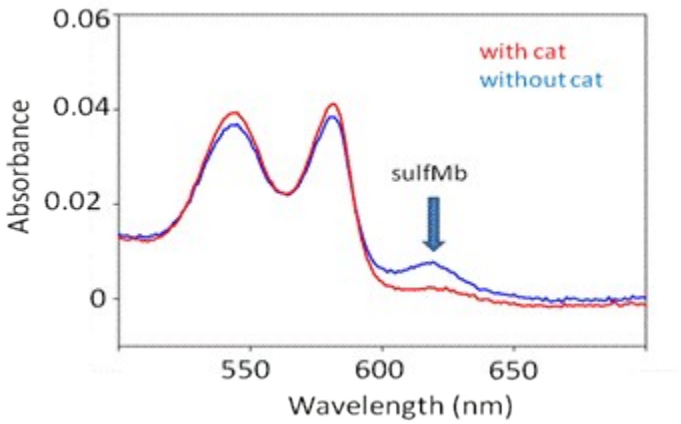
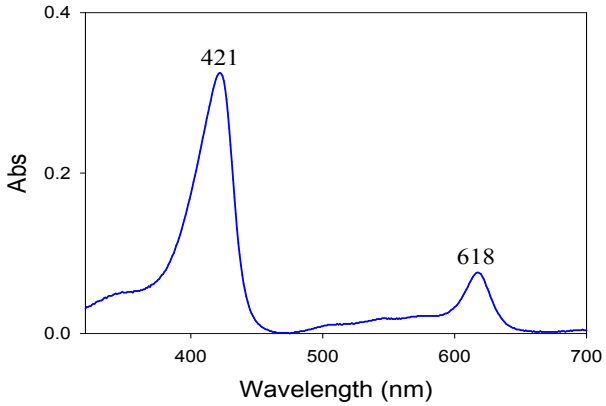



**Figure S10.** UV-Vis spectrum of the product obtained after mixing FerrylMb(IV) (2 µM) with $Na_2S$ (2 µM) in HEPES buffer (50 mM, pH 7.4, DTPA 1mM) under anaerobic conditions.



Supplementary references:

(1) Cheng, R. J.; Latosgrazynski, L.; Balch, A. L., Preparation and Characterization of Some Hydroxy Complexes of Iron(Iii) Porphyrins *Inorg. Chem.* **1982,***21* (6), 2412-2418.
(2) Derbesy, G.; Harpp, D. N.; Rather, B.; Carroll, G., Preparation and characterization of tert-butyl hydrodisulfide *Sulfur Lett.* **1992,***14* (4), 199-204.