

Supporting Information

REACTIVITY OF INORGANIC SULFIDE SPECIES TOWARD A HEME PROTEIN MODEL.

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Figure S1 - QM optimization at PBE 6-31G** DFT level were performed on a ferric low-spin hexacoordinated core-porphyrinate, with both an imidazole ring and SH^- as 5th and 6th ligand. An N-methyl acetamide molecule was used to provide a counterpart for hydrogen bonding to the imidazole ligand. Also, a control calculation (full-optimization at the same level of theory) was performed in the absence of N-methyl acetamide. Mülliken charge populations were computed for the optimized structures.

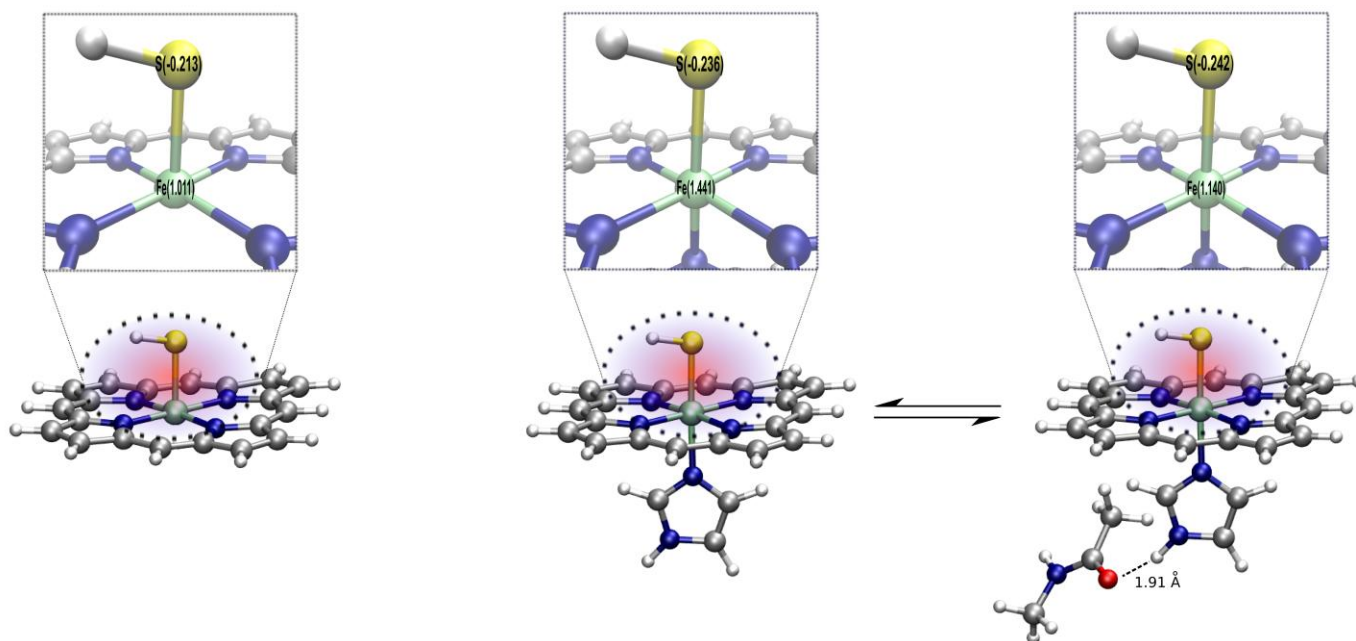


Figure S2 – Absorption spectra of 2.6×10^{-6} M Fe^{III} NACMP11 in the absence (dashed line) and in the presence (continuous line) of 4.5 mM cysteine. The optical path was 1 mm.

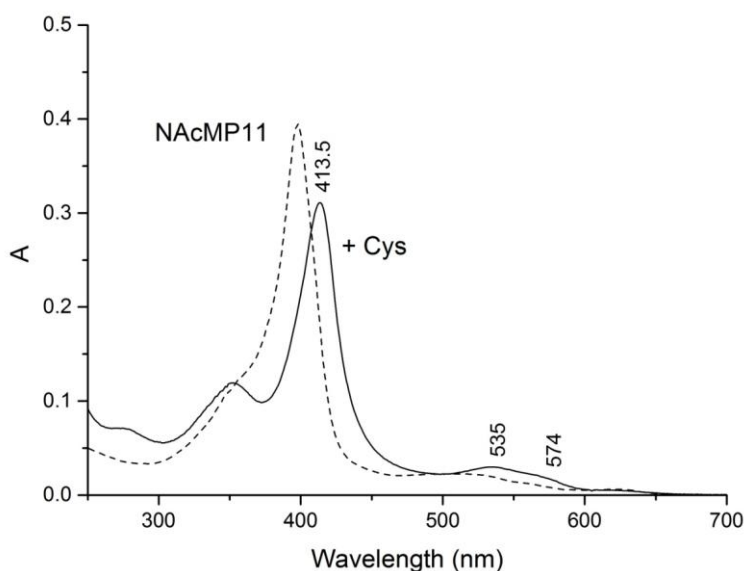


Figure S3A - Reactivity of the NAcMP11Fe^{III}-S(sulfide) toward 1-methylimidazole. **A:** 1) [Fe^{III}NAcMP11]= 5x10⁻⁶M, pH 6.8 (PO₄³⁻, 0.1M, 2.5mL, black line), 2) 10 μL 1-methylimidazole (red line), 3) 100μL H₂S (g) (blue line). The reaction of Fe^{III}NAcMP11 with 1-methylimidazole led to the formation of a [NAcMP11Fe^{III} (Imid)(His)] complex, with λ_{max}= 406 nm, at pH 6.8. This complex was indifferent to the addition of H₂S (g). **B:** 1) [Fe^{III}NAcMP11]= 5x10⁻⁶M, pH 6.8 (PO₄³⁻, 0.1M, 2.5mL, black line), 2) 100μL H₂S (g) (red line), 3) 10 μL 1-methylimidazole (blue line). The samples were deaerated under stream of argon, in quartz cuvettes (1 cm) with silicon septa prior to the addition of the reagent. The addition of 1-methylimidazole after the addition of H₂S shows the conversion of the 414 nm complex to the [NAcMP11Fe^{III} (1-MeIm)(His)], without modification of the Fe^{III} redox state in the process. Reagents are numbered according the order of addition to the solution in each experiment.

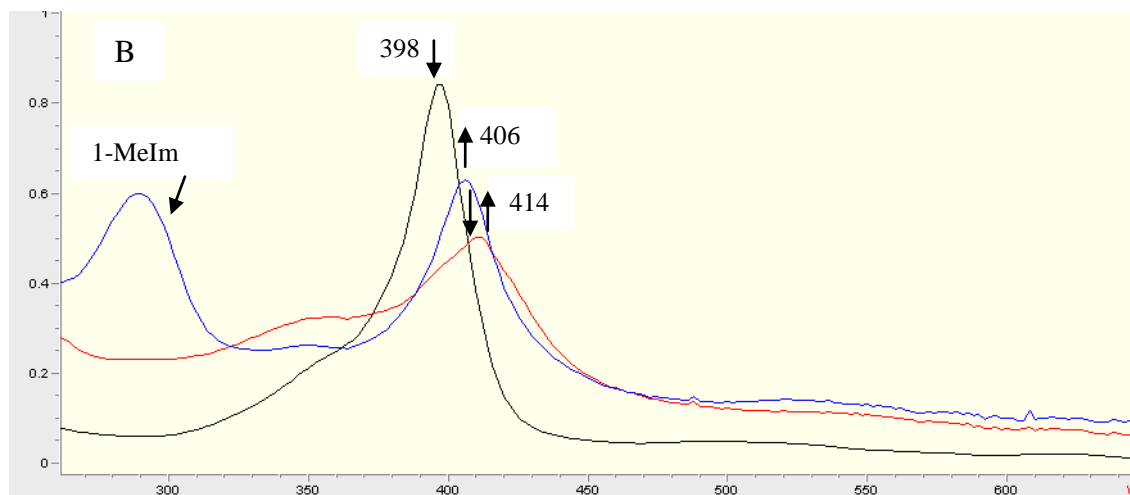
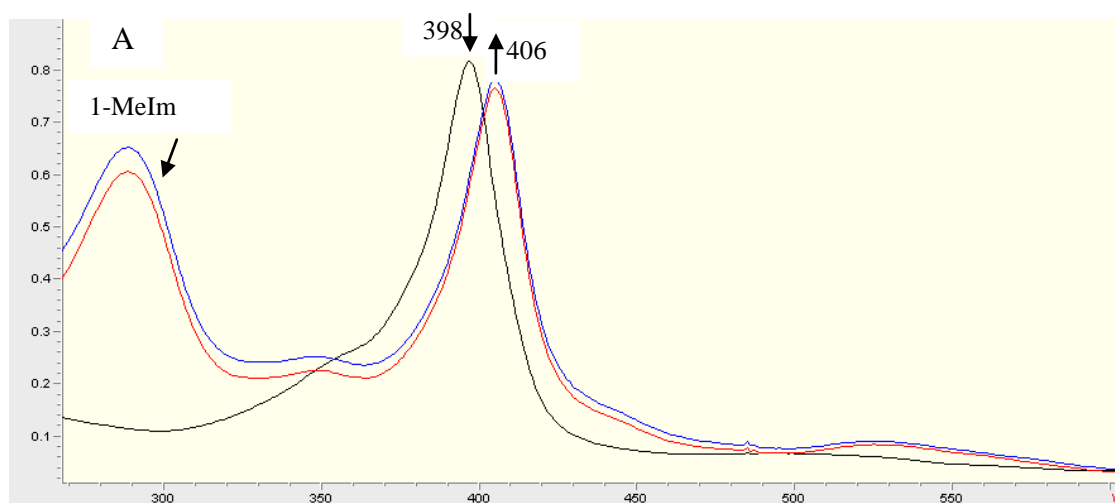
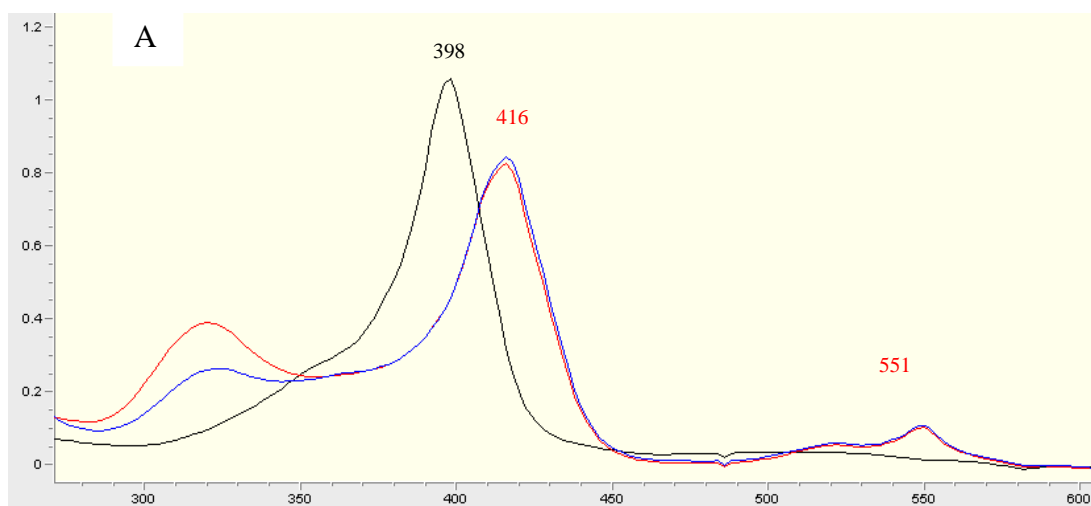
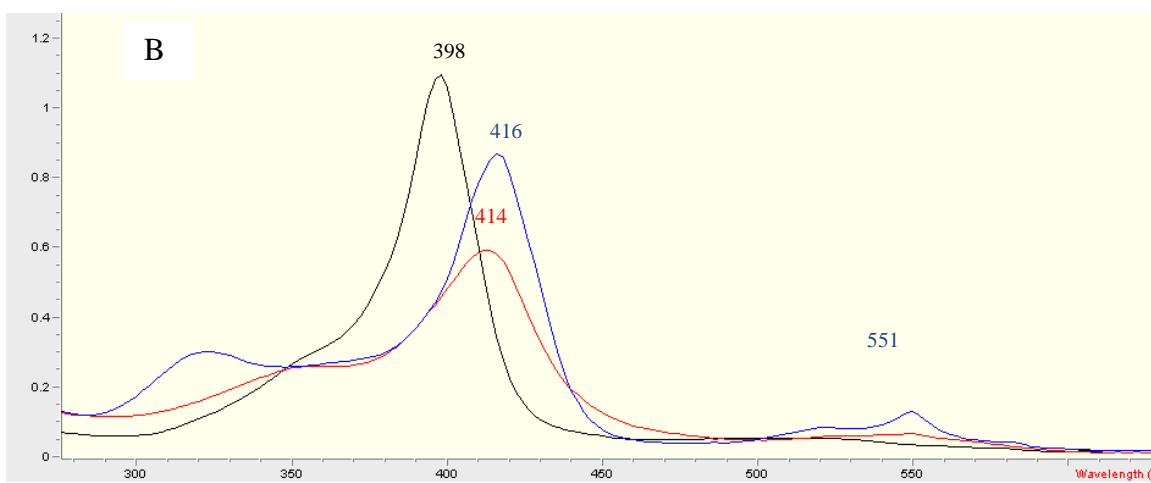


Figure S3B - Reactivity of the NAcMP11Fe^{III}-S(sulfide) toward the addition of dithionite. **A:** 1) [Fe^{III}NAcMP11]= 7x10⁻⁶M, pH 6.8 (PO₄³⁻, 0.1M, 2.5mL) (black line), 2) [S₂O₄²⁻]_{final conc}= 0.15mM (red line), 3) 200μL H₂S (g) (blue line). The Fe^{II}NAcMP11 is indifferent to the addition of H₂S (g). **B:** 1) [Fe^{III}NAcMP11]= 7x10⁻⁶M, pH 6.8 (PO₄³⁻, 0.1M, 2.5mL) (black line), 2) 200μL H₂S (g) (red line), 3) [S₂O₄²⁻]_{final conc}= 0.15M (blue line). The samples were deaerated under stream of argon, in quartz cuvettes (1 cm) with silicon septa prior to the addition of the reagent. The NAcMP11Fe^{III}-S(sulfide) reacts with sodium dithionite and yields the Fe^{II}NAcMP11 form. Reagents are numbered according the order of addition to the solution in each experiment.



1) [Fe^{III}NAcMP11]= 7x10⁻⁶M, pH 6.8 (PO₄³⁻ buffer, 0.1M, 2.5 mL) , 2) [S₂O₄²⁻]_{final conc}= 0.15M, 3) 200μL H₂S(g)



1) [Fe^{III}NAcMP11]= 7x10⁻⁶M, pH 6.8 (PO₄³⁻ buffer, 0.1M, 2.5 mL), 2) 200μL H₂S(g), 3) [S₂O₄²⁻]_{final conc}= 0.15M

Figure S4 - (middle trace) RR spectra of 2.6×10^{-5} M NAcMP11 with 4.5 mM cysteine, in comparison with the RR spectra of unbound and sulfide-bound ferric NAcMP11. The intensities are normalized to the intensity of the ν_4 band at $1372\text{--}1373\text{ cm}^{-1}$. The low-frequency region of the cysteine complex is expanded to allow for a better visualization. Experimental conditions: 413.1 nm excitation wavelength, 3 mW power, 1.2 cm^{-1} spectral resolution; low-frequency range: 30 min integration time; high-frequency range: 30 min (NAcMP11), 10 min (+ cysteine), 6 min (+ H_2S) integration time.

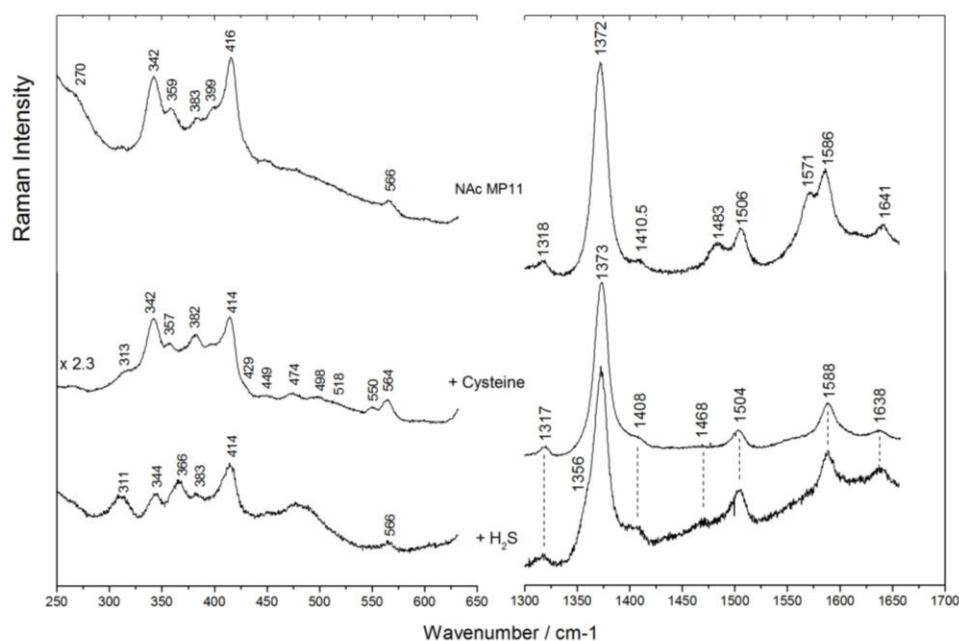
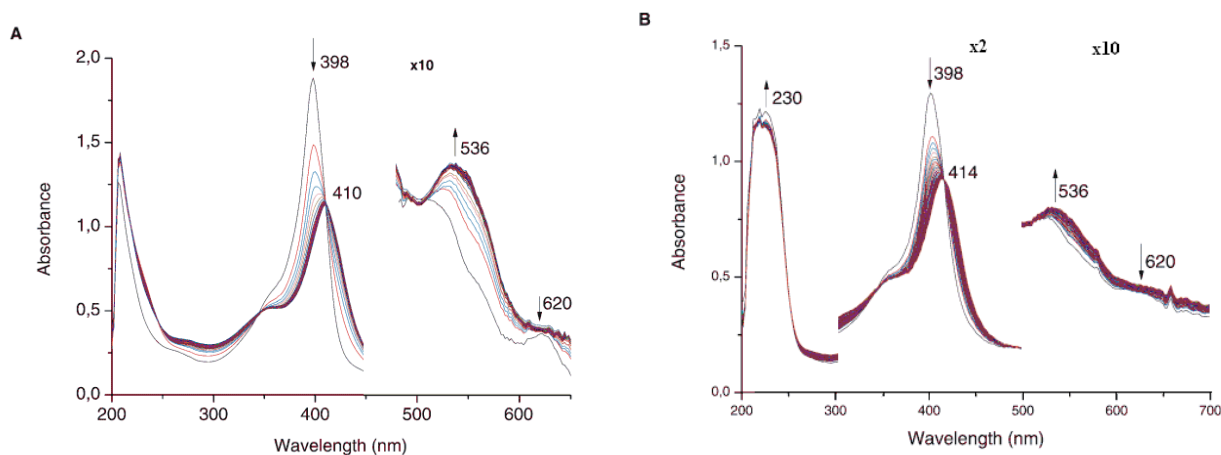
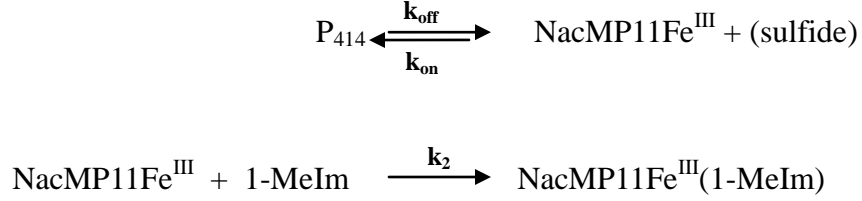


Figure S5. UV-Vis spectra of the Fe^{III} NAcMP11 toward Na_2S (anhydrous) solution. A) $[\text{Fe}^{\text{III}}\text{NAcMP11}] = [\text{Na}_2\text{S}(\text{anhydrous})] = 1.2 \times 10^{-5}\text{ M}$; B) $[\text{Fe}^{\text{III}}\text{NAcMP11}] = 8 \times 10^{-6}\text{ M}$, $[\text{Na}_2\text{S}(\text{anhydrous})] = 8 \times 10^{-4}\text{ M}$. Both reactions at pH 6.8; buffer PO_4^{3-} , 0.1M, 25°C .



S6. Dissociation kinetic constant

By assuming the following reaction scheme



Expressing the reaction rate as

$$v = v_2 = k_2 \cdot [\text{NacMP11Fe}^{\text{III}}] \cdot [1\text{-MeIm}] = \frac{\partial [\text{NacMP11Fe}^{\text{III}}(1\text{-MeIm})]}{\partial t}$$

and assuming steady-state for $[\text{NacMP11Fe}^{\text{III}}]$ the following relationship is obtained:

$$k_{\text{off}} \cdot [\text{P}_{414}] = k_{\text{on}} \cdot [\text{NacMP11Fe}^{\text{III}}] \cdot [\text{sulfide}] + k_2 \cdot [\text{NacMP11Fe}^{\text{III}}] \cdot [1\text{-MeIm}]$$

Thus, the reaction rate can be expressed as a function of the reactants

$$v = \frac{\partial [\text{NacMP11Fe}^{\text{III}}(1\text{-MeIm})]}{\partial t} = \frac{k_2 \cdot k_{\text{off}} \cdot [\text{P}_{414}] \cdot [1\text{-MeIm}]}{k_{\text{on}} \cdot [\text{sulfide}] + k_2 \cdot [1\text{-MeIm}]}$$

The previous expression can be simplified as follows:

$$\begin{array}{c}
 v = \frac{\partial [\text{NacMP11Fe}^{\text{III}}(1\text{-MeIm})]}{\partial t} = k_{\text{obs}} \cdot [\text{P}_{414}] \\
 \\
 \text{with } k_{\text{obs}} = \frac{k_2 \cdot k_{\text{off}} \cdot [1\text{-MeIm}]}{k_{\text{on}} \cdot [\text{sulfide}] + k_2 \cdot [1\text{-MeIm}]}
 \end{array}$$

At high concentration of $[1\text{-MeIm}]$, k_{obs} becomes independent of $[1\text{-MeIm}]$, and the following equivalence is derived:

$$k_{\text{obs}} = k_{\text{off}}$$

