Supporting information: Delving into the Magnetic, Electronic and Geometrical parameters of P450-I and CPO-I.

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S1 Active Space: Orbitals used

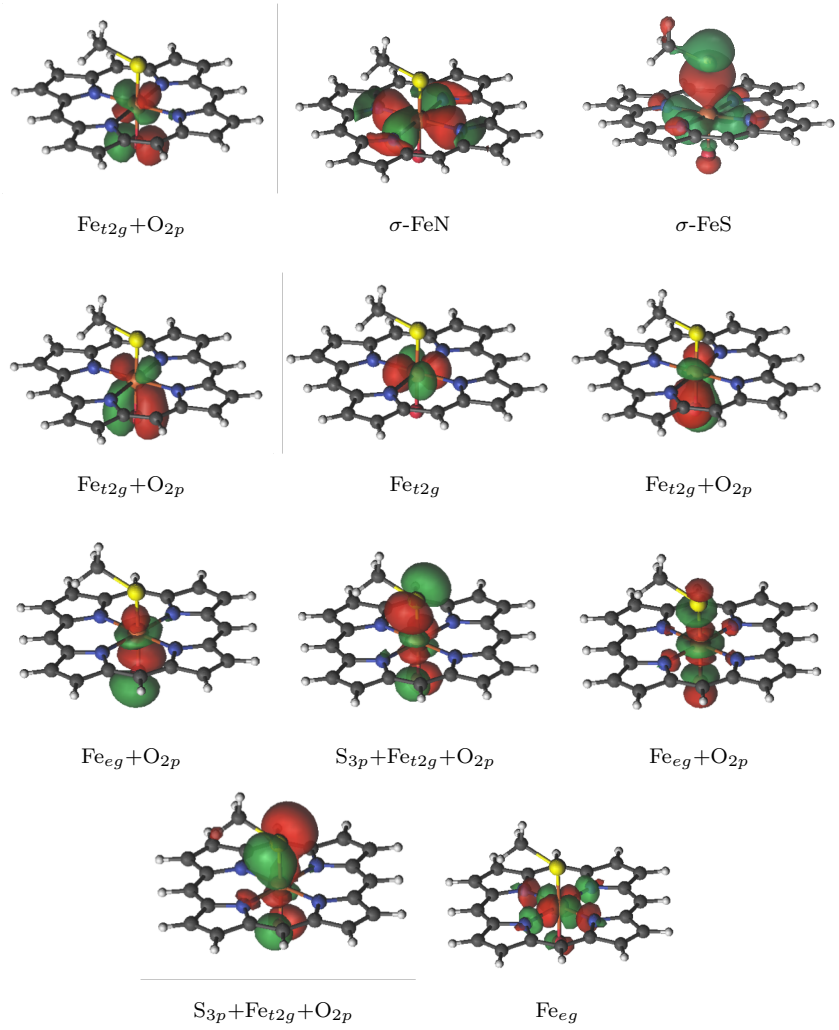
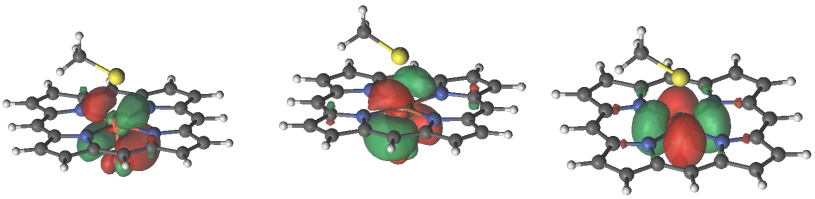
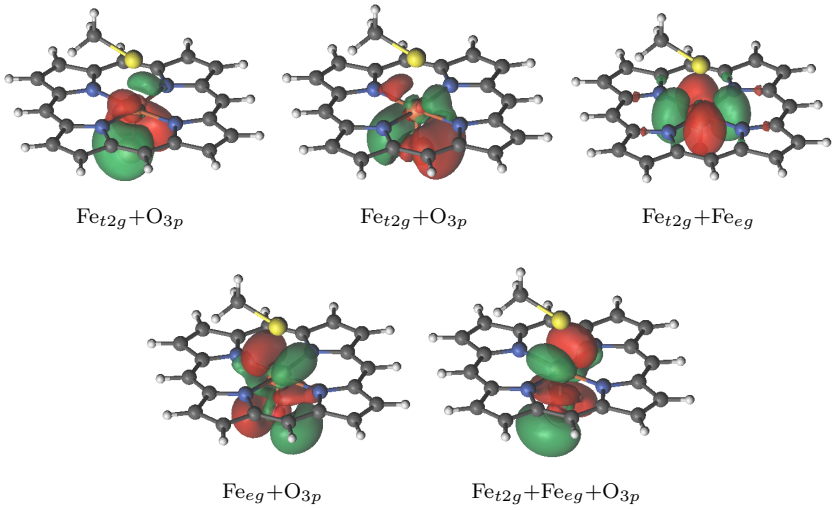


Figure S1.1: Minimum active space used, CAS(15,11).



Fe_{t2g} Fe_{t2g} Fe_{t2g}

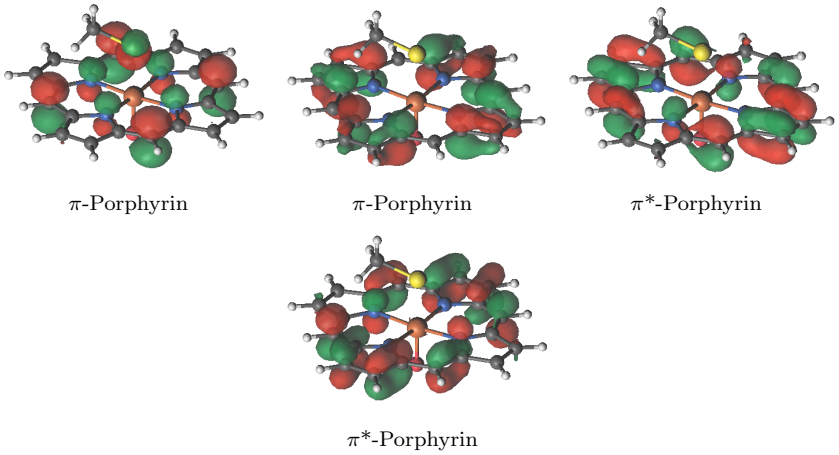
Figure S1.2: Inclusion of the Fe3d' orbitals, CAS(15,14).



Fe_{t2g}+O_{3p} Fe_{t2g}+O_{3p} Fe_{t2g}+Fe_{eg}

Fe_{eg}+O_{3p} Fe_{t2g}+Fe_{eg}+O_{3p}

Figure S1.3: Inclusion of the Fe3d' orbitals, CAS(15,16).



π-Porphyrin π-Porphyrin π*-Porphyrin

π*-Porphyrin

Figure S1.4: Inclusion of the π orbitals of the porphyrin, CAS(19,20).

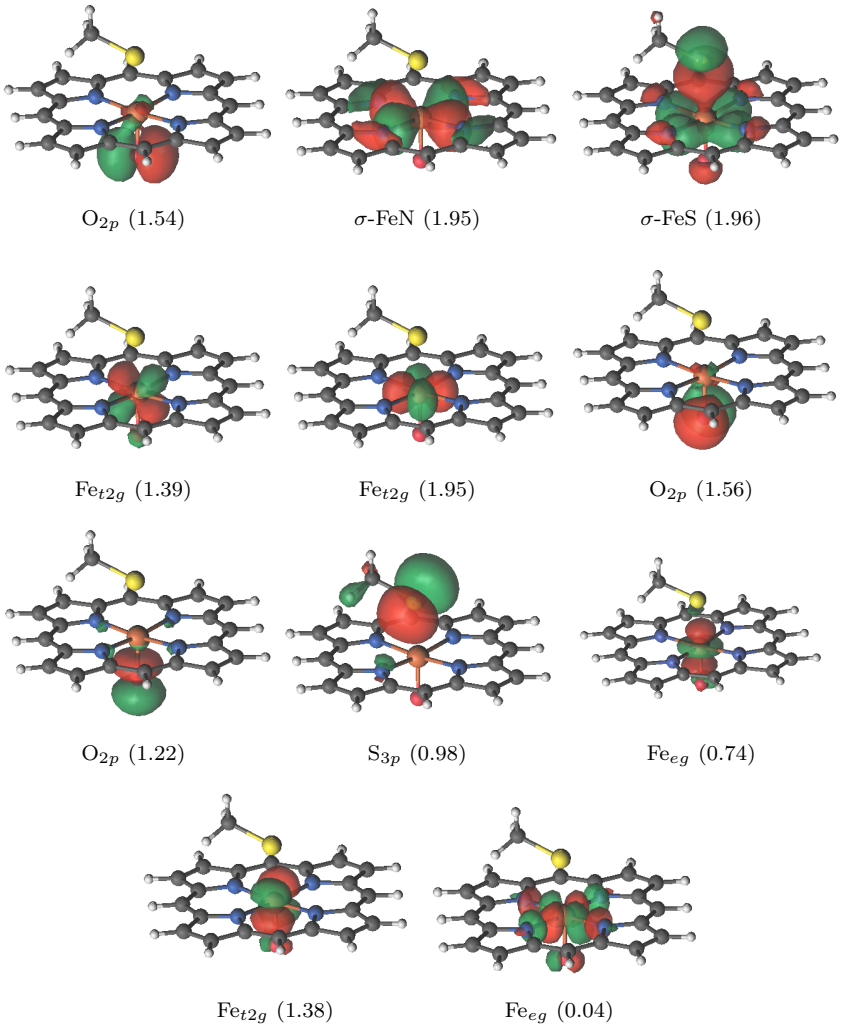


Figure S1.5: Localized orbitals of CAS(15,11) with the QGROT program. The natural occupation of the orbitals is shown in parenthesis. The quasi-XRAY structure has been used in this analysis.

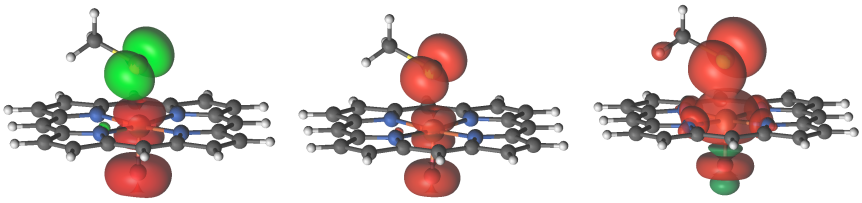


Figure S1.6: CASSCF spin density representation of the LS, IS and HS over the *o* point (corresponding to the P450-I geometry).

S2 Additional CASPT2 PES

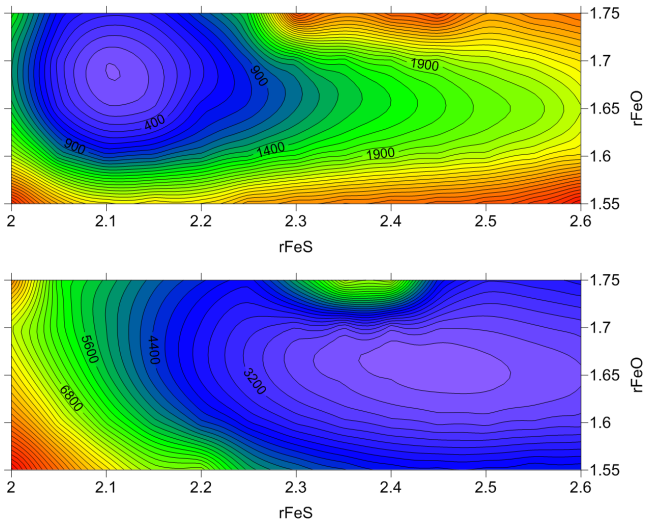


Figure S2.1: DFT/CASPT2 potential energy surface as function of the Fe-S and Fe-O distances (Å) of the lowest electronic doublet state of CAS(15,11) (top) and the lowest electronic quartet state of CAS(15,11). Energies (in cm^{-1}) are relative to the total energy of the LS minimum.

S3 Equations used

Model Hamiltonian for DDCI:

- $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B + D\left(\hat{S}^2_{z,A} - \frac{1}{3}\hat{S}^2_A\right)$
- $J^{SF} = \frac{2}{3}(E_{LS} - E_{IS})$

Model Hamiltonian for Broken Symmetry:

- $\hat{H} = -2 \cdot J\hat{S}_A \cdot \hat{S}_B$
- $J^{SF}_{BS} = \frac{2(E_{BS}-E_{IS})}{<S^2_{IS}>-<S^2_{BS}>}$

Basis functions $|S, M_S\rangle$:

- $|\frac{3}{2}, \frac{3}{2}\rangle = |Q_1\rangle = |\alpha\alpha\alpha\rangle$
- $|\frac{3}{2}, \frac{1}{2}\rangle = |Q_2\rangle = \left(|\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha\rangle\right)/\sqrt{3}$

- $|\frac{1}{2},\frac{1}{2}\rangle = |D\rangle = \left(|2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha\rangle\right)/\sqrt{6}$

Matrix representation of $\hat{H}$

$$\begin{array}{cccc} & |Q_1\rangle & |Q_2\rangle & |D\rangle \\ |Q_1\rangle & -\frac{1}{2}J + \frac{1}{3}D & 0 & 0 \\ |Q_2\rangle & 0 & -\frac{1}{2}J - \frac{1}{3}D & \frac{\sqrt{2}}{3}D \\ |D\rangle & 0 & \frac{\sqrt{2}}{3}D & J \end{array} \tag{1}$$