Supporting Information

for

Isocyanide or Nitrosyl Complexation to Hemes with Varying Tethered Axial Base Ligand Donors: Synthesis and Characterization

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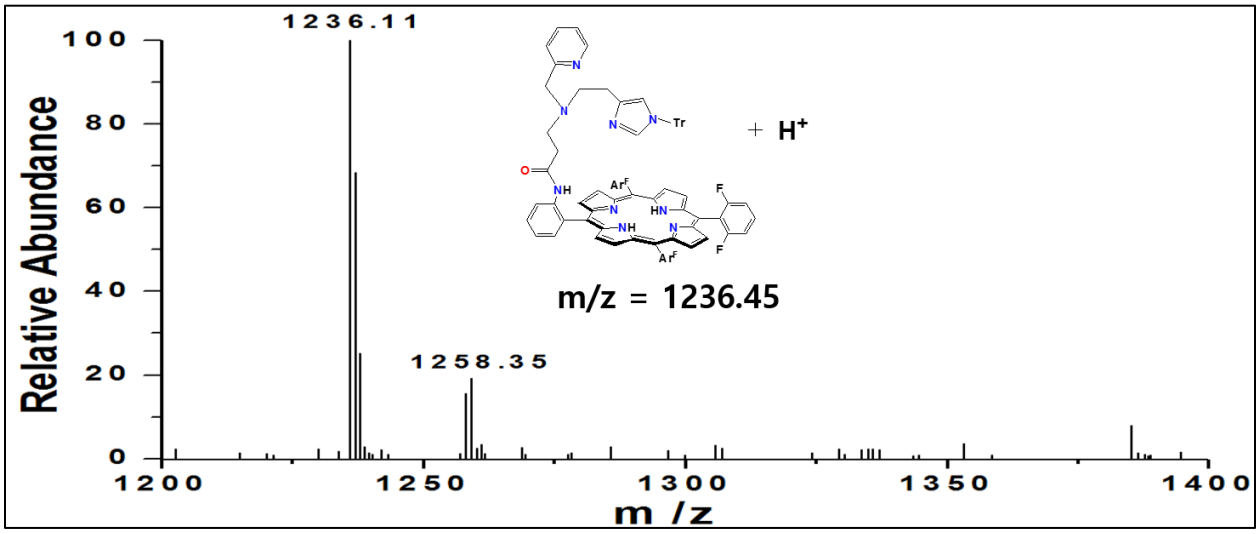

Fig. S1. ESI-MS of the porphyrin ligand P^{ImTr}, corresponding to $M+H^+$ and $M+Na^+$ (1258.35) in CH_2Cl_2 at 293 K.

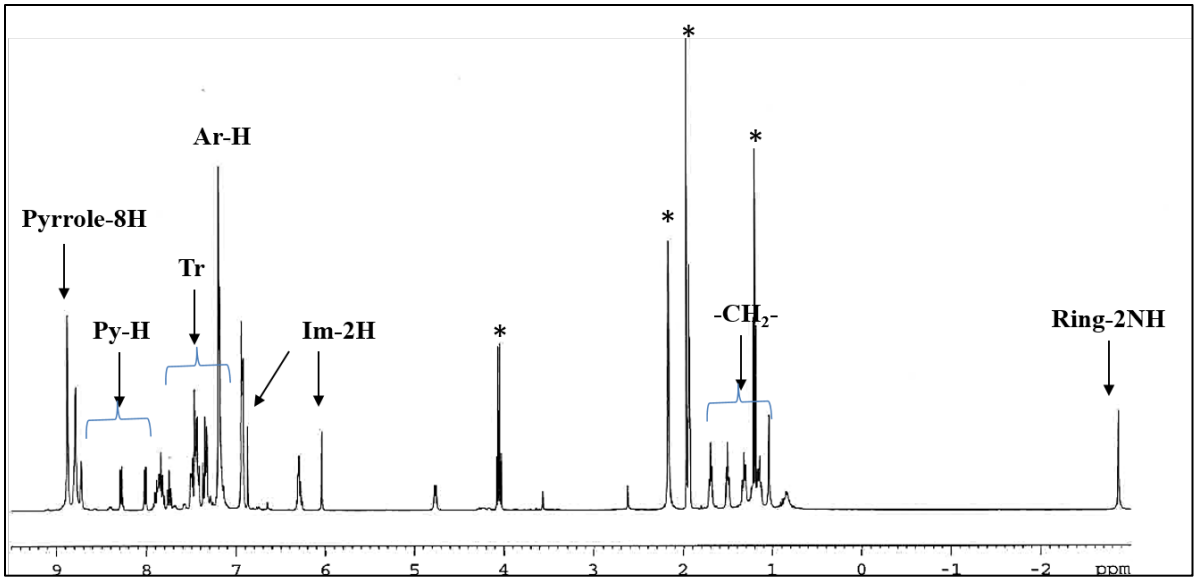

Fig. S2. ^{1}H-NMR spectra of covalently linked histamine containing porphyrin P^{ImTr} in CD_3CN at 293 K. (*) corresponds to solvent molecules, residual NMR solvent CH_3CN and ethyl acetate (used as an eluent for column chromatography.

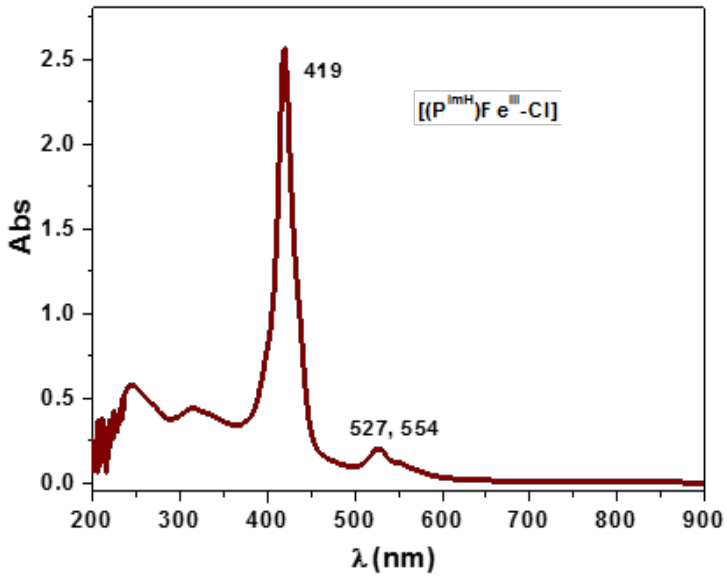

Fig. S3. UV-Vis spectra of heme iron(III) porphyrin, $[(P^{ImH})Fe^{III}\text{-}Cl]$ complex in CH_2Cl_2 at 293 K.

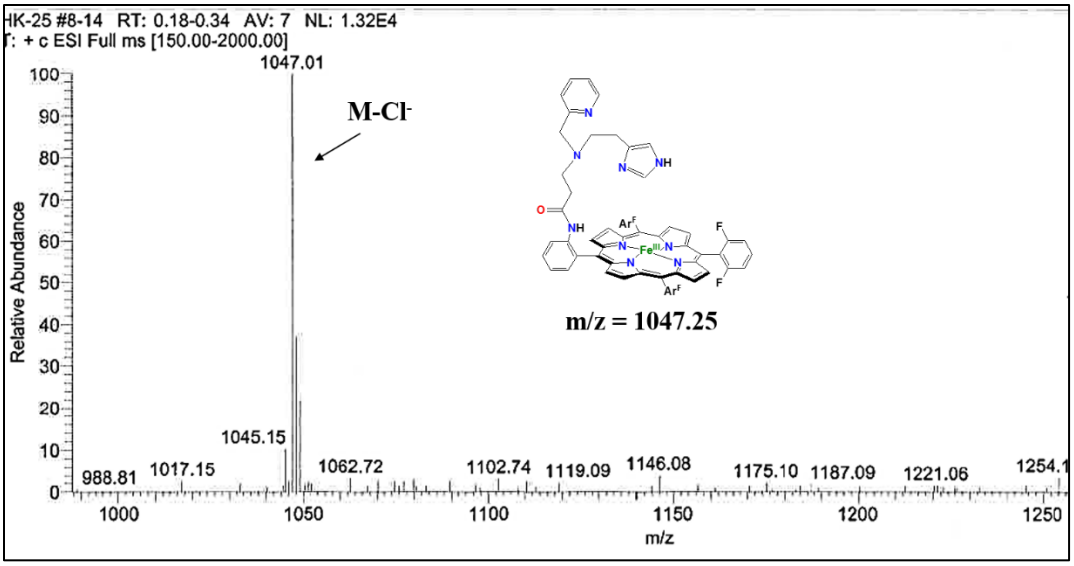

Fig. S4. ESI-MS of [(P^{ImH})Fe^{III}-Cl] in CH_2Cl_2 at 293 K; the peak at 1047.01 corresponds to M-Cl^-.

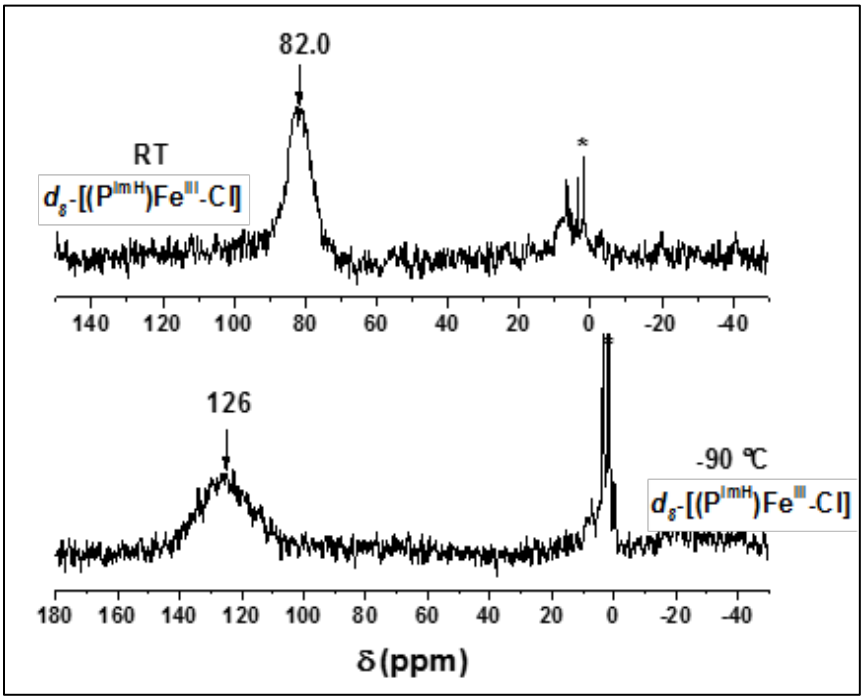

Fig. S5. (top) ^{2}H-NMR spectra of heme iron(III) complex d_8-[(P^{ImH})Fe^{III}-Cl] in THF ($\delta_{pyrrole}$ = 82.0 ppm) at 293 K. (bottom) ^{2}H-NMR spectra of heme iron(III) complex d_8-[(P^{ImH})Fe^{III}-Cl] in THF ($\delta_{pyrrole}$ = 126 ppm) at 183 K. (*) corresponds to solvent molecule THF.

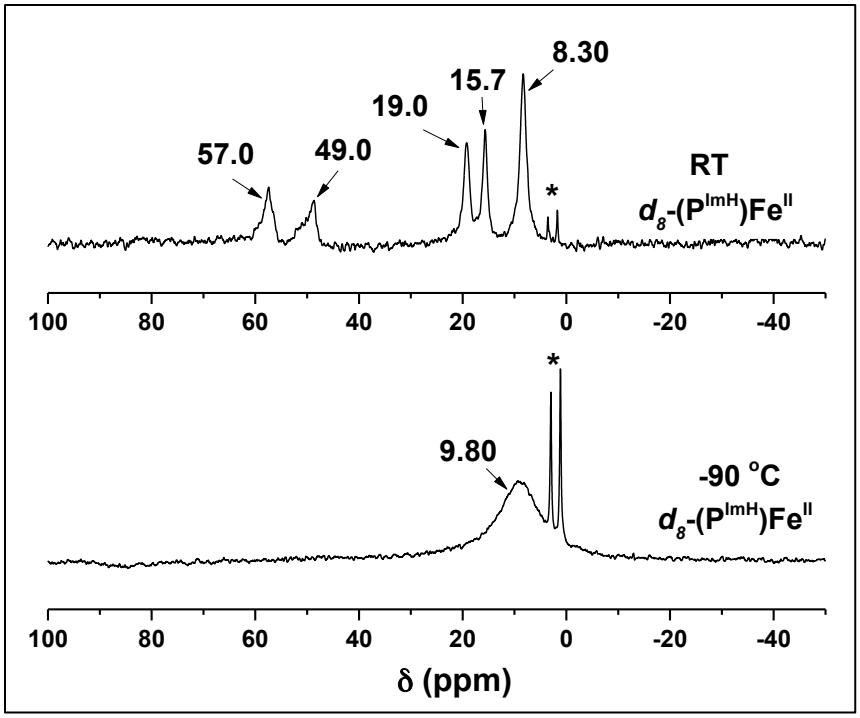

Fig. S6. (top) ^{2}H-NMR spectra of heme iron(II) complex d_8-[(P^{ImH})Fe^{II}] in THF ($\delta_{pyrrole}$ = 57.0, 49.0, 19.0, 15.7, 8.30 ppm) at 293 K, (ratio of pyrrole-H is 1:1:2:4). (bottom) ^{2}H-NMR spectra of heme iron(II) complex d_8-[(P^{ImH})Fe^{II}] in THF ($\delta_{pyrrole}$ = 9.80 ppm) at 183 K. See main text for detail. (*) corresponds to solvent molecule THF.

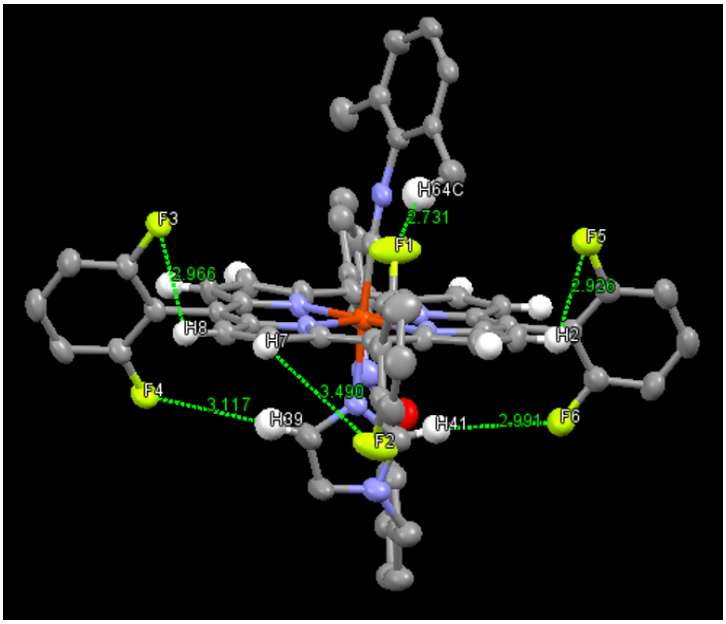

Fig. S7. Crystal structure of (**3**)-DIMPI, showing weak intramolecular CH…F interactions identified by the dotted green lines. See main text for detailed discussion.

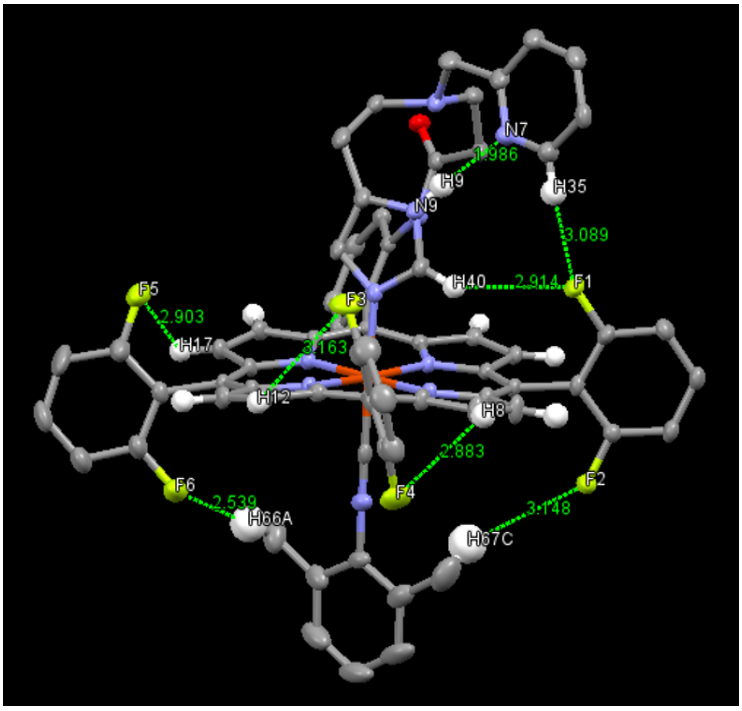

Fig. S8. Crystal structure of (**4**)-DIMPI, showing weak intramolecular CH…F interaction identified by the dotted green lines. See main text for detailed discussion.

UV-vis Spectral Titrations for (P)Fe^{II} + DIMPI. To a solution of (P)Fe^{II} (12 μM, THF; P = P^{Py}, P^{Im}, P^{ImH}) was added 0.1 – 2.5 equiv of DIMPI in 0.1 equiv increments from a stock solution in THF. UV-vis spectrum was taken after each addition of DIMPI, showing isosbestic conversion of (P)Fe^{II} to (P)Fe^{II}-DIMPI. The reaction mixture was allowed to equilibrate fully until no further spectral change was observed prior to the next equivalent of DIMPI. A plot of the change in absorbance at 430 nm vs DIMPI resulted in the binding curve shown in Fig. S9 – S11 and could be well fit by a 1:1 binding model, eq 1–4. Using this equation, the best fit of the plot for P^{Py}, P^{Im} and P^{ImH} system gives K_a = 2.29 x 10^7 M^{-1}, 1.19 x 10^7 M^{-1} and 1.29 x 10^7 M^{-1}.

$$(P)Fe^{II} + DIMPI \rightleftharpoons (P)Fe^{II}\text{-}DIMPI \qquad (P) = P^{Py}, P^{Im}, P^{ImH} \qquad (1)$$

$$K_a = \frac{[(P)Fe^{II}\text{-}DIMPI]}{[(P)Fe^{II}][DIMPI]} \qquad (2)$$

$$\frac{(A - A_0)}{(\varepsilon_{FeII\text{-}DIMPI} - \varepsilon_{FeII})} = [(P)Fe^{II}\text{-}DIMPI] \qquad (3)$$

$$[(P)Fe^{II}\text{-}DIMPI] = \frac{1}{2}\left[\left\{[DIMPI] + [(P)Fe^{II}]_i + \left(\frac{1}{Ka}\right)\right\} - \sqrt{\left([DIMPI] + [(P)Fe^{II}]_i + \left(\frac{1}{Ka}\right)\right)^2 - 4\,[DIMPI][(P)Fe^{II}]_i}\right] \qquad (4)$$

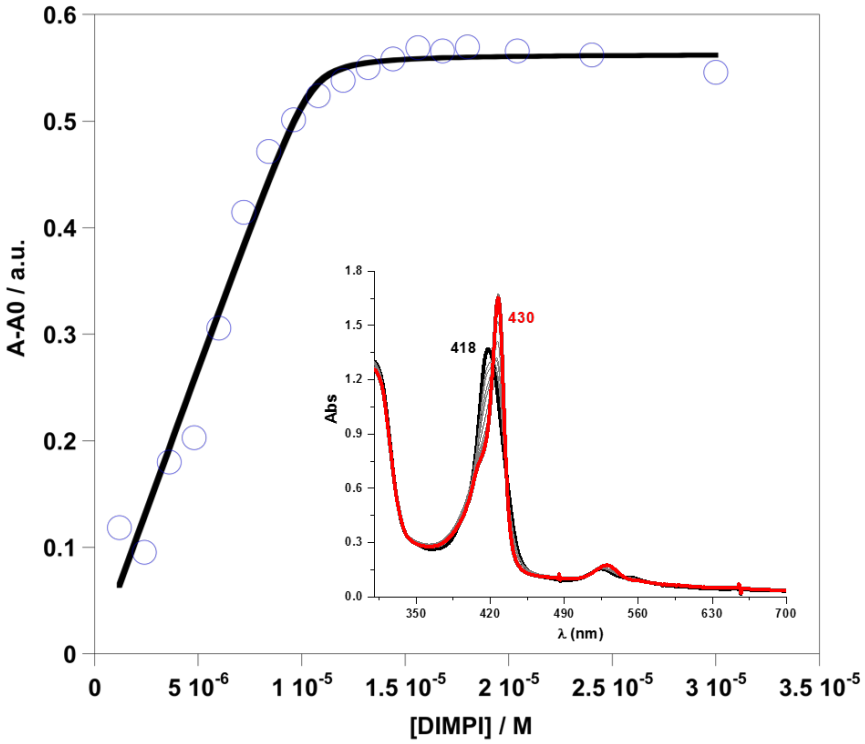

Fig. S9. Binding isotherm at 430 nm resulting from the reaction of $(P^{Py})Fe^{II}$ (12 μM in 2.5 mL Tetrahydrofuran, THF, black) and DIMPI (red, $(P^{Py})Fe^{II}$-DIMPI). $K_a = 2.29 \times 10^7\ M^{-1}$ See main text for detailed discussion.

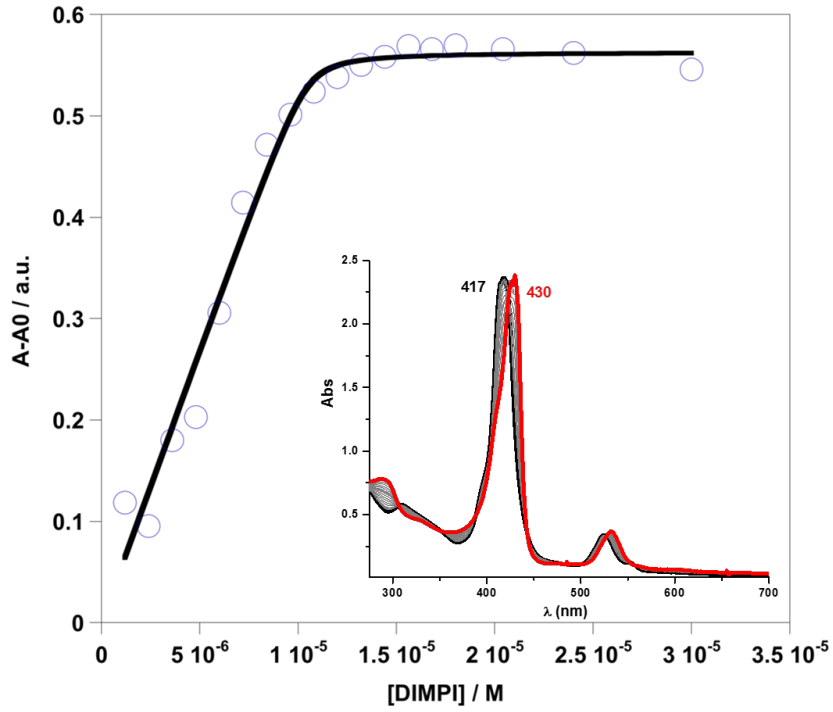

Fig. S10. Binding isotherm at 430 nm resulting from the reaction of $(P^{Im})Fe^{II}$ (12 μM in 2.5 mL Tetrahydrofuran, THF, black) and DIMPI (red, $(P^{Im})Fe^{II}$-DIMPI). $K_a = 1.19 \times 10^7\ M^{-1}$ See main text for detailed discussion.

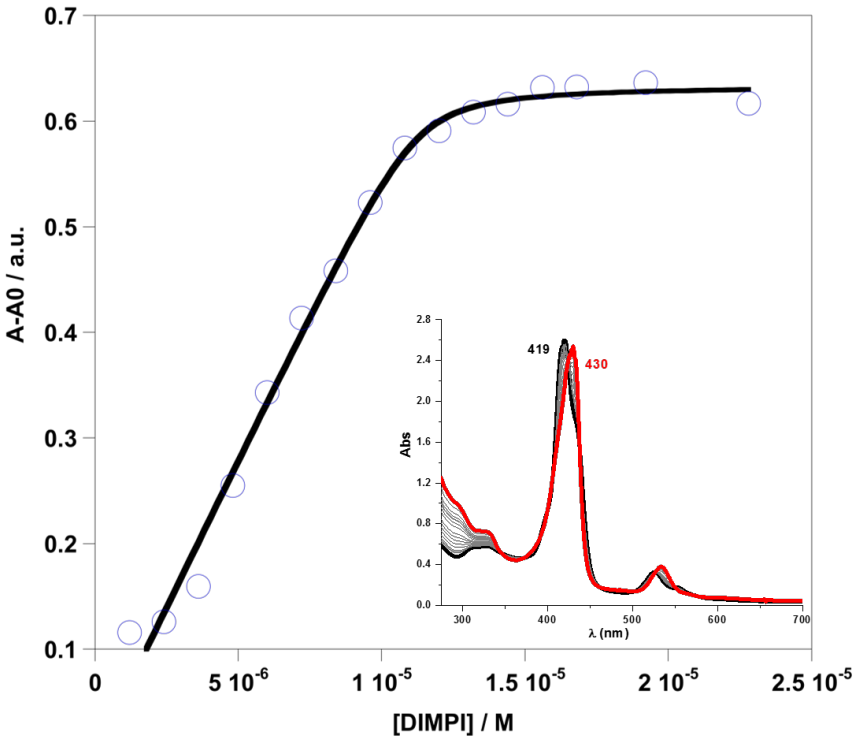

Fig. S11. Binding isotherm at 430 nm resulting from the reaction of $(P^{ImH})Fe^{II}$ (12 µM in 2.5 mL Tetrahydrofuran, THF, black) and DIMPI (red, $(P^{ImH})Fe^{II}$-DIMPI). K_a = 1.29 x 10^7 M^{-1}. See main text for detailed discussion.

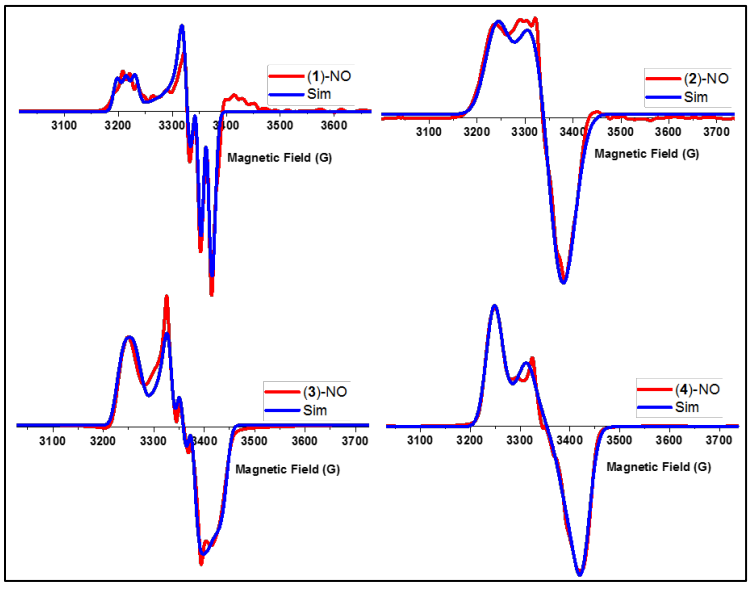

Fig. S12. X-band EPR spectroscopy of ferrous heme-NO complexes recorded at 8K in frozen THF (**red**) and fit of the spectrum using the program Easy Spin [1] (**blue**). Fit parameters:
(a) (**1**)–NO (g_1 = 2.0918, g_2 = 2.0074, g_3 = 2.0052; N hyperfine: $^{NO}A_1$ = 48.78, $^{NO}A_2$ = 67.63, $^{NO}A_3$ = 35.68)
(b) (**2**)–NO (g_1 = 2.0746, g_2 = 2.0081, g_3 = 1.9904; N hyperfine: $^{NO}A_1$ = 4.0, $^{NO}A_2$ = 60.4, $^{NO}A_3$ = 35.8; $^{Py}A_1$ = 18.1, $^{Py}A_2$ = 20.1, $^{Py}A_3$ = 19.1)

(c) (**3**)–NO (g_1 = 2.0686, g_2 = 2.002, g_3 = 1.9662; N hyperfine: $^{NO}A_1$ = 44.10, $^{NO}A_2$ = 63.18, $^{NO}A_3$ = 47.45; $^{Im}A_1$ = 22.94, $^{Im}A_2$ = 1.29, $^{Im}A_3$ = 16.84)
(d) (**4**)–NO (g_1 = 2.0690, g_2 = 2.0050, g_3 = 1.9643; N hyperfine: $^{NO}A_1$ = 14.68, $^{NO}A_2$ = 23.97, $^{NO}A_3$ = 71.75; $^{ImH}A_1$ = 2.0, $^{ImH}A_2$ = 4.3, $^{ImH}A_3$ = 10.2)

Reference

1. S. Stoll and A. Schweiger (2006) Journal of Magnetic Resonance 178:42-55; http://easyspin.org/