Iron Strap Porphyrins with Carboxylic Acid Groups Hanging Over the Coordination Site: Synthesis, X-ray Characterization, and Dioxygen Binding

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Supporting information.

α-5,15-*Bis*-{2,2'[3,3'-(2,2-(diethoxycarbonyl)propane-1,3-diyl)dibenzoylamino]diphenyl)}-β-10,20-*bis*-{2,2'[3,3'-(*N*-(pyridin-3-ylmethyl-amine)-dibenzoylaminodiphenyl)}]-iron carbonyl porphyrin 2aFeCO. In a dry box, compound **2aFe(III)** was dissolved in toluene (5 mL) and a saturated aqueous solution of $Na_2S_2O_4$ was added. After 5 min of stirring, the organic layer was dried over $MgSO_4$ and evaporated. The resulting product was precipitated and dried under vacuum. The compound was dissolved in $CDCl_3$ and placed into a Young NMR tube. The NMR sample was degassed using a freeze-pump-thaw procedure (5 cycles), then placed under a saturated O_2 atmosphere to yield **2aFeO2**. This complex was degassed using a freeze-pump-thaw procedure (5 cycles) and placed under a saturated CO atmosphere to yield the expected compound **2aFeCO**. ^{1}H NMR (500.13 MHz, $CDCl_3$, 298 K): δ = 8.95 (2H, d, *J* = 8.5 Hz, H_{aro}), 8.77 (6H, m, $H_{aro}+H_{\beta pyr}$), 8.64 (4H, m, $H_{\beta pyr}$), 8.61 (2H, s, NHCO), 8.02 (2H, d, *J* = 8 Hz, H_6), 7.82 (2H, t, *J* = 7.5 H, H_{aro}), 7.75 (2H, t, *J* = 7.5 H, H_{aro}), 7.63 (2H, d, *J* = 7.5 Hz, H_{aro}), 7.43 (2H, m, NHCO), 7.29 (6H, m, H_{aro} + $H_{6'}$ + H_5), 7.11 (2H, d, *J* = 6.5 Hz, H_{aro}), 7.01 (2H, d, *J* = 7.5 Hz, H_4), 6.79 (2H, t, *J* = 7.7 Hz, $H_{5'}$), 6.61 (2H, d, *J* = 7.7 Hz, $H_{4'}$), 6.12 (2H, s, H_2), 6.11 (1H, d, *J* = 7 Hz, H_{4pyr}), 6.03 (2H, s, $H_{2'}$), 5.38 (1H, t, *J* = 7 Hz, H_{5pyr}), 3.78 (2H, m, CH_{2ester}), 3.49 (2H, q, *J* = 7.3 Hz, CH_{2ester}), 2.89 (2H, d, *J* = 12.5 Hz, CH_{2bz}), 2.68 (1H,

s, H$_{2pyr}$), 2.4 (2H, d, J = 13 Hz, CH$_{2bz}$), 1.65 (2H, d, J = 14 Hz, CH$_{2bz}$), 1.64 (1H, d, H$_{6pyr}$), 0.91 (3H, t, J = 7.3 Hz, CH$_{3ester}$), 0.52 (3H, t, J = 7 Hz, CH$_{3ester}$).

Equilibrium measurements for **1aFe**, **2aFe**, and **2bFe**. In the case of **1bFe**, the intramolecular coordination of a carboxylic acid to the iron(II) cation precluded the measurement by this method.

The O$_2$ affinities were measured spectrophotometrically under equilibrium conditions with a Uvikon XL spectrometer. Measurements were performed with benzene solutions thermostated in the spectrometer to 25.0 $\pm$ 0.3 °C with a Lauda RL6 constant-temperature bath and circulator. Dioxygen (or diluted dioxygen in nitrogen) was added in defined aliquots using a syringe to the samples taken out a dry box in a sealed tonometer. An identical volume of gas was removed from the tonometer before addition of dioxygen to maintain constant pressure within the tonometer. After addition of dioxygen, the sample was shaken vigorously and then allowed to equilibrate before the next absorbance spectrum was taken. Finally, after completion of the measurement, a large excess of carbon monoxide was introduced into the tonometer to verify the lack of oxidation of the dioxygen adduct by UV-vis monitoring.

The equilibrium between the metalloporphyrin (MP) with an intramolecular fifth ligand and O$_2$ can be expressed as follows:
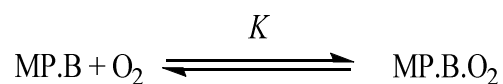
$$\text{MP.B} + \text{O}_2 \xrightleftharpoons{K} \text{MP.B.O}_2$$

The equilibrium constant K is defined by:

$$K = [\text{MP.B.O}_2]/[\text{MP.B}].p(\text{O}_2)$$

If C_0 is the total concentration of (MP.B), then at $t = 0$ (without dioxygen) : C_0 = [MP.B].

With a dioxygen partial pressure $p(\text{O}_2)$, C_0 = [MP.B] + [MP.B.O$_2$]. Then:

$$K = [\text{MP.B.O}_2]/((C_0 - [\text{MP.B.O}_2]).p(\text{O}_2))$$

Only (MP.B) and (MP.B.O$_2$) have absorbance in UV-Vis absorbance. The Beer-Lambert law can be written as follow:

When $t = 0$: $A\text{o} = \varepsilon_{MP.B}.C\text{o} = \varepsilon_{MP.B}.[MP.B] + \varepsilon_{MP.B}.[MP.B.O_2]$ and at any t: $A = \varepsilon_{MP.B}.[MP.B] + \varepsilon_{MP.B.O_2}.[MP.B.O_2]$.

Then $A - A\text{o} = (\varepsilon_{MP.B.O_2} - \varepsilon_{MP.B}).[MP.B.O_2]$ or $\Delta A = \Delta\varepsilon.\,[MP.B.O_2]$

The equilibrium constant K could be defined by:

$$K = \Delta A/((C_0\Delta\varepsilon - \Delta A).p(O_2))\ \text{or}\ K^{-1} = ((C_0\Delta\varepsilon/\Delta A).p(O_2)) - p(O_2)$$

The partial pressure of dioxygen ($p(O_2)$) could be defined as:

$$p(O_2) = ((C_0\Delta\varepsilon/\Delta A).p(O_2)) - K^{-1}$$

This is the equation of a straight line with a slope of $C_0\Delta\varepsilon$ and an intercept of $-1/K$.

When the metalloporphyrin is half-oxygenated: $[MP.B] = [MP.B.O_2]$ and then $1/K = P_{1/2}(O_2)$. The partial pressure of oxygen at which 50% of metalloporphyrin sites are bound with O$_2$ is defined as $P_{1/2}(O_2)$. The details of these measurements have been reported in a previous communication.[1]
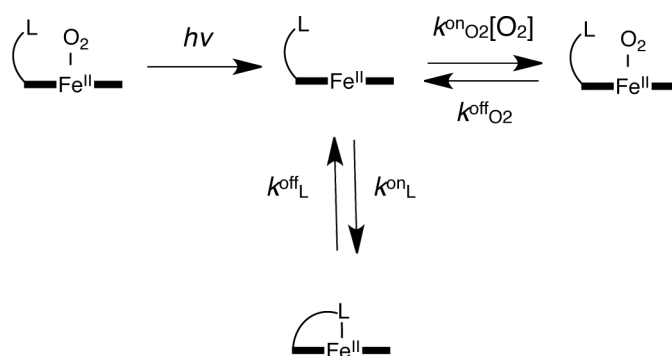
Scheme S1. Oxygen binding behavior for **1bFe(II)** after flash photolysis.

[1] Hijazi, I.; Roisnel, T.; Fourmigué, M.; Weiss, J.; Boitrel, B. Coordination Studies of Bis-Strapped-Hanging-Carboxylate Porphyrins. X-ray. Characterization of a Five-Coordinate Iron(II) Complex with a Built-in Axial Base. *Inorg. Chem.* **2010,** 49, 3098-3100.
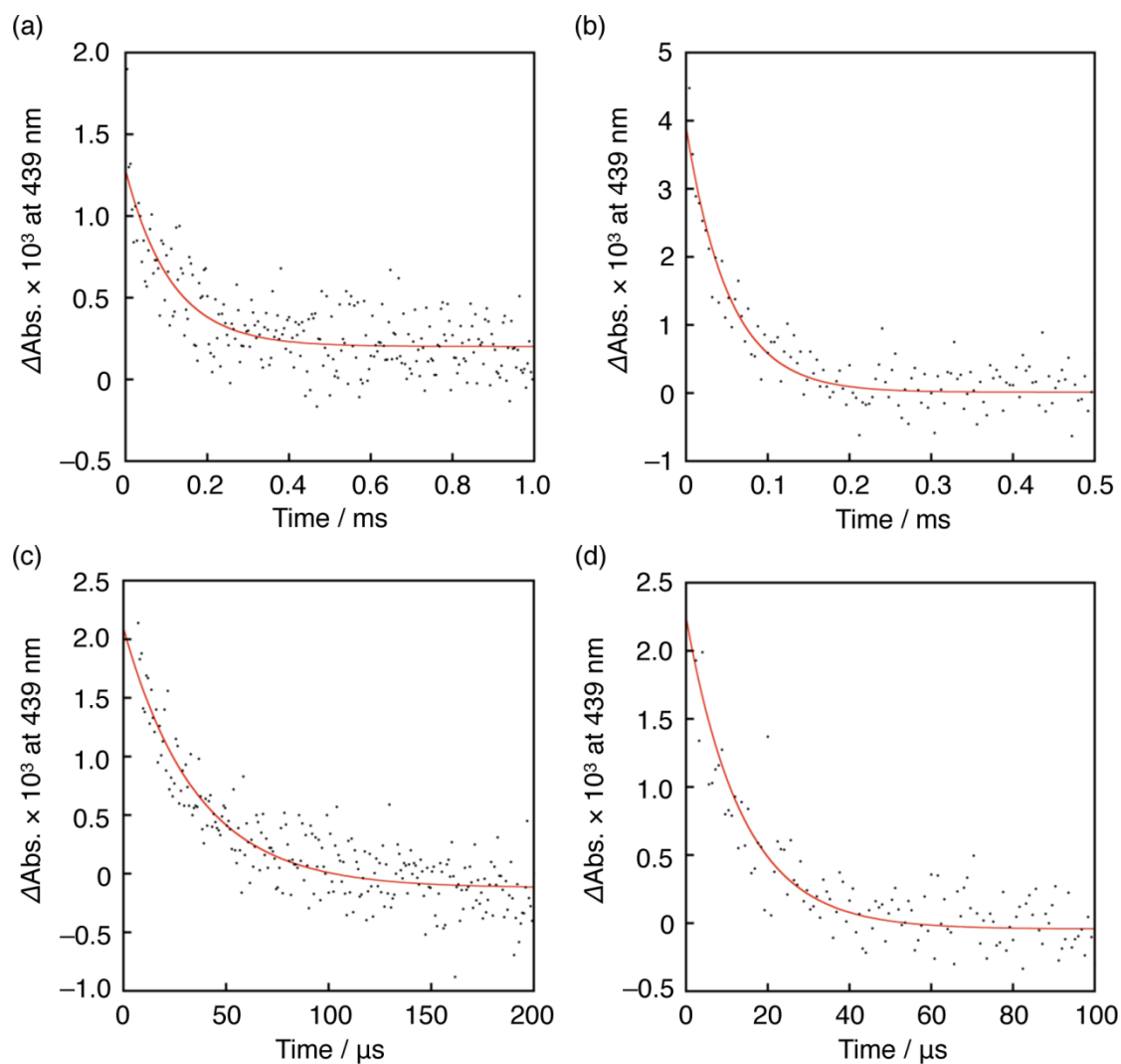
Figure S1. Time course absorption changes of **1bFe(II)** after flash photolysis under the various partial pressures of O_2: (a) 0.1, (b) 0.2, (c) 0.5 and (d) 1.0 atm. Red lines are fitting curves using following equation: ΔAbs. $= A_0 + A_1 \times \exp(-k_{obs} \times t)$, where t is time.
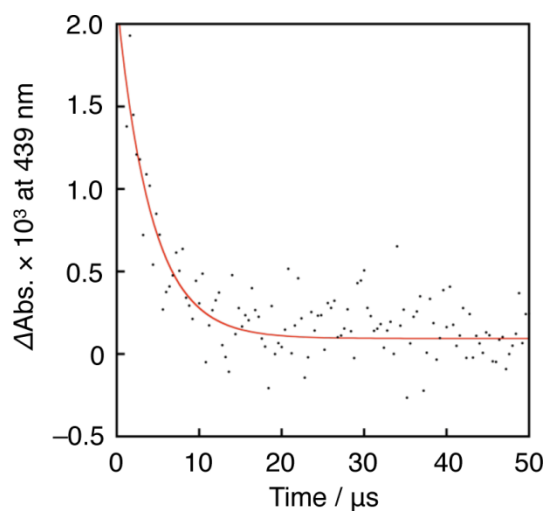
Figure S2.Time course absorption changes of **2bFe(II)** after flash photolysis under 0.1 atm of partial pressures of O_2. Red line is a fitting curve using following equation: ΔAbs. $= A_0 + A_1 \times \exp(-k_{obs} \times t)$, where t is time.
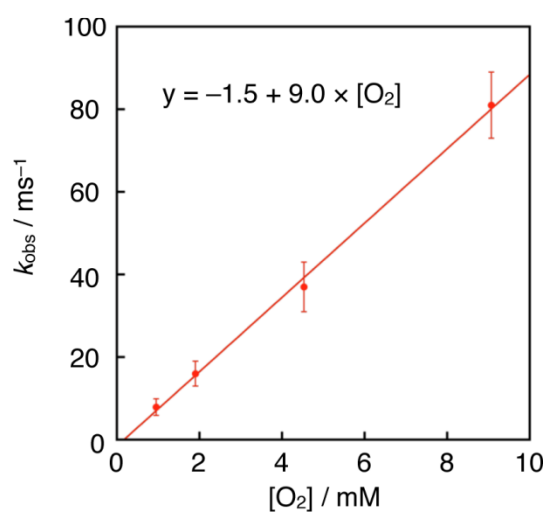

$$y = -1.5 + 9.0 \times [O_2]$$

Figure S3. Plots of k_{obs} for **1bFe(II)** against dissolved concentration of O_2. Red line is a fitting curve with $k_{obs} = k^{on}_{O2}[O_2] + k^{off}_{O2}$.

Figure S4. UV-vis spectroscopy monitoring of dioxygen and carbon monoxide binding on complex **2aFe(II)**.