

Supporting Information for

**Transient Absorption Studies of the Pacman Effect in Spring-loaded
Diiron(III) μ -oxo Bisporphyrins**

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Estimate of maximum TA signal of OAT photoproduct

Our estimate of the maximum possible TA signal generated by the diferrous form is based on the application of Beers law. We measured $\epsilon(\text{PFe}^{\text{II}}/\text{PFe}^{\text{II}}) = 1.73 \times 10^7 \text{ M}^{-1}\text{cm}^{-1}$ at 541.5 nm. (because this is an isosbestic point for the photogenerated $\text{PFe}^{\text{II}}/\text{PFe}^{\text{IV}}\text{O}$ intermediates, i.e. their contribution to $\Delta\text{OD} = 0$, thus it is at this wavelength that the photoproduct can be measured relative to a zero background intensity). The maximum possible concentration of this photoproduct that could be detected is the initial diiron μ -oxo bisporphyrin concentration ($5 \times 10^{-5} \text{ M}$) multiplied by the product quantum yield (greatest measured $\Phi_p = 7.4(7) \times 10^{-4}$ for $(\text{DPD})\text{Fe}_2\text{O} + 0.2 \text{ M P(OMe)}_3$) and scaled by 0.5 to take account of the greatest effective concentration that can be detected when both pump and probe are polarized parallel to each other). Thus $c_{\text{max}}(\text{PFe}^{\text{II}}/\text{PFe}^{\text{II}}) = 1.9 \times 10^{-8} \text{ M}$. This conservatively assumes that every molecule being probed had previously absorbed an excitation photon into the photoactive LMCT transition, which is clearly an overestimation. Nevertheless, a maximum ΔOD can be estimated based on the most positive assumptions, given $\Delta\text{OD}_{\text{max}} = \Delta(\epsilon c l) \sim \epsilon(\text{PFe}^{\text{II}}/\text{PFe}^{\text{II}}) \times c_{\text{max}}(\text{PFe}^{\text{II}}/\text{PFe}^{\text{II}}) \times \ell$ (Φ_p is low enough that the concentration of the diiron μ -oxo bisporphyrin reformed after excitation is virtually the same as it was initially, accordingly it needn't be accounted for in the ΔOD estimate). On this basis, $\Delta\text{OD}_{\text{max}} \sim 5 \times 10^{-5}$ which is already at least 2 orders of magnitude less than the TA signals measured in this study for the photogenerated $\text{PFe}^{\text{II}}/\text{PFe}^{\text{IV}}\text{O}$ intermediate. Under more realistic assumptions and in less efficient systems, ΔOD for the photoproduct appearance could be several orders of magnitude smaller than 5×10^{-5} .

Estimate of lower limit for Φ_{spring}

The lower limit for Φ_{spring} is also based on the application of Beers law. The measured TA spectrum of the $\text{PFe}^{\text{II}}/\text{PFe}^{\text{IV}}\text{O}$ species can be rescaled from ΔOD to $\Delta\epsilon$, with the resulting scaling factor being the inverse of the concentration of the 'sprung open' form multiplied by the cell pathlength. In order to rescale to $\Delta\epsilon$ we observe that the TA spectrum in the 530-620 nm region consists of the bleach of the ground-state Q-bands (565, 590 nm) overlaid by a positive

transient absorption. Thus we estimate that the bleach of the 565-nm band for the bisporphyrin ($\Delta\epsilon = -19000 \text{ M}^{-1}\text{cm}^{-1}$) corresponds to $\Delta\text{OD} \sim -0.015$ in the TA spectrum. This method of scaling ΔOD to $\Delta\epsilon$ using the Q-band bleach as a metric has been employed before in porphyrin TA spectroscopy.¹ After taking account of the effective concentration that can be detected when both pump and probe are polarized and set at the magic angle with respect to each other ($c_{\text{eff}} = 0.29 \times c_0$ assuming that the dipole moments of the porphyrin transitions probed are orthogonal to that of the LMCT excited), we find that the minimum concentration of the $\text{PFe}^{\text{II}}/\text{PFe}^{\text{IV}}\text{O}$ species that could produce this ΔOD signal is; $\Delta\text{OD} / (\Delta\epsilon \times \ell) \times (c_0 / c_{\text{eff}}) = 1.4 \times 10^{-5} \text{ M} = 0.28 \times \text{initial concentration of diiron } \mu\text{-oxo bisporphyrin}$. Once again this analysis conservatively assumes that every molecule probed had previously absorbed a photon into the photoactive LMCT transition. Thus we can conservatively set a lower limit for $\Phi_{\text{spring}} = 0.25$.

References

- (1) Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500 - 6506.

Figure S1. Spectra of probe light generated by focusing 810-nm, 100-fs pulses into spinning CaF₂ (solid), and sapphire (dashed).

