

Intramolecular Single-turnover Reaction in a Cytochrome *c* Oxidase Model bearing a Tyr²⁴⁴ Mimic

(Supporting Information)

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Instrumentation¹

EPR Spectroscopy: Bruker EMX spectrometer; X-band; microwave power, 10.08 mW; microwave frequency: 9.3075 GHz, modulation frequency: 100.0 kHz; modulation amplitude: 20.0 G, Receiver gain: 5.02×10^3 ; Resolution in X: 1024; T = 77K. Sample: (0.5-1.0 mM, 100 μ L) in 2.8 mm o.d diameter EPR tube sealed with a septum (Kontes Stopper Sleeve, Size 7, 774250-0007) and parafilm. Concentration in porphyrin 0.5-2.0 mM

Mass spectrometry. Nanospray: Advion/Nanomate; ***Electrospray***: Waters/Micromass Q-ToF Api-vs. Porphyrin in solution in scintillation vial sealed with septum or in borosilicate glass culture tubes (6x50 mm, disposable, Kimble) sealed with a Kontes-septum.

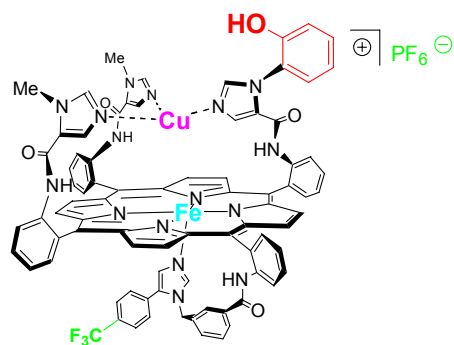
NMR spectroscopy. Inova-500. ¹H-NMR carried out at 500 MHz, PTFE-capped NMR tube filled with porphyrin solution (400 μ L, mm of solvent)

Resonance Raman spectroscopy. Spectra were obtained using 407 nm excitation (Kr⁺ laser, Coherent I90C-K), power 10 mW. Concentration in porphyrin 0.5-2.0 mM

UV/Vis spectroscopy Hewlett Packard apparatus 8452. Glass cuvette (3 mL capacity) sealed with a 14/24 septum, solvent: THF. Concentration in porphyrin 2×10^{-6} M- 2×10^{-5} M.

Syntheses and Reactivity

Model 1- [Copper (I) [Cis- α_2 -(*o*-4-(3-methylimidazolyl)-amidophenyl)- α -(*o*-4-(3-(2-hydroxyphenylimidazolyl)-amidophenyl)- β -(*o*-3-(1-(5-*p*-trifluoromethylphenyl)imidazolyl methyl)benzamidophenyl) iron (II) porphyrin] hexafluorophosphate, {Cu(I)[Fe(II)(α_2 (*N*-MeIm) α (*N*-(PhOH)Im) β F₃T-T)]⁺ {PF₆}⁻, Fe/Cu[*N*-Me][*N*-PhOH]PF₆ (**1**)]
A mixture of free base porphyrin H₂[*N*-Me]₂[*N*-PhOH]² (10.6 μ mol, 15 mg) and FeBr₂ (32 μ mol, 7mg) in MeOH/THF (1:4 vol., 10 mL) was heated for 1h at reflux. The volume was reduced to a 1/3rd then 0.1 M aqueous Na₂.EDTA (1 mL) was introduced and the resulting mixture was stirred for 10 min. Then the volume was expanded with benzene (15 mL), water was added (15 mL) and stirring was continued for 10 more min. The organic phase was then washed with water (4 x 15 mL), and dried by addition of Na₂SO₄ and stirring for 10 min. After filtration of the porphyrin solution through a glass wool plug, the solvents were distilled under reduced pressure to yield Fe[*N*-Me]₂[*N*-PhOH] (12.5 mg, 80% yield). An aliquot of Fe[*N*-Me]₂[*N*-PhOH] (4.1 μ mol, 6 mg) in THF (1 mL) was mixed with 1 equiv. of CuPF₆MeCN₄ (100 μ L taken from a 41 mM stock solution in MeCN (15.3 mg/mL)). The resulting solution was stirred for 10 min and the solvents were removed under vacuum, yielding **1** quantitatively (6.8 mg).



Fe/Cu [N-Me]₂[N-PhOH] (1)

¹H NMR (500 MHz, CDCl₃/CD₃CN/THF-*d*₈/1 atm CO) δ 9.07 (d, 1H, J = 8.0 Hz), 8.79-8.70 (m, 6H), 8.63-8.61 (m, 2H), 8.53 (d, 1H, J = 8.5 Hz), 8.50 (d, 1H, J = 8.5 Hz), 8.45 (d, 1H, J = 8.5 Hz), 8.29-8.23 (m, 3H), 8.18 (d, 1H, J = 7.5 Hz), 7.66-7.82 (m, 7H), 7.42-7.55 (m, 5H), 7.38 (s, 1H), 7.11 (m, 3H), 7.02 (m, 2H), 6.97 (m, 2H), 6.85 (s, 1H), 6.66 (t, 1H, J = 7.5 Hz), 6.61 (d, 1H, J = 7.0 Hz), 6.57 (d, 1H, J = 7.5 Hz), 6.08 (d, 2H, J = 8.5 Hz), 5.57 (s, 1H), 5.32 (s, 1H), 5.09 (s, 1H), 4.13 (s, 1H), 3.99 (s, 2H), 3.52 (s, 3H), 3.37 (s, 3H), 2.23 (s, 1H), 1.36 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃/CD₃CN/THF-*d*₈ 0.1:4:1 vol./1 atm CO): δ -64.1 (s, 3F), -73.4 ppm (d, 6F, J_{FP} = 708 Hz). ³¹P NMR (162 MHz, CDCl₃/CD₃CN/THF-*d*₈/1 atm CO): δ 66.9 (7uplet, 1P, J_{PF} = 708 Hz). HR-MS (ESI⁺): *m/z* = 1521.3240 [M-PF₆]⁺ (Calcd for C₈₂H₅₇CuF₃FeN₁₆O₅: 1521.3395). UV-Vis. (CH₂Cl₂) λ (10⁻³ x ε/ mol⁻¹ L cm⁻¹): 425 (230), 543 (10).

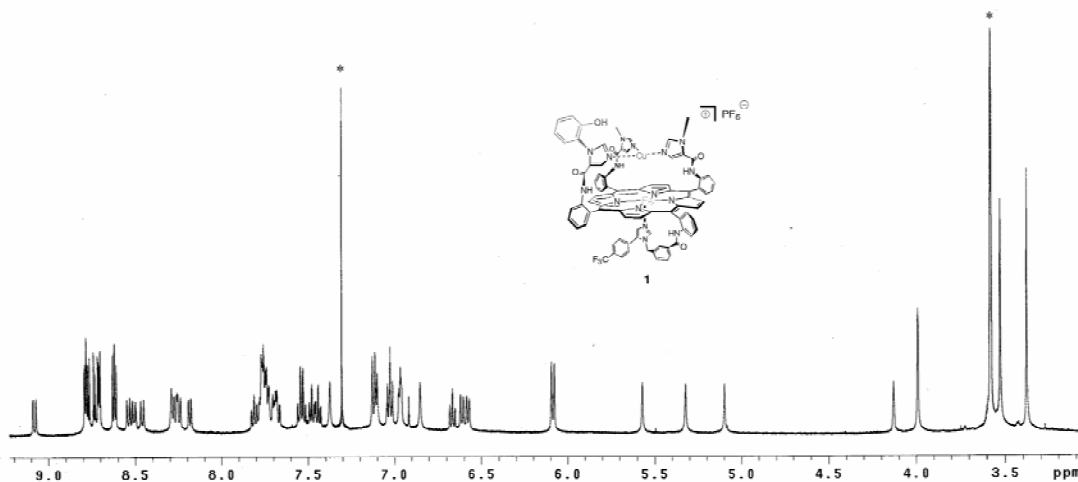


Fig. S1. ¹H-NMR spectrum of Model **1** in CDCl₃/THF-*d*₈/CD₃CN under 1 atm of CO. (solvent peaks are marked with *).

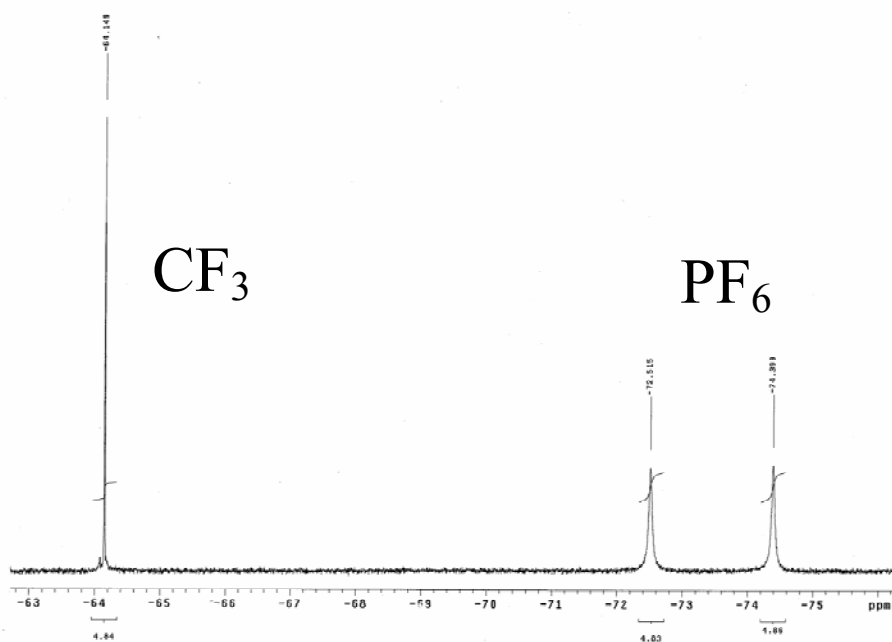


Fig. S2. ¹⁹F-NMR spectrum indicating a 1:1 ratio porphyrin (CF₃ marker): copper (PF₆ counter ion). Integration shows 4.84 (CF₃), 4.83 (PF₆), and 4.86 (PF₆).

Models Oxy-1 and 2. A vessel containing a solution of **1** in DMF was frozen, evacuated, back-filled with 1 atm of 100%-O₂, thawed at -60 °C for 15s, and subjected to three freeze-pump-thaw (-60 °C) cycles. The vessel was plunged in a bath at -40 °C in the dark, and frozen after 20-60 min for EPR and resonance Raman analyses. For reactivity experiments 3 equiv. of PPh₃ were introduced, the mixture was warmed to room temperature and analyzed by TLC and GC as previously described, and showed the formation of triphenylphosphine oxide after comparison with an authentic standard.¹

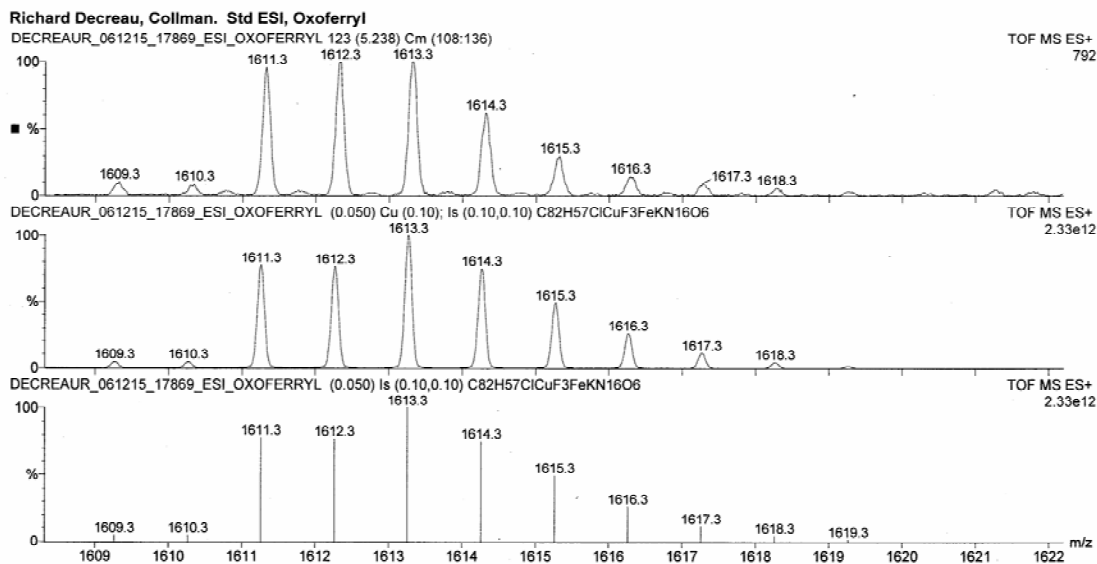


Fig. S3. Experimental (top) and simulated (middle and bottom) mass spectra of a potassium chloride adduct of **2**.

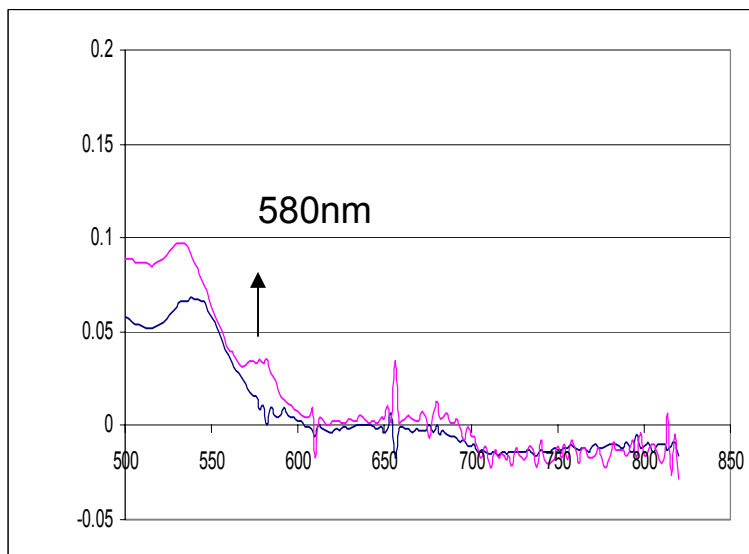


Fig. S4. UV-Vis spectrum of oxy-1 (black) and 2 (purple) in THF.

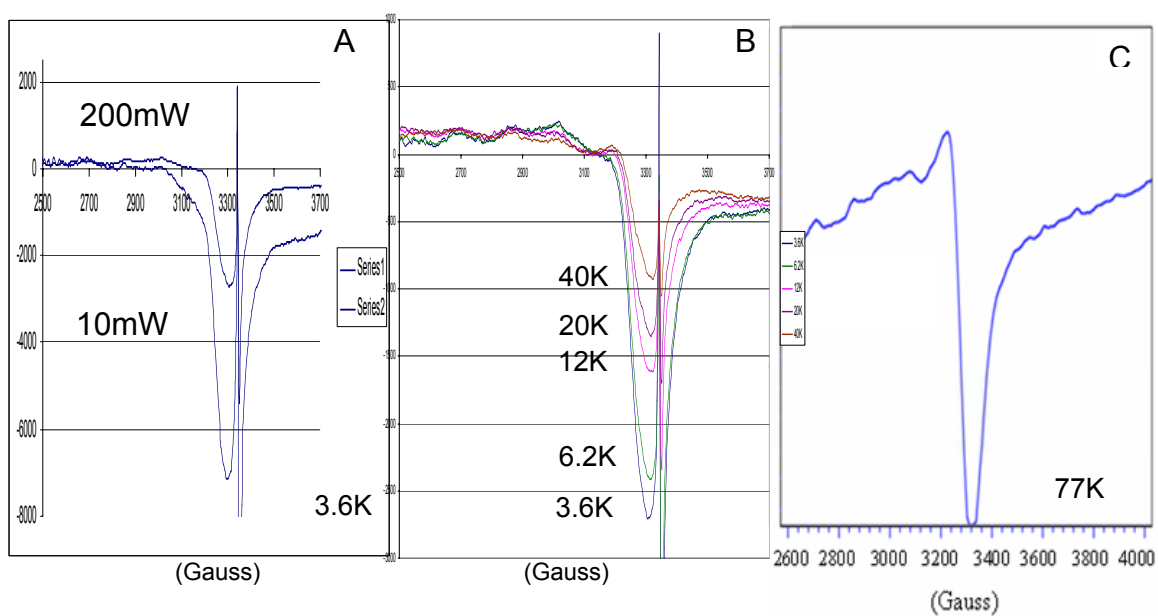


Fig. S5. A- Power dependence of the signal; B- T dependence; C- At 77K

References

- 1- Conditions were adapted from that previously reported for an intermolecular reaction between phenols and an Fe(III)-superoxide-Cu(I) CcO model: Collman, J. P.; Decréau, R. A.; Sunderland, C. E. *Chem. Com.* **2006**, 3894.
- 2- Collman, J. P.; Decréau, R. A.; Zhang, C. *J. Org. Chem.* **2004**, 69, 3546