

Supporting Information for:

Single-turnover intermolecular reaction between a Fe^{III}-superoxide-Cu^I cytochrome *c* oxidase model and Tyr²⁴⁴ mimics.

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EPR. Experimental conditions: 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.

Intermolecular Reaction.

EPR experiments. A solution of **1** in CH₂Cl₂ (0.5-1.0 mM, 100 μL) in 2.8 mm i.d diameter EPR tube sealed with a septum (Kontes Stopper Sleeve, Size 7, 774250-0007) was frozen, pumped, refilled with 25% O₂ mixture, melt and stir while cold (-40 °C, acetonitrile/dry ice bath) for 15s then frozen again. After two freeze-pump-thaw cycles, the solution of phenol **2** was introduced (7 μL from 50 μL capacity air-tight Hamilton syringe) and the mixture was stirred by putting the tube upside-down quickly. The tube was plunged in a water bath at room temperature in the dark, shaken every 5 mins then frozen after reaction time was up.

UV/Vis experiments: the reaction was carried out in a UV/Vis cuvette sealed with a 14/24 septum, on a 100-300 μL scale from a 0.5 mM stock solution in **1**. The experimental conditions (mixing etc.) were the same as the one described for the EPR experiment, then the mixture was diluted accordingly for UV/Vis measurements by dilution with O₂-free CH₂Cl₂.

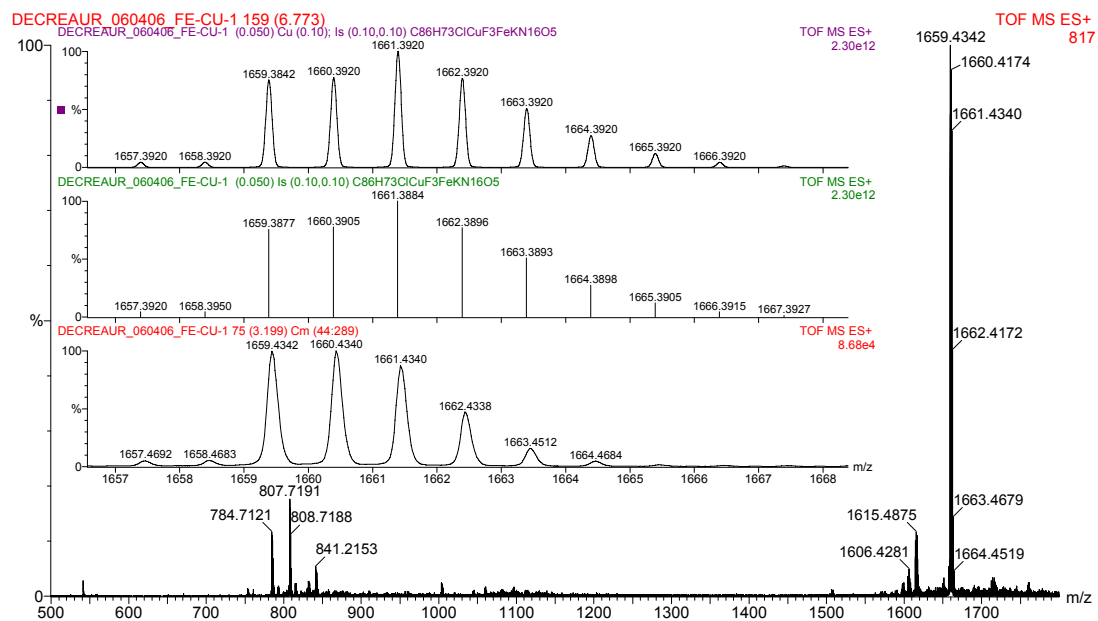
Mass spectrometry analysis and reactivity experiments: A stock solution of **1** (300 μL, 3.5 mM) was placed in borosilicate glass culture tubes (6x50 mm, disposable, Kimble) sealed with a Kontes-septum. For MS experiment, the introduction of the solution of phenol, and the reaction were both carried out at -40°C in CH₃CN. After introducing the phenol and allowing the reaction to proceed for ca 10 min (RT in CH₂Cl₂ with shaking tube occasionally), 3 equiv. PPh₃ were introduced. The mixture was allowed to stand for

ca. 20 min before TLC and GC analyses. For GC analysis the mixture was filtered through a short silica plug, washed with CH₂Cl₂ to remove the unreacted PPh₃ then diethyl ether to isolate PPh₃O. The ether solution was evaporated and redissolved in a 0.5 mM solution of nitrobenzene in CH₂Cl₂ (200 μL). The yield of triphenyl phosphine oxide (45%) was determined from nitrobenzene used as an internal standard.

2,6-Di-*tert*-4-methoxy-butylphenoxy radical (2a[•]). In the glovebox, a 21.2 mM solution of **2** in toluene (50 mg / 10 mL) was mixed with a solution of 0.5 g K₃Fe^{II}CN₆ in 2N KOH (1.12 g KOH in 10 mL H₂O) under vigorous stirring for 5-15 min. The concentration of phenoxy radical was assessed by iodometric titration. A series of standard solutions of phenoxy radical was prepared (0.1-2.0 mM range). The EPR tubes were filled with *ca* 200 μL of solution and frozen immediately. UV/Vis (CH₂Cl₂) λ (10³ x ε M⁻¹.cm⁻¹) 298 (7.3), 338 (3.8), 387 (1.7), 406 (2.4), 542 (0.12) nm.

2,6-Di-*tert*-4-methoxy-butylphenol-*d* (2a-D) 2,6-Di-*tert*-4-methoxy-butylphenol (0.13g) was dissolved in DMSO-*d*₆ (3.0 mL) along with NaH (0.010 g) under inert atmosphere. The mixture was stirred for 16h and then quenched with D₂O (5.0 mL). The white precipitate was collected by filtration, washed with D₂O and dried under high vacuum for several days (90%). ¹H-NMR (500 MHz, CDCl₃): δ (ppm) 7.20 (s, 2H), 1.45 (s, 9H), 1.30 (s, 3H). mp (°C). UV/Vis (CH₂Cl₂) 310 nm. MS (ESI+): 237.4 (Calcd for C₁₅H₂₃DO₂).

Actual and simulated (MassLynk) Mass-Spectra of the reaction mixture containing **4**.



Absorbance of phenoxyl radical **2a** at two different concentrations

