Supporting Information

Hangman Effect on Hydrogen Peroxide Dismutation by Fe(III) Corroles

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Index Page

Materials and Methods S2
Synthesis of Compounds S2–S4
NMR Spectra of 2-py and 3-Et2O S5–S8
UV-Vis Spectra of 2-py in pentane and in THF S9
UV-Vis Spectra of 2-py and 3-Et2O in THF S10
Mass Spectra S11–S12

S1
Materials and Methods

$^1$H NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz spectrometer. All $^1$H NMR spectra were referenced to deuterated benzene (C$_6$D$_6$) as an internal standard (measured values for δ are given in parts per million (ppm) and for J in Hertz (Hz)). $^{19}$F NMR spectra were referenced to CFCl$_3$ in CDCl$_3$. Electrospray ionization mass spectra (ESI-MS) were obtained using a Bruker Daltonics APEXIV 4.7 T FT-ICR-MS instrument at the DCIF facility of MIT.

UV-vis spectra were recorded at room temperature in 10 mm path length quartz cuvettes on compound dissolved in anhydrous THF or pentane on a Varian Cary 5000 UV-vis-NIR spectrophotometer employing the software Cary WinUV. In a glovebox, the quartz cuvette was filled with 3.0 mL of solvent. From a stock solution, Fe(III) corrole was added to the cuvette, which was sealed and removed from the glovebox.

4-Formyl-5-bromo-2,7-di-tert-butyl-9,9-dimethylxanthene$^1$ 5-pentafluorophenyl-dipyrromethane,$^2$ 5,10,15-tris(pentafluorophenyl)corrole,$^3,4$ and 1-py$^5$ were prepared as described in the literature. THF (anhydrous), DMF (anhydrous), pyridine (anhydrous), methanol (anhydrous), diethyl ether (anhydrous), pentane (anhydrous), 30 wt % H$_2$O$_2$ in H$_2$O and pyridine were reagent grade and were used as received. ESI-MS data was measured on corroles in Ar-saturated EtOAc.

The procedure to measure H$_2$O$_2$ disproportionation is as follows. 1 μmol of the iron corrole was placed in an oven-dried vial containing magnetic stirbar and 1,5-dicyclohexyl-imidazole (6.0 mg, 26 μmol). Under an inert atmosphere, dry THF (1.5 mL) was added, and the vial was sealed with a septum and secured with a plastic zip-tie. A cannula needle was inserted into the vial and was purged thoroughly with Ar. The cannula needle was removed. of Ar-saturated MeOH (0.5 mL) and Ar-saturated H$_2$O$_2$ (0.11 mL, 30% wt in H$_2$O, 1.0 mmol, 1000 eq.) were added to the solution at time = 0, the syringe plunger was retracted to 0.11 mL and removed. The increase in the headspace volume due to generation of O$_2$ was measured through insertion of one end of the cannula needle into a 25 mL graduated pipette, which had been filled with water, inverted and submerged in water. Volume was converted to moles with the ideal gas law. Turnover frequencies were calculated from the amount of O$_2$ evolved after 20 seconds.

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Synthesis of Compounds

10-(4-(5-bromo-2,7-di-tert-butyl-9,9-dimethyl-xanthene)-5,15-bis(pentafluorophenyl)corrolatoiron(III) pyridine adduct (2-py). Following published procedures for Fe insertion into corroles,5 10-(4-(5-Bromo-2,7-di-tert-butyl-9,9-dimethyl-xanthenyl))-5,15-bis(pentafluorophenyl) corrole (20.0 mg, 19.4 μmol) was dissolved in dry pyridine (10 mL) in a 100 mL 3-necked round bottom flask. After thorough purging with Ar, anhydrous FeCl₂ (40 mg, 0.31 mmol, 16 mole equiv.) was added under strong Ar flow, and the solution was immediately refluxed in a pre-heated 125 °C oil bath. After 30 min the flask was removed from the oil bath and volatiles were removed in vacuo. The flask was transferred to a glovebox and the solids were filtered through a celite plug with Et₂O. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. 1H NMR (300 MHz, C₆D₆, 20 °C): δ = 31.80 (br, py–H), 22.16 (br, py-H), 2.057 (corrole β-H, 2H), −59.79 (br, corrole β-H, 2H H), −65.58 (br, corrole β-H, 2H), −125.42 (br, corrole β-H, 2H). Hangman backbone 1H resonances unidentifiable. 19F NMR (300 MHz, C₆D₆, 20 °C): δ = −95.4 (ortho-F, 2F), −111.8 (ortho-F, 2F), −150.8 (para-F, 2F), −156.3 (meta-F, 2F), −156.9 (meta-F, 2F). M = C₅₅H₃₆BrF₁₀FeN₄O: 1081.1262, (M + pyridine): 1160.1684; Found for ESI-MS: ((M + H) + + pyridine): 1162.1630; ((M–Br)+ + pyridine) = 1181.25.

λmax,abs/nm (ε × 10⁻³) (pentane) = 407 (24), 556 (8.1), 758 (1.4), λmax,abs/nm (ε × 10⁻³) (THF) = 406 (24), 556 (8.5), 737 (1.7)

10-(4-(5-Hydroxycarbonyl-2,7-di-tert-butyl-9,9-dimethyl-xanthene)-5,15-bis(pentafluorophenyl)corrolatoiron(III) diethyl ether adduct (3-Et₂O). Following published procedures for Fe insertion into corroles,5 10-(4-(5-hydroxycarbonyl-2,7-di-tert-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl)corrole (27.4 mg, 27.4 μmol) was dissolved in dry DMF (10 mL) in a 100 mL 3-necked round bottom flask. After purging with Ar, anhydrous FeCl₂ (60 mg, 0.50 mmol, 20 equiv.) was added under strong Ar flow. The solution was immediately placed in a pre-heated 150 °C oil bath and brought to reflux. After 30 min the flask was removed from the oil bath and volatiles were removed in vacuo. The flask was transferred to a glovebox and the solids were filtered through a celite plug with Et₂O. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed in vacuo and the resulting solids were filtered through a celite plug with pentane. 1H NMR (300 MHz, C₆D₆, 20 °C): δ = 13.90 (br, corrole β-H, 2H), 9.72 (br, corrole β-H, 2H), 59.27, (br, corrole β-H, 2H), 112.8 (br, corrole β-H, 2H). Hangman backbone 1H resonances unidentifiable. 19F NMR (300 MHz, C₆D₆, 20 °C): δ = −95.4 (ortho-F, 2F), −111.8 (ortho-F, 2F), −150.8 (para-F, 2F), −156.3 (meta-F, 2F), −156.9 (meta-F, 2F). M = C₅₅H₃₇F₁₀FeN₄O₃: 1047.2055, (M + pyridine): 1121.2787; Found for ESI-MS: ((M–H) + + diethylether): 1120.28 λmax,abs/nm (ε × 10⁻³) (THF) = 406 (31), 556 (11), 737 (1.9)

10-(4-(5-Bromo-2,7-di-tert-butyl-9,9-dimethylxanthenyl))-5,15-bis(pentafluorophenyl)corrolatoiron chloride (2-Cl). Following the published procedure,5 in a
scintillation vial, 2-py (1.2 mg, 1.0 μmol) was dissolved in DCM and washed with 4% HCl in H₂O (10 mL). The organic layer was dried over Na₂SO₄ and evaporated to dryness.

10-(4-(5-Hydroxycarbonyl-2,7-di-tert-butyl-9,9-dimethylxanthenyl))-5,15-bis-(pentafluorophenyl)corrolato Iron Chloride (3-Cl). Following the published procedure, 3-Et₂O (1.1 mg, 1.0 μmol) was placed in an oven dried scintillation vial and dissolved in DCM and washed with 4% HCl (10 mL) in H₂O. The organic layer was dried over Na₂SO₄ and evaporated to dryness.
Figure S1. $^1$H NMR spectrum of 2-py in C$_6$D$_6$ at room temperature.
Figure S2. $^{19}$F NMR spectrum of 2-py in C$_6$D$_6$ at room temperature.
Figure S3. $^1$H NMR spectrum of 3-Et$_2$O in C$_6$D$_6$ at room temperature.
**Figure S4.** $^{19}\text{F}$ NMR spectrum of 3-Et$_2$O in C$_6$D$_6$ at room temperature.
**Figure S5.** Absorption spectra of 2-py in pentane (---) and in THF (—).
Figure S6. Absorption spectra of 2-py (---) and 3-Et$_2$O (—) in THF.
Figure S7. ESI-MS spectrum of 2-py.
Figure S8. ESI-MS spectrum of 3-Et$_2$O.