Supporting Information

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

Daniel J. Graham, Dilek K. Dogutan, Matthias Schwalbe and Daniel G. Nocera*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

nocera@mit.edu

Index *Page*

Materials and Methods S2

Synthesis of Compounds S2–S4

NMR Spectra of **2-py** and **3-Et$_2$O** S5–S8

UV-Vis Spectra of **2-py** in pentane and in THF S9

UV-Vis Spectra of **2-py** and **3-Et$_2$O** in THF S10

Mass Spectra S11–S12

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_6D_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_2O_2 in H_2O 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_2O_2 disproportionation is as follows. 1 μmol of the iron corrole was placed in an oven-dried vial containing magnetic stirbar and 1,5-dicyclohexylimidazole (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_2O_2 (0.11 mL, 30% wt in H_2O, 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.

---

[1] C. J. Chang,C. H. Yeh and D. G. Nocera, *J. Org. Chem.*, 2002, **67**, 1403.

[2] J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Process Res. Dev.*, 2003, **7**, 799.

[3] D. K. Dogutan, S. A. Stoian, R. McGuire Jr., M. Schwalbe, T. S. Teets and D. G. Nocera, *J. Am. Chem. Soc.*, 2011, **133**, 131.

[4] Schwalbe, M.; Dogutan, D. K.; Stoian, S. A.; Teets, T. S.; Nocera, D. G. *Inorg. Chem.*, 2011, **50**, 1368.

[5] L. Simkhovich, I. Goldberg and Z. Gross, *Inorg. Chem.*, 2002, **41**, 5433.

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 $FeCl_2$ (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 Et_2O. The volatiles were removed *in vacuo* and the resulting solids were filtered through a celite plug with pentane. The volatiles were removed *in vacuo* to afford **2-py** as a dark red solid (21.3 mg, 94.6% yield). ^1H NMR (300 MHz, C_6D_6, 20 ^oC): 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. ^{19}F NMR (300 MHz, C_6D_6, 20 ^oC): 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 = $C_{54}H_{36}BrF_{10}FeN_4O$: 1081.1262, (M + pyridine): 1160.1684; Found for ESI-MS: ((M + H)$^+$ + pyridine): 1162.1630; ((M–Br)$^+$ + pyridine) = 1181.25. $\lambda_{max,abs}$/nm ($\varepsilon \times 10^{-3}$) (pentane) = 407 (24), 556 (8.1), 758 (1.4), $\lambda_{max,abs}$/nm ($\varepsilon \times 10^{-3}$) (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-Et_2O). 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 $FeCl_2$ (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 Et_2O. The volatiles were removed *in vacuo* and the resulting solids were filtered through a celite plug with pentane to afford **3-Et_2O** as a dark red solid (29.5 mg, 96.0%). ^1H NMR (300 MHz, C_6D_6, 20 ^oC): 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. ^{19}F NMR (300 MHz, C_6D_6, 20 ^oC): δ = –92.4 (*ortho*-F, 2F), –106.6 (*ortho*-F, 2F), –148.0 (*para*-F, 2F), –153.6 (meta-F, 2F), –154.3 (*meta*-F, 2F). M = $C_{55}H_{37}F_{10}FeN_4O_3$: 1047.2055, (M + diethylether): 1121.2787; Found for ESI-MS: ((M–H) + diethylether): 1120.28 $\lambda_{max,abs}$/nm ($\varepsilon \times 10^{-3}$) (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 H_2O (10 mL). The organic layer was dried over Na_2SO_4 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,[5] **3-Et$_2$O** (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 H_2O. The organic layer was dried over Na_2SO_4 and evaporated to dryness.

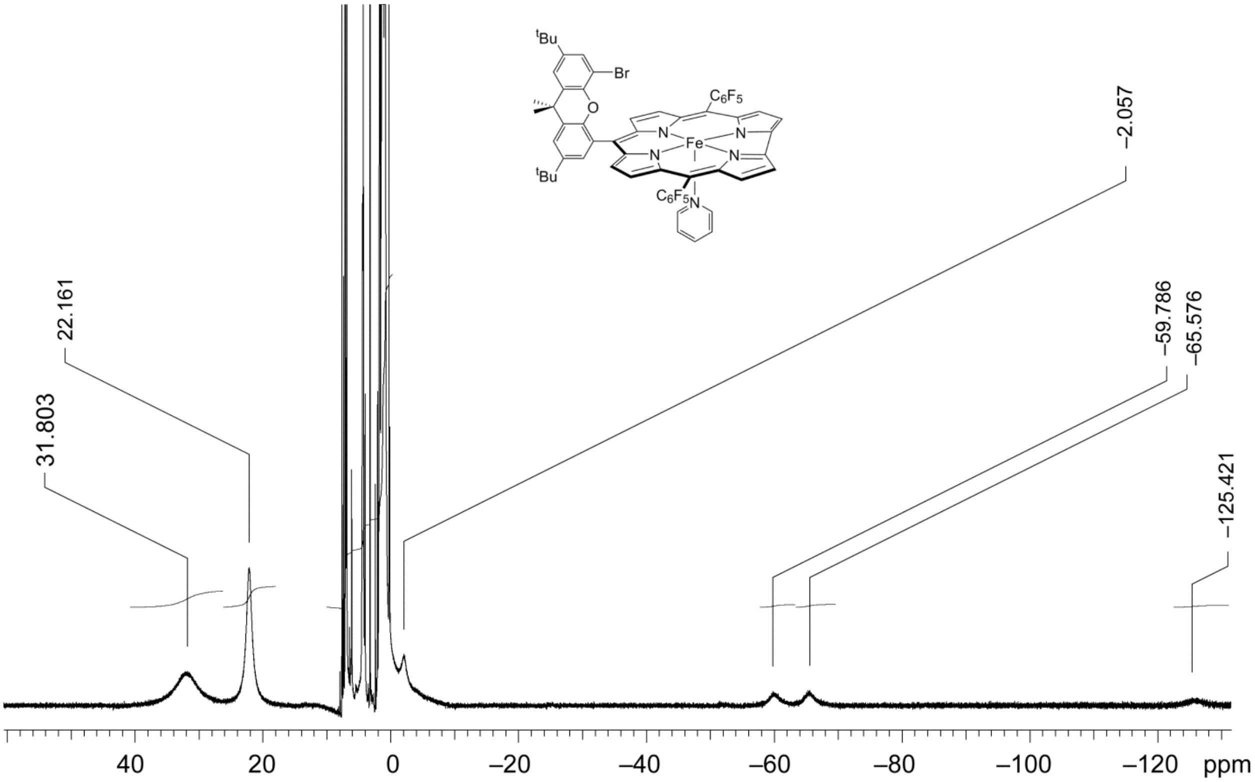

Figure S1. ^{1}H NMR spectrum of **2-py** in C_6D_6 at room temperature.

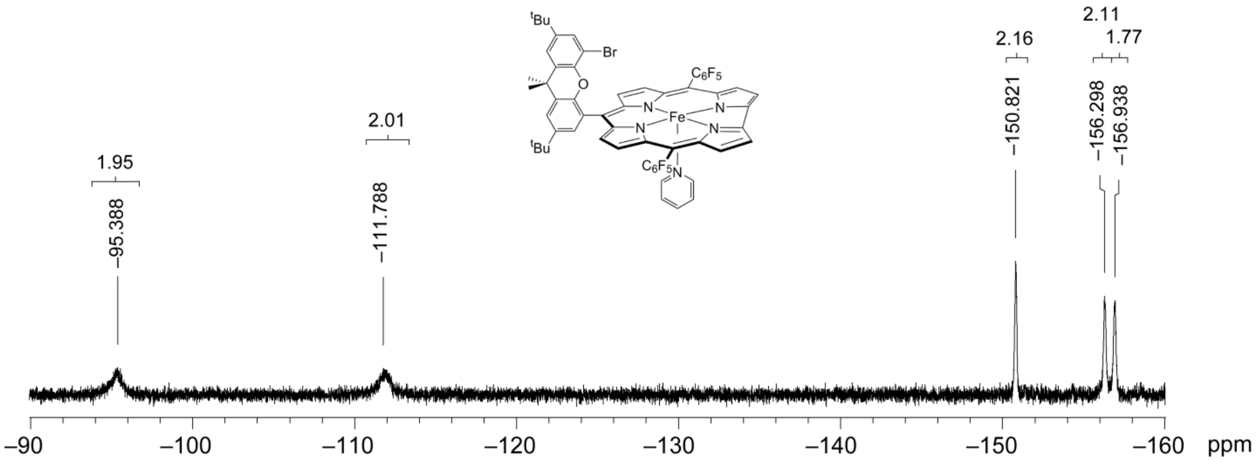

Figure S2. ^{19}F NMR spectrum of **2-py** in C_6D_6 at room temperature.

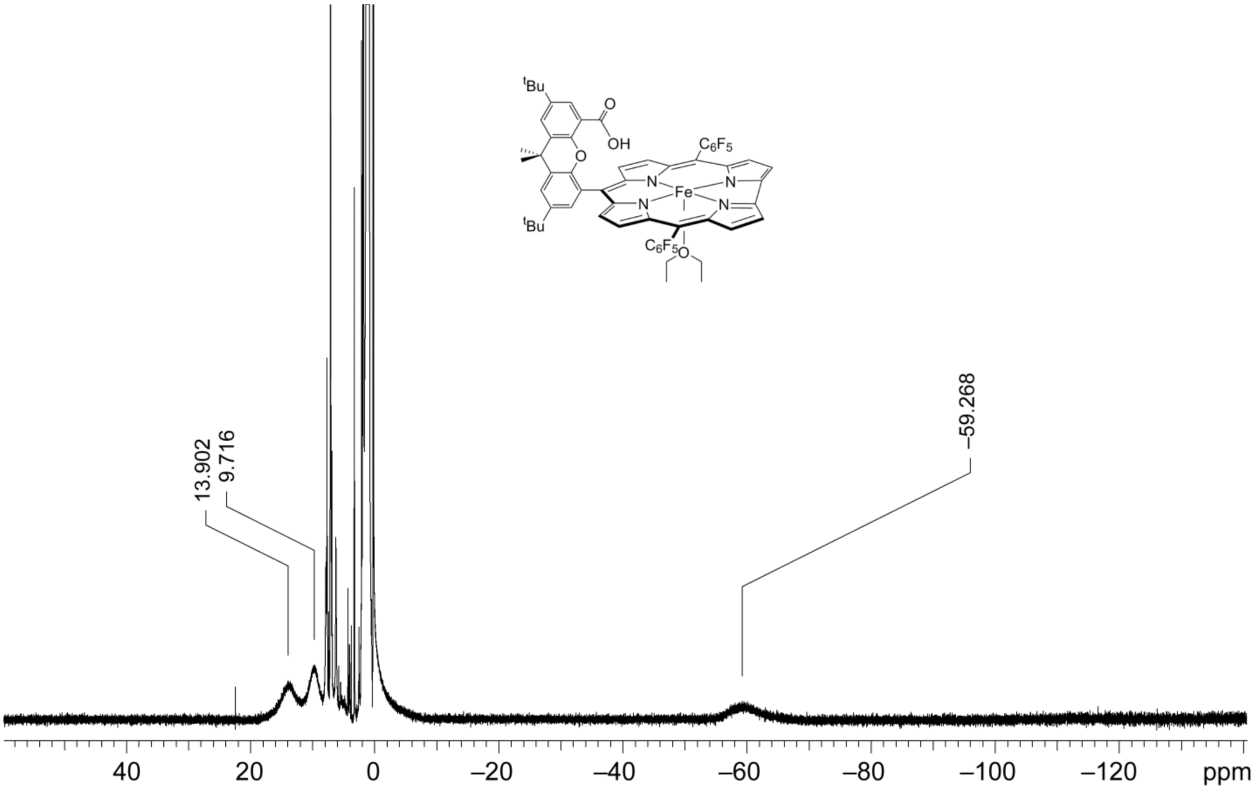

Figure S3. ^{1}H NMR spectrum of **3-Et$_2$O** in C_6D_6 at room temperature.

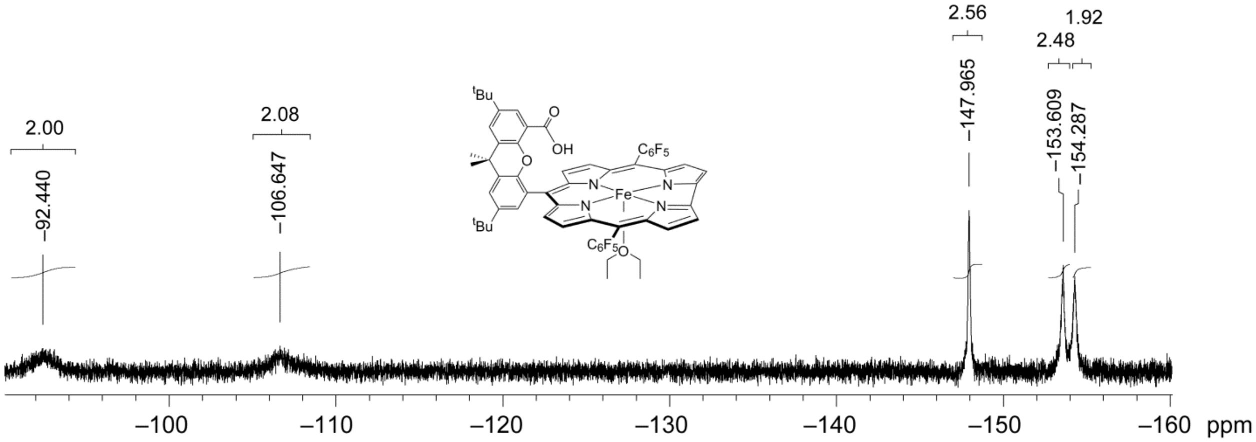

Figure S4. ^{19}F NMR spectrum of **3-Et$_2$O** in C_6D_6 at room temperature.

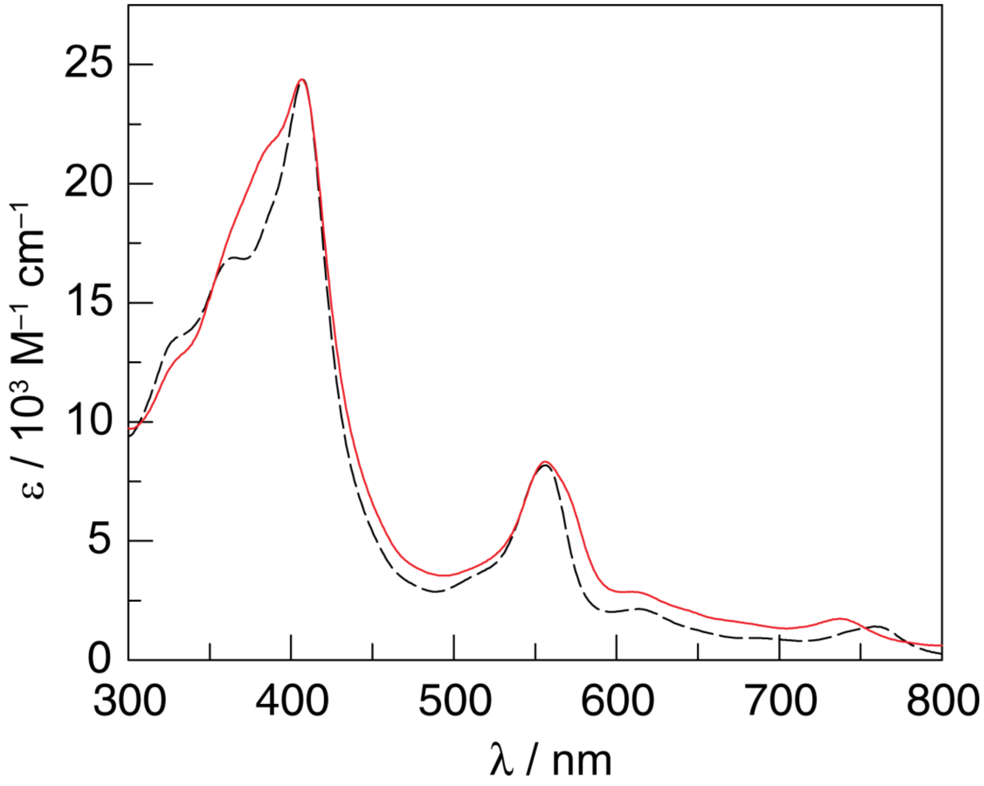

Figure S5. Absorption spectra of **2-py** in pentane (- - -) and in THF (—).

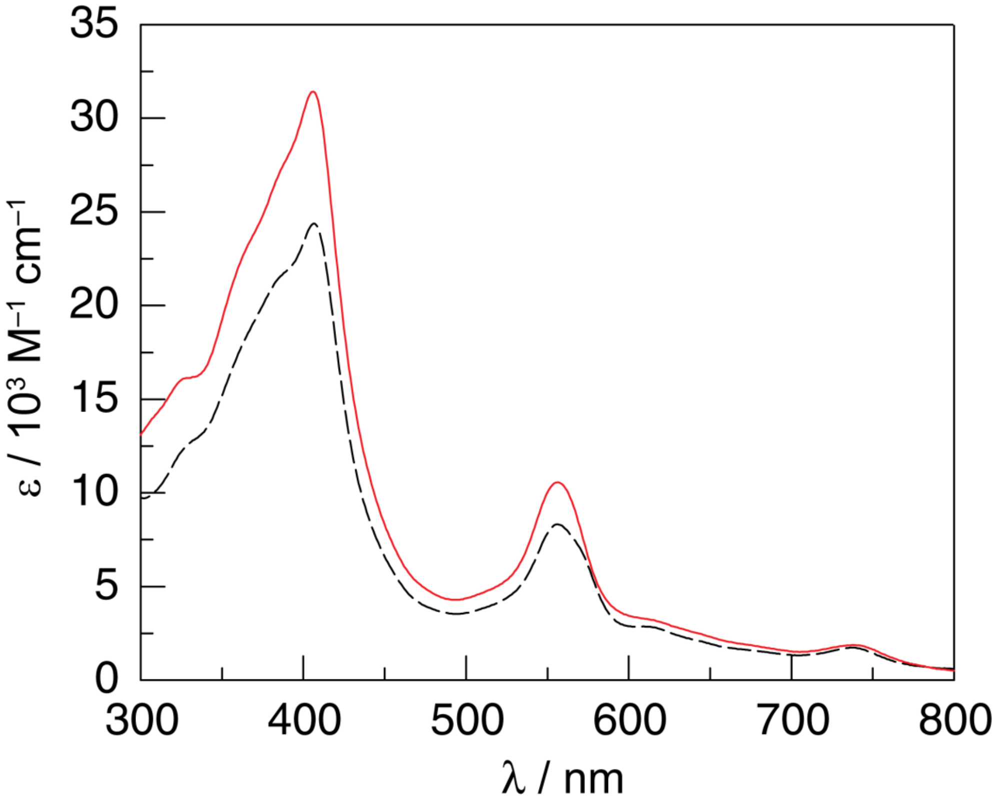

Figure S6. Absorption spectra of **2-py** (- - -) and **3-Et$_2$O** (—) in THF.

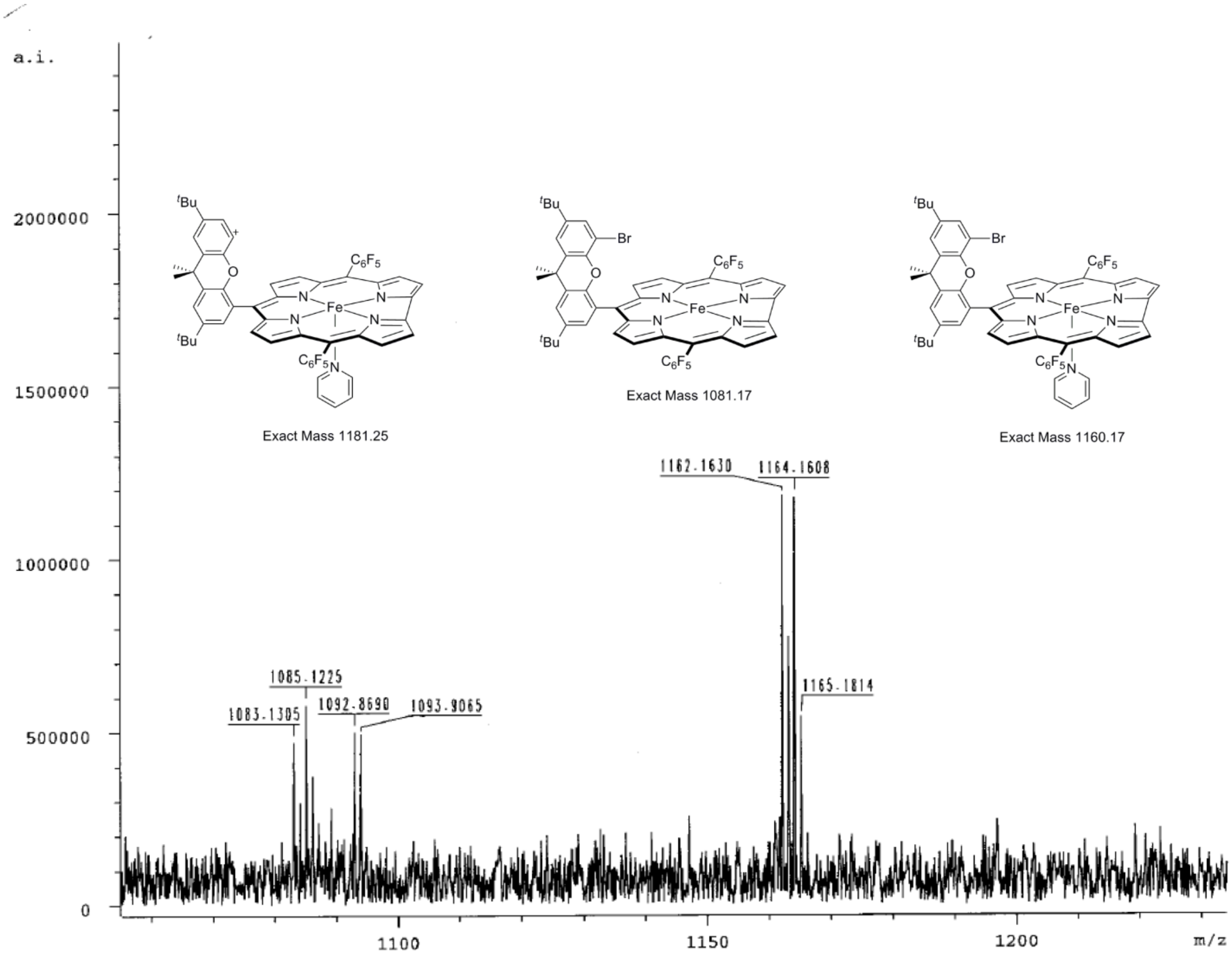

Figure S7. ESI-MS spectrum of **2-py**.

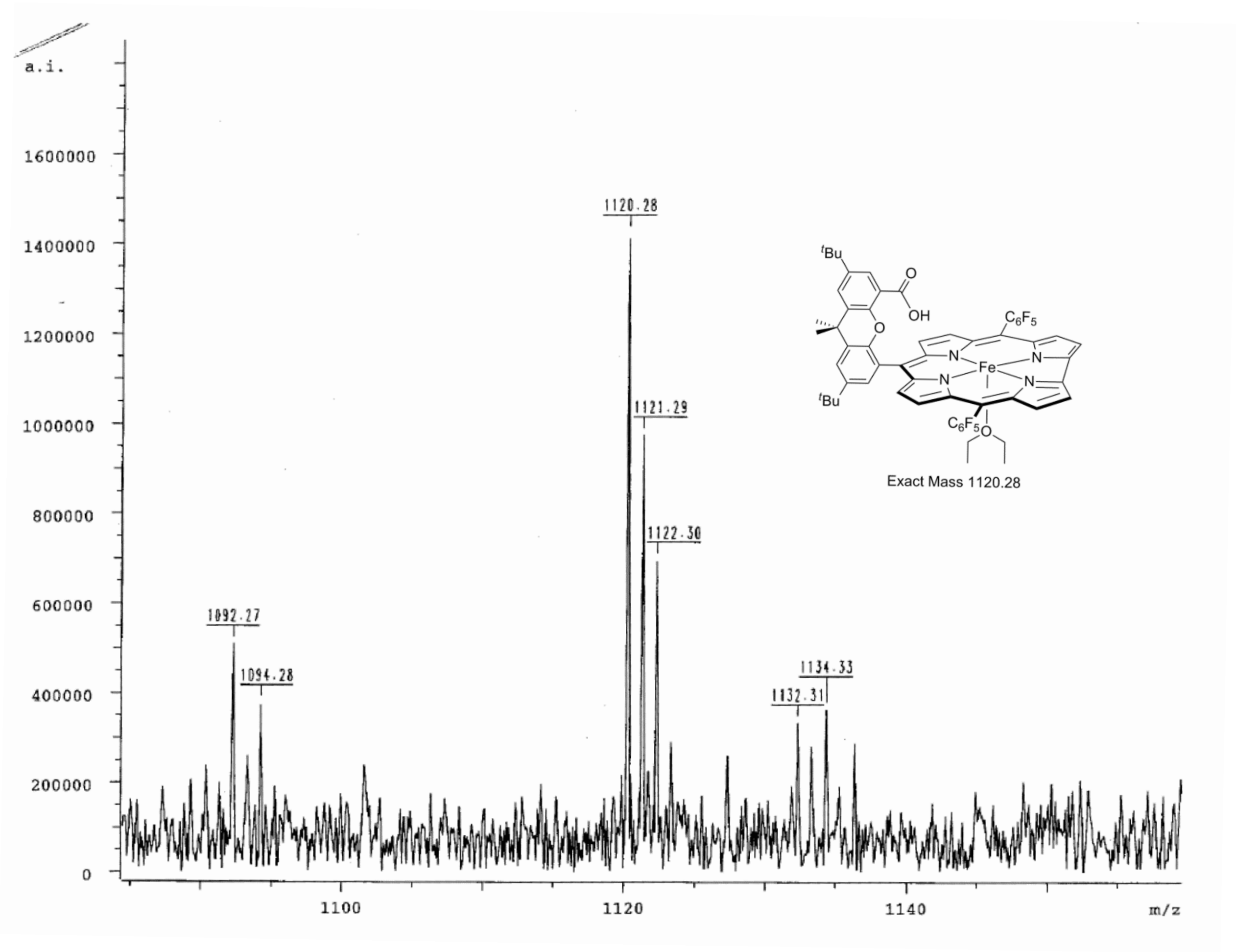

Figure S8. ESI-MS spectrum of **3-Et$_2$O**.