

Electronic supplementary information (ESI)

Materials

Xanthine, xanthine oxidase, ferricytochrome c, EDTA, were purchased from Sigma. Complexes **1-Fe**, **1-Mn**, **1-Cu**, **3-Mn**, **4-Mn** and **5-Mn** were previously reported and available from previous research [13, 16-19].

Synthesis of the iron(III) complex of 2,17-bis-sulfonato-5,10,15-tris(4-methoxy-2,3,5,6-tetrafluorophenyl)corrole, **2-Fe**, was accomplished by the three step procedure outlined below.

Step 1: 5,10,15-tris(pentafluorophenyl)corrole ($H_3(tpfc)$, 200 mg) was dissolved in 100 mL of a sodium methoxide solution (0.5 M in methanol). The solution was heated to reflux for 6 h under argon, followed by evaporation of the solvent. The product was purified by two subsequent silica gel columns (ethanol as eluent for the first column and CH_2Cl_2/n -hexane 2:1 for the second column), affording 160 mg (77% yield) of 5,10,15-tris(4-methoxy-2,3,5,6-tetrafluorophenyl)corrole, $H_3(tpomc)$.

1H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.02 (d, $J = 4.0$ Hz, 2H), 8.73(d, $J = 4.8$ Hz, 2H), 8.54 (d, $J = 4.8$ Hz, 2H), 8.51 (d, $J = 4.0$ Hz, 2H), 4.31 (s, 9H).

^{19}F NMR (282.4 MHz, $CDCl_3$, δ in ppm): -139.6(dd, $J_1 = 22$ Hz, $J_2 = 7$ Hz, 2F), -140.1 (dd, $J_1 = 22$ Hz, $J_2 = 7$ Hz, 4F), -158.2 (dd, $J_1 = 22$ Hz, $J_2 = 7$ Hz, 4F), -158.6 (dd, $J_1 = 22$ Hz, $J_2 = 7$ Hz, 2F).

MS (TOF LD⁻) m/z (%) 832.0 (100%) [M].

Step 2: 100 mg of $H_3(tpomc)$ and 10 mL of sulfuric acid were stirred at room temperature for 4 h, after which the reaction mixture was cooled by an ice bath and treated with small ice chips. The acid was neutralized by sodium carbonate, and the product was freed from the sodium sulfate via addition of ethanol, filtration and evaporation. The product was further purified by a silica gel column (CH_2Cl_2 /ethanol 2:1 as eluent), affording 80 mg (67% yield) of 2,17-bis-sulfonato-5,10,15-tris(4-methoxy-2,3,5,6-tetrafluorophenyl)corrole, $H_3(tpomc)(SO_3H)_2$.

1H NMR (300 MHz, CD_3OD , δ in ppm): 9.67 (s, 1H), 8.57 (s, 1H), 8.38 (d, $J = 4.8$ Hz, 1H), 8.22 (d, $J = 4.5$ Hz, 1H), 8.15 (d, $J = 4.8$ Hz, 1H), 8.14 (d, $J = 4.5$ Hz, 1H), 4.24 (s, 3H), 4.23 (s, 3H), 4.21 (s, 3H).

^{19}F NMR (282.4 MHz, CD_3OD , δ in ppm): -140.9 (dd, $J_1 = 24$ Hz, $J_2 = 8$ Hz, 2F), -141.9 (dd, $J_1 = 24$ Hz, $J_2 = 8$ Hz, 2F), -142.1 (dd, $J_1 = 24$ Hz, $J_2 = 8$ Hz, 2F), -161.6 (dd, $J_1 = 24$ Hz, $J_2 = 8$ Hz, 2F), -162.1 (dd, $J_1 = 24$ Hz, $J_2 = 8$ Hz, 2F), -164.3 (dd, $J_1 = 24$ Hz, $J_2 = 8$ Hz, 2F).

MS (TOF LD⁻) m/z (%) 1011.9 (100%) [$M^{2+} + Na^+$]; MS (Electro-spray) m/z (%) 494.90 (100%) [$M^{2+}/2$].

Step 3: One portion of $FeCl_2 \cdot 4H_2O$ (100 mg) was added at once to a pyridine solution (10 mL) of $H_3(tpomc)(SO_3H)_2$ (100 mg) and the mixture was heated immediately to reflux for 10 min. The product was purified by silica gel column (starting with ether/ethanol 3:1 as eluent and gradually changing to ether/ethanol 1:2), affording 75 mg (71% yield) of $Fe(tpomc)(SO_3H)_2$.

^{19}F NMR (282.4 MHz, CD_3OD , δ in ppm): -109.2 (2F), -119.3 (4F), -153.4 (2F), -154.8 (2F), -157.4(2F).

MS (TOF LD) m/z (%) 1065.9 (100%) [$M^{2+} + Na^+$]; MS (Electro-spray) m/z (%) 521.49 (100%) [$M^{2+}/2$].

Methods

Spectral analyses: The NMR spectra were recorded on Bruker 300 instrument and the electronic spectra were recorded on HP 8452A diode array spectrophotometer.

Cyclic voltammetry: Measurements of lipophilic corroles were performed on a portable USB potentiostat and analyzed with AfterMath software (Pine [Research Instrumentation](#)). The system consists of platinum as working electrode, a platinum wire as counter electrode and Ag/AgCl KCl 3 M as the reference electrode. The experiments were performed in acetonitrile solutions with 0.5 mM substance and 0.1 M of n-tetrabutylammonium perchlorate (TBAP, Fluka, recrystallized three times from absolute ethanol) or tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte. The scan rate was 0.1 Vs⁻¹.

Measurements in phosphate buffer solutions pH 7.4 were performed on EG&G potentiostat model number 263 and 270/250 Research Electrochemistry 4.00 software. The system consists of a glassy carbon electrode as working electrode, calomel electrode as the reference electrode and platinum wire as a counter electrode. Solution contained 0.01 M phosphate buffer pH 7.4 and 0.5 mM substance. The scan rate was 0.1 Vs⁻¹.

All $E_{1/2}$ values are reported in the manuscript vs. NHE by adding 235 mV to the values obtained relative to the Ag/AgCl electrode.

Superoxide Dismutase activity: The two main methods used for evaluating SOD activity were the Cytochrome c assay and pulse radiolysis [4, 20]

Cytochrome c assay: Catalysis of dismutation of superoxide was measured by using Xanthine oxidase plus Xanthine (40 μ M xanthine) as a source of superoxide and cytochrome c (11 μ M) as the indicating scavenger of superoxide. The reduction of cytochrome c was followed at 550 nm. Assays were conducted at 25 ± 1 °C, in 0.05 M phosphate buffer, pH 7.8 and 0.1 mM EDTA. IC_{50} was determined by plotting $(v_0 - v_i) - 1$ versus concentration of corrole metal complex (v_0 is the rate of reduction of cytochrome c by superoxide; v_i is the rate of reduction of cytochrome c inhibited by corrole metal complex) when $(v_0 - v_i) - 1 = 1$. Rate constants for reaction of metal corrole complexes with superoxide were based upon the competition with cytochrome c for reaction with superoxide, using $k_{\text{cyt c}} = 2.6 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Superoxide was produced at rate of 1.2 $\mu\text{M min}^{-1}$ [4, 21, 22].

Pulse Radiolysis: The pulse radiolysis experiments were carried out using a linear electron accelerator in the Hebrew University of Jerusalem. The dose of fast electrons per pulse was controlled by varying the pulse duration of a 200 mA current of 5 eV electrons. Pulse durations ranged from 0.1 to 1.5 μ s. Absorbance data were collected by passing light from 150 W xenon arc lamp three times through a 4 or 1 cm Suprasil cell to give a 12.3 cm or 3 cm pathlength, respectively. Superoxide was formed by pulse irradiation of oxygenated pH 7.4 buffer solutions containing 0.02-0.1 M formate and 0.01 M phosphate buffer. Under such conditions, all the primary radicals formed by the radiation are converted into superoxide anion radical [20].

The experiments were performed under conditions designed for allowing the reactions to obey pseudo-first order kinetics. The experiment condition for the determination of k_{cat} was $[O_2^-] \gg [\text{Metal-complex}]$, while in the experiment of mechanism investigation the relative concentrations were $[O_2^-] < [\text{Metal-complex}]$.

In the experiments where k_{cat} were determined, a sequential series of six pulses were delivered within 100ms in order to obtain measurable OD for the O_2^- formed. The technique was previously described in: I. Zilbermann, E. Maimon, H. Cohen, R. van Eldik, D. Meyerstein *Inorg.Chem.Comm.* 1998, **1**, 46.