Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information of

Influence of the Distal Guanidine Group on Rate and Selectivity of O_2 Reduction by Iron Porphyrin

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1. Experimental Details

1.1. Materials

All reagents were of highest grade commercially available product. Thiourea, sodium hydride (60% in mineral oil), Boc anhydride, $HgCl_2$, triethylamine, hydrochloric acid, collidine Na_2SO_4, NaN_3, and pyrrole were purchased from spectrochem Ltd. Diethyl ether, THF, acetonitrile, dichloromethane, DMF, chlorobenzene, acetic acid, and methanol were purchased from Merck. Anhydrous ferrous bromide ($FeBr_2$), 2,4,6-collidine, 11-Bromo undecan-1-ol ($BrC_{11}OH$), Methane sulfonyl chloride (OMsCl), Potassium thioacetate (KSAc), Octanethiol (C_8SH), potassium hexafluorophosphate (KPF_6), cyclohexanone, benzylalcohol, and all buffers were purchased from Sigma-Aldrich. Disodium hydrogen phosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$), potassium chloride (KCl), imidazole (Imd), conc. Hydrochloric acid (HCl), cyclohexane, and cyclohexanol were purchased from Merck. Au wafers were purchased from Platypus Technologies (1000 Å of Au on 50 Å of Ti adhesion layer on top of a Si(III) surface) and Au discs for the Rotating Ring Disc Electrochemistry (RRDE) experiments were purchased from Pine Instruments, U.S.A.

1.2. Instrumentation

All electrochemical experiments were carried out using CH instruments (model CHI700E, CHI710D Electrochemical Analyzer). Biopotentiostat, reference electrodes, Teflon plate material evaluating cell (ALS Japan) were purchased from CH Instruments. The RRDE set up from Pine Research Instrumentation (E6 series ChangeDisk tips with AFE6M rotor) was used to obtain the RRDE data. All the NMR spectra were recorded on a Bruker DPX-400 or DPX-500 spectrometer at room temperature. The mass spectra were recorded by QTOF Micro YA263 instrument. UV−vis absorption data were taken in an Agilent technologies spectrophotometer model 8453 fitted with a diode-array detector. The EPR spectra were recorded on a JEOL instrument.

1.3. Electrochemical Measurements

1.3.1. Cyclic Voltammetry

All CV experiments were done in pH 7 buffer containing 100 mM $Na_2HPO_4 \cdot 2H_2O$ and 100 mM KPF_6 (supporting electrolyte) using Pt wire as the counter electrode and Ag/AgCl as the reference electrode.

1.3.2. Rotating Disc electrochemistry (RDE)

The RDE measurements were performed on a CHI 700E bi-potentiostat with a Pine Instruments Modulated speed rotor fitted with an E6 series changedisc tip. The graphite surface was cleaned by polishing it uniformly on a Silicon carbide grinding paper. The complex was physiadsorbed on the disc as described above. The RDE experiment was done at different rotations 50 rpm, 100 rpm, 150 rpm, 200 rpm, 250 rpm, and the 2nd order rate constant was calculated using Koutecky–Levich analysis. Koutecky–Levich equation,

$i^{-1} = i_K(E)^{-1} + i_L^{-1}$, where $i_K(E)$ is the potential dependent kinetic current expressed as $nFA[O_2]k_{cat}\Gamma_{catalyst}$, and i_L is the Levich current. i_L is expressed as $0.62nFA[O_2](D_{O2})^{2/3}\,\omega^{1/2}\,\nu^{-1/6}$, where n is the number of electrons transferred to the substrate, F is the faraday constant, A is the macroscopic area of the disc (0.192 cm^2), $[O_2]$ is the concentration of O_2 in an air saturated buffer (0.26 mM) at 25 ° C,[1, 2] k_{cat} is the 2nd order rate of catalytic O_2 reduction, $\Gamma_{catalyst}$ is the catalyst concentration in moles/cm^2 , D_{O2} is the diffusion coefficient of O_2 (2.2 x 10-5 $cm^2\ s^{-1}$) at 25 ° C,ω is the angular velocity of the disc and v is the kinematic viscosity of the solution (0.009 cm2 s -1) at 25 ° C.[3] The plot of i^{-1} at multiple rotation rates vs. the inverse square root of the angular rotation rate ($\omega^{-1/2}$) is linear. The number of electrons (n) involved in the O_2 reduction by a catalytic species may be calculated from the slope and rate of catalysis (k_{cat}) from the intercept of this linear plot.

1.3.3. Partially Reduced Oxygen Species (PROS)

The Pt ring and the Au disc were both polished by alumina powder (grit sizes: 1 µm, 0.3 µm, and 0.05 µm) and electrochemically cleaned and inserted into the RRDE tip (Figure 3A) which was then mounted on the rotor and immersed into a cylindrical glass cell equipped with Ag/AgCl reference and Pt counter electrodes. The collection efficiency (CE) of the RRDE setup was measured in a 2 mM $K_3Fe(CN)_6$ and 0.1 M KNO_3 solution at 10 mV/S scan rate and 300 rpm rotation speed. A 20 ± 2% CE was generally recorded during these experiments (Figure 3B). The potential at which the ring was held during the collection experiments at pH 7 for detecting H_2O_2 was obtained from literature.[4]

1.4. DFT Calculation

The geometry of all compounds is optimized in gradient corrected B3LYP Functional in unrestricted formalism using Gaussian 03 version C03. For hydroperoxide models, Fe, N and O atoms are optimised using 6-311G(d) basis set and 6-31G(d) for other all atoms. For the protonated hydroperoxide models all atoms are optimized with 6-311G(d) basis set in a Polarizable continuum model with water.[5, 6] An energy minimum is confirmed by performing frequency calculation on the fully optimized structure using the same basis set used for optimization to ensure no imaginary mode is present for all these compounds. The final energy calculations were performed using 6311+G(d) basis set on all atoms in PCM model using water as a solvent and convergence criterion of 10^{-10} Hartree.[7] All the ferric-superoxide geometries have been optimised considering broken symmetry approximation using the same basis set as mentioned above and B3LYP functional for all atoms. To obtain the broken symmetry ground state of the Fe-O_2 adducts, first the triplet wave function was obtained from single point (SP) calculation. The broken symmetry singlet ground state could be obtained by performing a singlet calculation using the triplet wavefunction as an initial guess. The geometries were then optimized by vertically shifting the virtual orbitals using the Vshift keyword.

2. Synthesis:

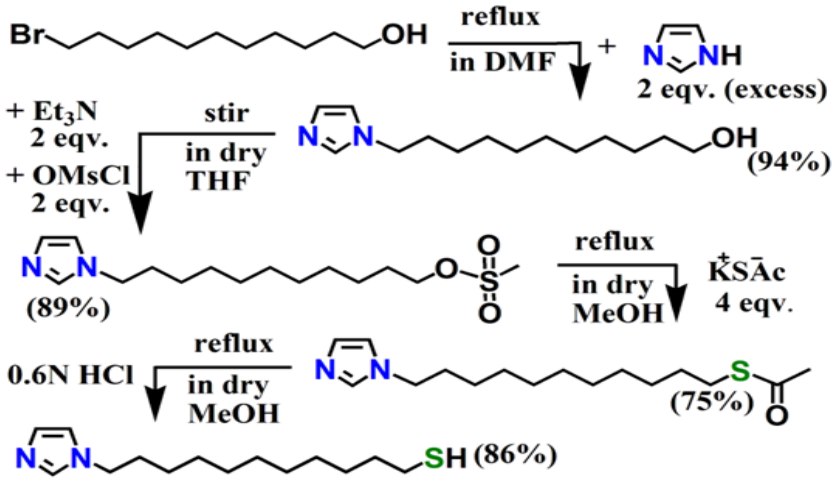
2.1. 11-Imidazoyl Undecan-1-thiol (ImdC_{11}SH)

11-Imidazoyl Undecan-1-thiol was synthesised according to the reported procedure (Scheme S1).[8]

^{1}H NMR (500 MHz, $CDCl_3$): 1.19 (m, 16H), 1.31 (m, 2H), 2.60 (t, 1H, J=7.5 Hz), 2.87 (t, 1H, J=7.5 Hz, 7.0 Hz), 4.03 (t, 2H, J=7.5 Hz, 7.0 Hz), 6.95 (s, 1H), 7.13 (s, 1H), 8.31 ppm (s, 1H).

ESI-MS (+ve ion mode, methanol): m/z = 254.03 (93%), [M]+; m/z = 285.98 (100%), [M+CH_3OH]

Scheme S1. Schematic representation of the synthesis of ImdC_{11}SH



2.2. *o*-Monoguanidiniotetraphenyliron(III)-Porphyrin (Fe^{III}Cl-MARG)

Fe-Marg was synthesised according to the reported procedure.[9]

Maximum yield: (62 mg, 90 ±2%)

MARG: Elemental analysis calculated (%) (C45H34N7Cl): C 76.31, H 4.84, N 13.84. Found: C 76.10, H 5.01, N 13.79. 1H NMR (500 MHz, CDCl3, 25°C): δ, ppm = 8.98−9.12 (m, 8H), 8.540−8.55 (d, 1H), 8.41−8.46 (dd, 6H), 7.91−7.95 (m, 10H), 7.54−7.57 (m, 2H), 5.28 (s, 1H), 7.86 (s, 2H) − 2.37 (s, 2H)

ESI-MS (positive ion mode in ACN): m/z (%) = 672.09(100). Fe-MARG: Elemental analysis calculated. (%) (C45H32N7Cl2Fe): C 67.77, H 4.04, N 12.29 Found: C 67.50, H 4.10, N 12.20. 1H NMR (500 MHz, $CDCl_3$,25 °C): δ, ppm = 78.80 (β-pyrrolic protons). UV−vis (ACN) λmax = 415, 510, 588, 645 nm. UV−vis (5%v/v H2O-ACN) λmax = 415, 510, 567, 620 nm. ESI-MS (positive ion mode in ACN): m/z (%) = 725.156(100).

2.3. *o*-Monomethylguanidiniotetraphenyliron(III)-Porphyrin ($Fe^{III}Cl$-MeMARG)

N-Methyl-N'-tert-butoxycarbonylthiourea: A mixture of N-methylthiourea(1.69 g, 18.7 mmol) and hexane washed NaH (0.9 g, 22.5 mmol, 60% in mineral oil) was added in 250 mL of dry THF and was stirred for 15 min under Ar at 273K. Di-tert-butyl dicarbonate (4.25 g, 19.5 mmol) was added in a dropwise manner. An off-white slurry formed within 15 min, which was stirred for another 3 h at room temperature. The reaction mixture was quenched with 50 mL of saturated aqueous $NaHCO_3$. Excess THF was evaporated and extracted with ethyl acetate. The ethyl acetate layer was dried over Na_2SO_4 and concentrated under vacuum producing a colourless slurry. The reaction mixture was separated on silica column with ethyl acetate/hexane (1: 5) to afford 2.11 g (59%) of desired product. ^1H NMR ($CDCl_3$) δ 9.68 (1H, br s), 7.92 (1H, br s), 3.17 (3H, d), 1.48 (9H, s).

Ligand MeMARG: o-monoaminotetraphenyl porphyrin (629mg,1mmol), N-Methyl-N'-tert-butoxycarbonylthiourea (330mg,1.2mmol) and 3.5 equivalents of triethylamine (726 µl, 5.25mmol) 1.2 equivalents of mercury (II) chloride (489 mg, 1.8mmol) were added in dimethylformamide (5 mL) at 273K in stirring condition. The temperature was maintained at 273K for 30 min and continued to stir for next 24hr at room temperature. The reaction mixture was filtered through Celite column to isolate the ligand from HgS. The celite column was rinsed with Et_2O and the organic layer was washed first with saturated ammonium chloride and then with brine (50 mL). The organic layer was dried over anhydrous MgSO4. Dark purple coloured ligand MeMarg was collected by evaporating Et2O. We avoided any chromatographic separation at this

stage. Ligand (2) was diluted with 5mL MeOH followed by addition of 1mL conc HCL and continued to stir for 12hrs. The reaction mixture was neutralized by 33% v/v ammonia solution followed by evaporation of MeOH. The reaction mixture was separated with DCM from DCM-water bilayer. The organic layer was dried over Na_2S0_4 and concentrated under vacuum.

Fe-MeMARG: To a solution of the MeMarg (67 mg, 0.08 mmol) in 20 mL of dry degassed THF, 2,4,6-collidine (25 µL, 0.195 mmol) was added and was stirred for 10 min in a glovebox. $FeBr_2$ (70 mg, 0.328 mmol) dissolved in THF was added dropwise and was stirred for 20 h. The reaction mixture was worked up with 0.5 N HCl followed by the addition of DCM. The organic layer was washed with brine solution and collected. It was dried over anhydrous Na_2SO_4 and purified by column chromatography with neutral alumina using 5% v/ v MeOH−DCM mixture as eluent (Scheme S2). Yield: (61mg, 85±2%)

MeMarg: ^{1}H NMR (400 MHz, CDCl3, 25°C): δ, ppm = 8.85-8.89 (m, 8H), 8.544-8.554 (d, 1H), 8.137-8.269 (dd, 6H), 7.984-8.102 (m, 10H), 7.58-7.67 (m, 2H), 5.032 (s, 1H), 1.351 (s, 3H), -2.826 (s, 2H) ESI-MS (positive ion mode in ACN): m/z (%) = 686.28(100) (MH^+). Fe-MeMarg: Elemental analysis calculated. (%) ($C_{47}H_{35}N_7Cl_4Fe$): C 63.04, H 3.94, N 10.95 Found: C 66.60 H 3.81 N 8.95. ^{1}H NMR (400 MHz, CDCl3, 25°C): δ, ppm = 78.80 (β-pyrrolic protons). ESI-MS (positive ion mode in ACN): m/z (%) = 775.23(100) (MH^+). UV-Vis (in ACN) λ_{max} = 416, 510, 574, 612

2.4. *o*-Monophenylguanidiniotetraphenyliron(III)-Porphyrin ($Fe^{III}Cl$-PhMARG)

N-phenyl-N'-tert-Butyloxycarbonylthiourea: A mixture of N-phenylthiourea (1.75g, 23.03 mmol) and hexane washed NaH (4.14 g, 103.6 mmol, 60% in mineral oil), was added in THF (250 mL) and stirred for 15 minutes. After that di-tert-butyl dicarbonate (11.04 g, 50.66 mmol) was added dropwise over the period of 15 minutes. An off-white slurry formed within 15 min, which was stirred for another 12 h at room temperature. The reaction mixture was quenched with 50 mL of saturated aqueous $NaHCO_3$. Excess THF was evaporated and extracted with ethyl acetate. The ethyl acetate layer was dried over Na_2SO_4 and concentrated under vacuum producing a colourless slurry. The reaction mixture was separated on silica column with ethyl acetate/hexane

(1: 7).1H NMR (400 MHz, CDCl3): δ 11.55 (br s, 1H,), 8.24 (br s, 1H), 7.66 (d, 2H), 7.42 (dd, 2H), 7.28 (t, 1H CH), 1.55 (s, 9H).

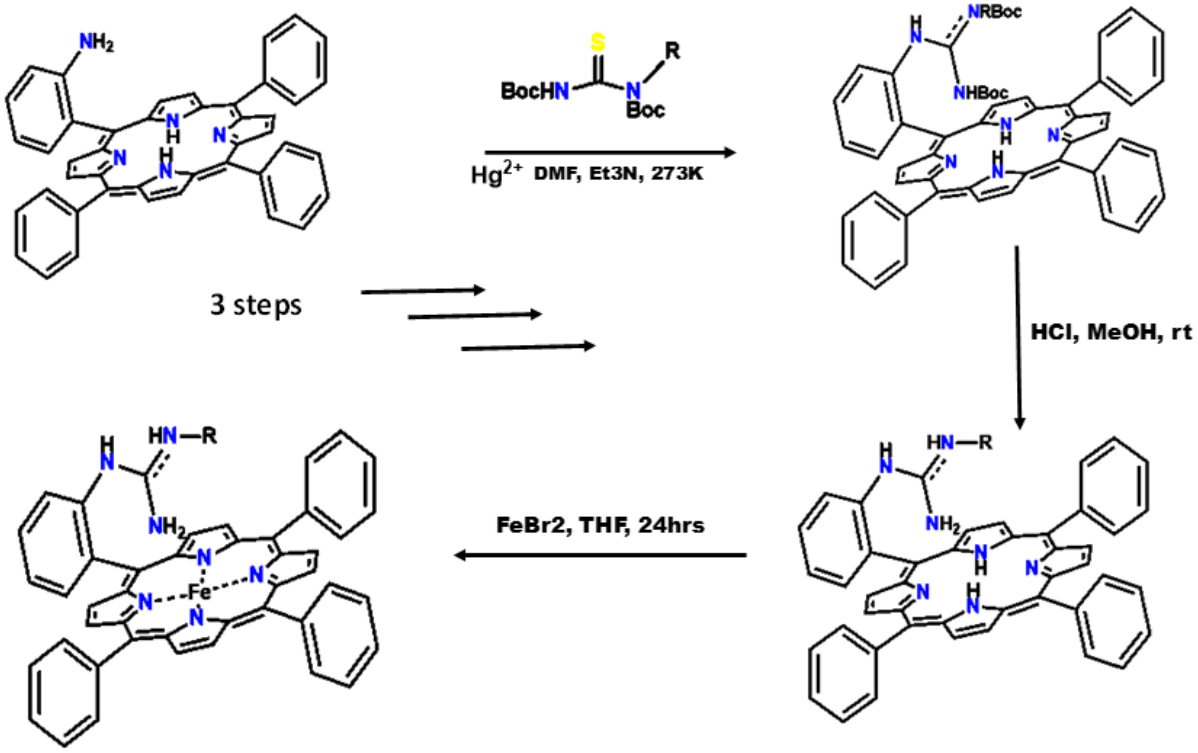
Ligand PhMARG: o-monoaminotetraphenyl porphyrin (629mg, 1mmol), N-Methyl-N'-tert-butoxycarbonylthiourea (330mg,1.2mmol) and 3.5 equivalents of triethylamine (726 µl, 5.25mmol) 1.2 equivalents of mercury (II) chloride (489 mg, 1.8mmol) were added in dimethylformamide (5 mL) at 273K in stirring condition. The temperature was maintained at 273K for 30 min and continued to stir for next 24hr at room temperature. The reaction mixture was filtered through Celite column to isolate the ligand from HgS. The celite column was rinsed with Et_2O and the organic layer was washed first with saturated ammonium chloride and then with brine (50 mL). The organic layer was dried over anhydrous $MgSO_4$. Dark purple coloured ligand MeMarg was collected by evaporating Et_2O. We avoided any chromatographic separation at this stage. Ligand (2) was diluted with 5mL MeOH followed by addition of 1mL conc HCL and continued to stir for 12hrs. The reaction mixture was neutralized by 33% v/v ammonia solution followed by evaporation of MeOH. The reaction mixture was separated with DCM from DCM-water bilayer. The organic layer was dried over Na_2S0_4 and concentrated under vacuum.

Fe-PhMARG: To a solution of the PhMarg (71 mg, 0.08 mmol) in 20 mL of dry degassed THF, 2,4,6-collidine (25 µL, 0.195 mmol) was added and was stirred for 10 min in a glovebox. FeBr2 (70 mg, 0.328 mmol) dissolved in THF was added dropwise and was stirred for 20 h. The reaction mixture was worked up with 0.5 N HCl followed by the addition of DCM. The organic layer was washed with brine solution and collected. It was dried over anhydrous Na2SO4 and purified by column chromatography with neutral alumina using 5% v/ v MeOH−DCM mixture as eluent (Scheme S2). Yield: (67mg, 88±2%)

PhMarg: ^{1}H NMR (400 MHz, CDCl3, 25°C): δ, ppm = 8.925-9.049 (m, 8H), 8.341-8.387 (d, 1H), 8.17-8.24 (dd, 6H), 7.632-7.847 (m, 10H), 7.450-7.463 (m, 2H), 6.415 (s, 1H), 6.265 (s, 2H), 5.814 (s, 2H) 5.295 (s, 1H), -2.539 (s, 2H) ESI-MS (positive ion mode in ACN): m/z (%) = 748.29(100).(MH^+) Fe-PhMarg: Elemental analysis calculated. (%) (C51H36N7ClFe): C 73.08, H 4.33, N 11.70 Found: C 72.07 H 3.68 N 10.91. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ, ppm = 78.80 (β-

pyrrolic protons). ESI-MS (positive ion mode in ACN): m/z (%) = 837.25(100) (MH^+). UV-Vis (in ACN) λ_{max} = 411, 515, 568, 612

Scheme S2. Synthetic scheme of the desired complexes **Fe-MeMARG** and **Fe-PhMARG** (R= Me, Ph accordingly)



2.5. Fe-Marg-N-MeImd

Fe-Marg was synthesised according to the reported procedure.[9] At first 20 mg of Fe-Marg was dissolved in DCM. To that solution almost 5 eq. of N-Methylimidazole solution (10 µL) was added. The mixture was then sonicated. To the mixture excess pentane was added. The mixture was then centrifuged for 15 mins. and the extract was collected. To the extract a mixture of pentane and DCM was added. The mixture was again centrifuged for some time. Then a red extract was obtained which was monitored through UV-Vis spectra to confirm the formation of Fe-Marg-N-MeImd (Fig. S2).

Fe-Marg-N-MeImd: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ, ppm = 81.405 (β-pyrrolic protons). UV-Vis (in ACN) λ_{max} = 324, 413, 558

3. Construction of the Electrodes

3.1 Formation of mixed SAM (ImdC_{11}SH SAM)

Au wafers and discs were cleaned electrochemically by sweeping several times between 1.5 V to −0.3 V in 0.5 M H_2SO_4. 10mL 0.4 mM SAM solution in ethanol was prepared using 0.2 mole fraction of the linker ImdC_{11}SH and C_8SH was used as the diluent. Au wafers and discs were rinsed with milli-q water, ethanol, purged with N_2 gas and immersed in the depositing solution for 48 hours.

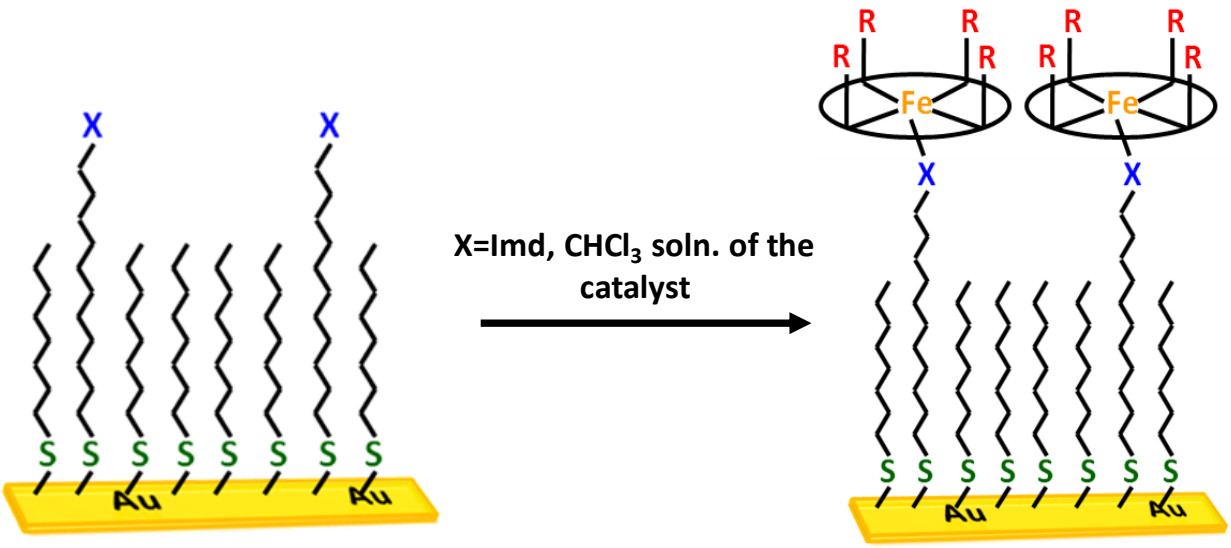
Similarly, 10 mL 0.4mM C_8SH and C_{16}SH SAM was prepared with the diluent C_8SH and C_{16}SH.

3.2. Attachment of the Catalysts on the ImdC_{11}SH SAM

Au wafers and discs were taken out before experiments and rinsed with ethanol followed by milli-q water and then dried with N_2 gas. The wafers were then inserted into a Plate Material Evaluating Cell (ALS Japan), and the discs were mounted on a platinum ring disc assembly (Pine Instruments, U.S.A.). Solutions of the catalysts were prepared in chloroform. Chloroform solution of the catalyst was drop casted over SAM functionalised Au discs and wafers and kept

for 2 hours. After the time the surfaces were thoroughly rinsed with chloroform, ethanol, and triple distilled water before the electrochemical experiments. This is the way to form bio inspired electrode (scheme 2).

Scheme S3. Formation of bio-inspired electrode using mixed SAM ImdC_{11}SH and catalysts solution.

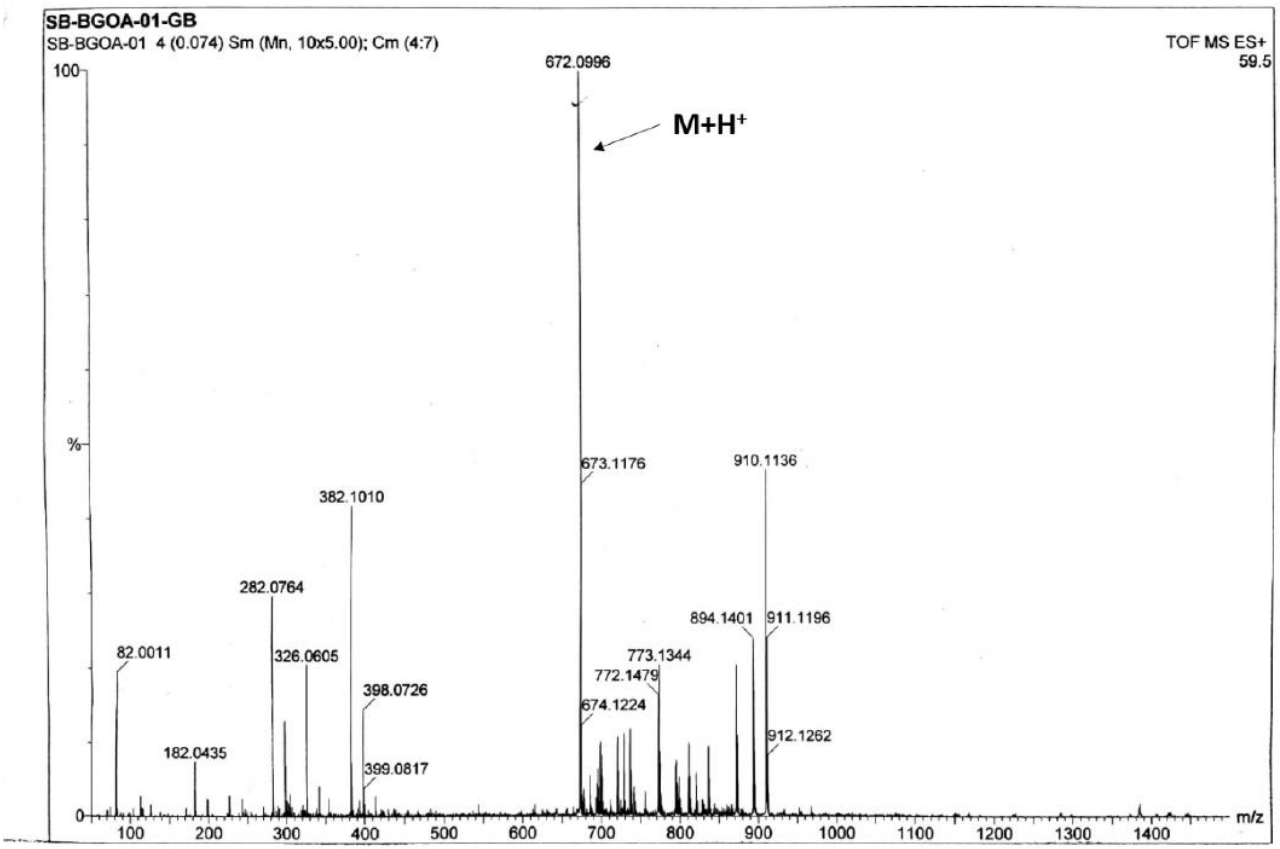


3.3. Physiadsorption of the catalyst on EPG, C_8SH, C_{16}SH SAM covered Au electrodes

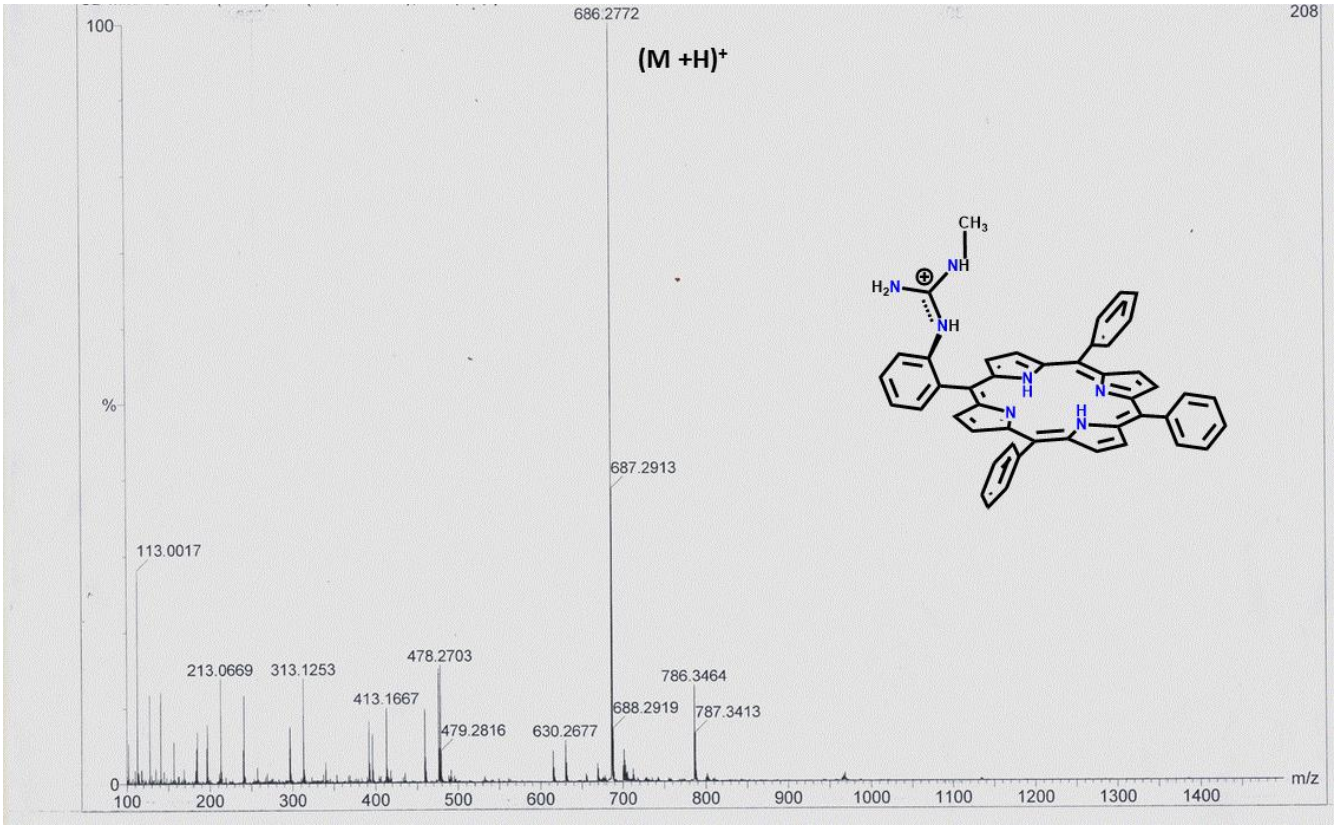
A 50 µL portion of catalyst from a 1 mM solution of the respective catalysts in chloroform (CHCl3) is deposited on a freshly cleaned EPG electrode, or on Au discs taken out from C8SH and C16SH SAM solution and mounted on a RDE setup. After the evaporation of the solvent, the surface is thoroughly dried with N_2 gas and sonicated in ethanol. Finally, before using it for electrochemical experiments, the modified electrodes are washed with milli-q water.

4. Spectral data.

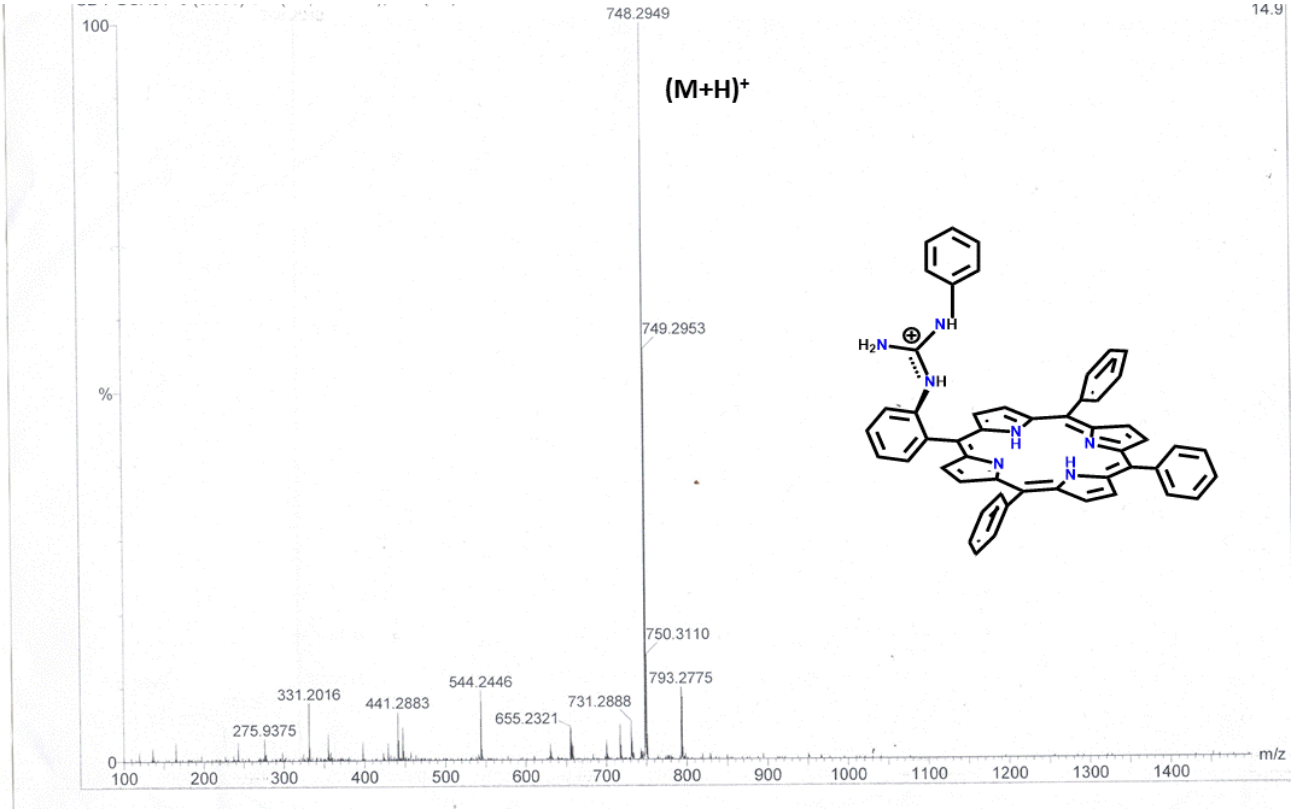
4.1.1. ESI-MS of free ligand MARG



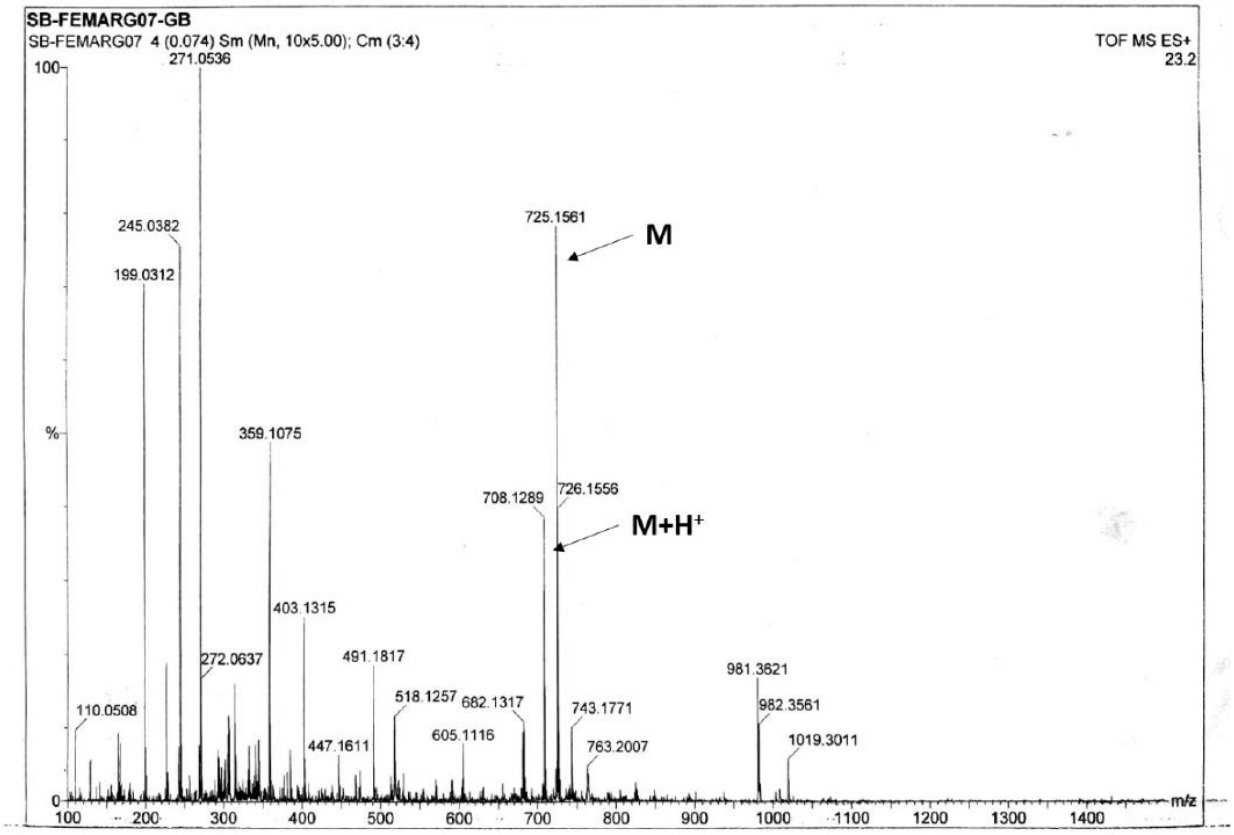
4.1.2. ESI-MS of free ligand MeMARG



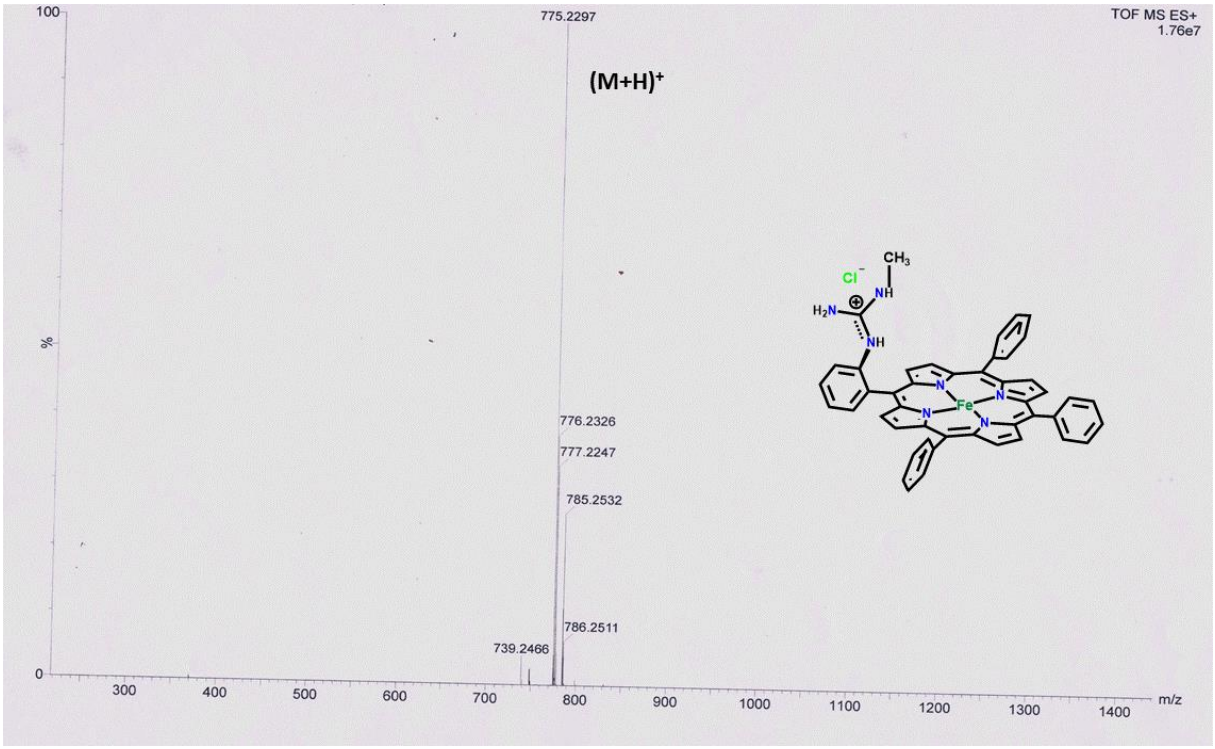
4.1.3. ESI-MS of free ligand PhMARG



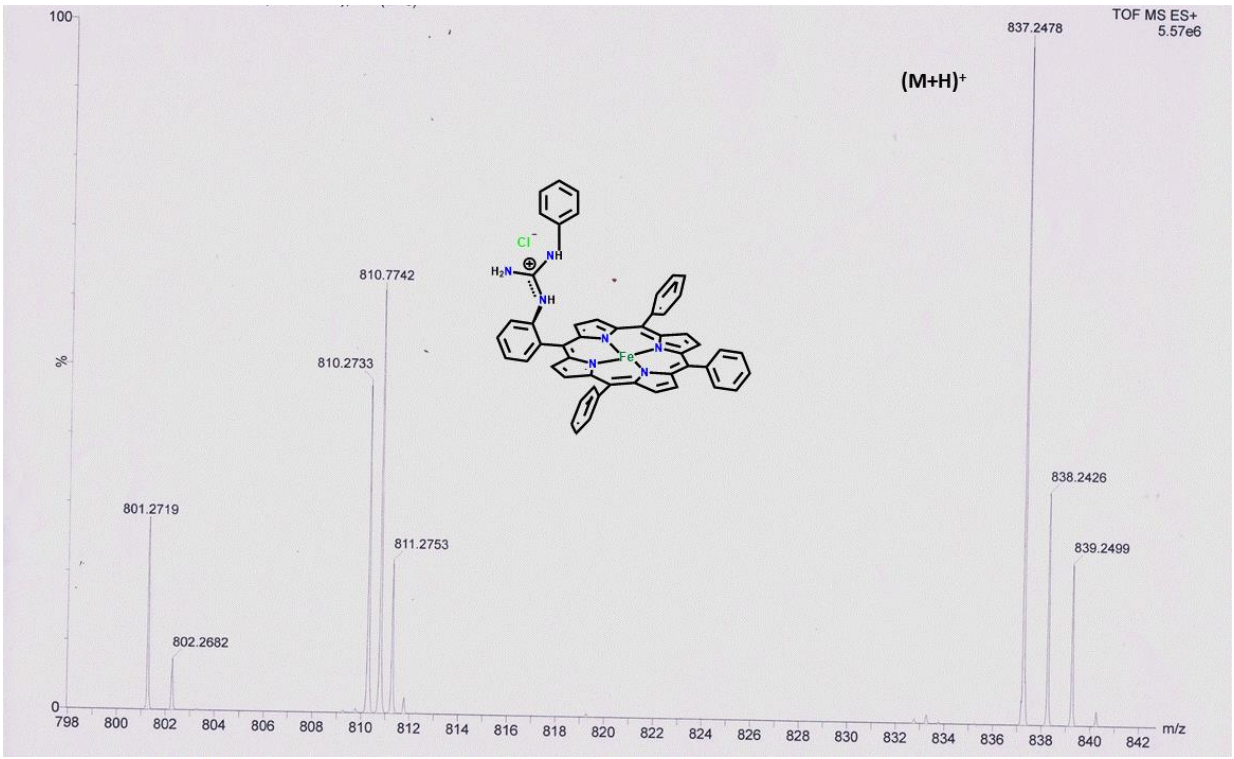
4.1.4. ESI-MS of Fe-MARG



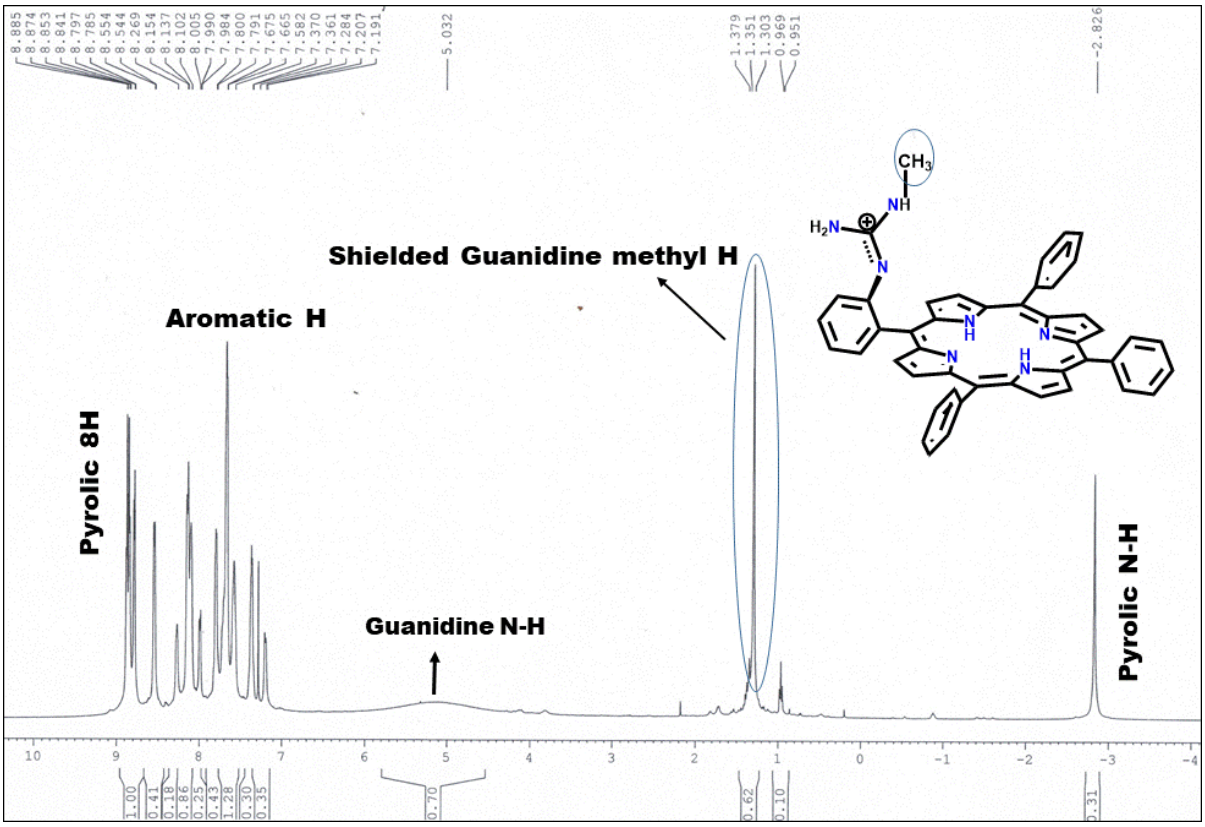
4.1.5. ESI-MS of Fe-MeMARG



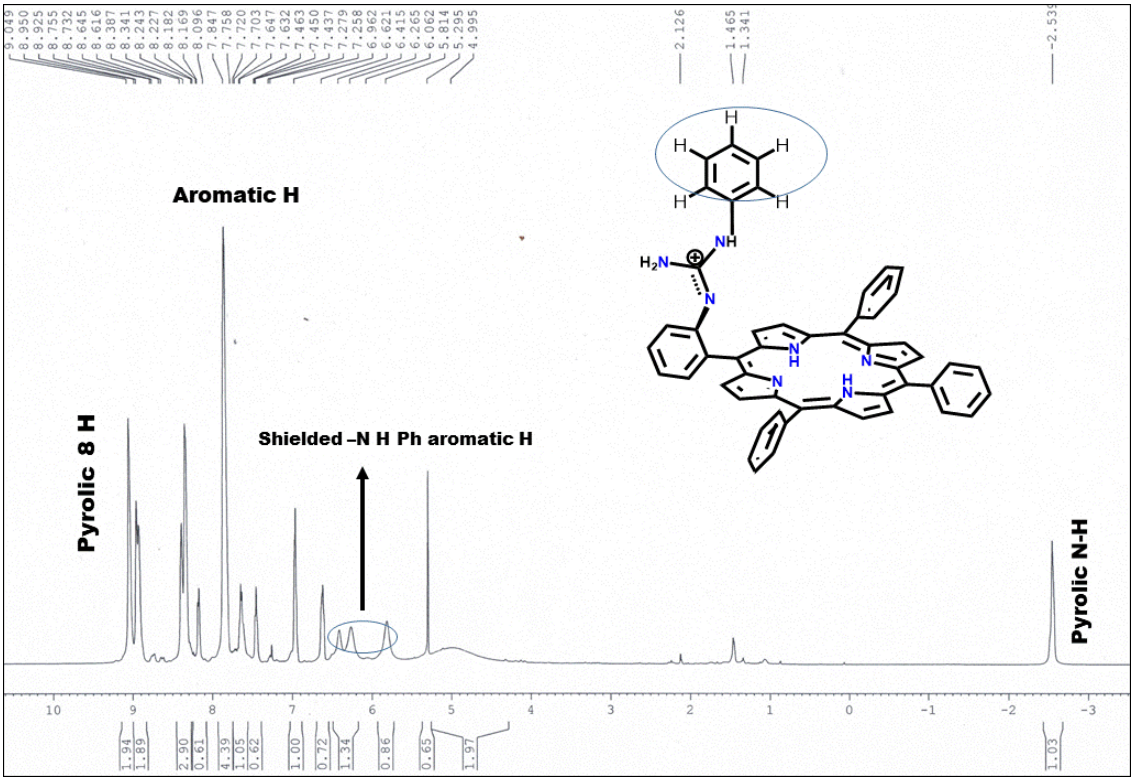
4.1.6. ESI-MS of Fe-PhMARG



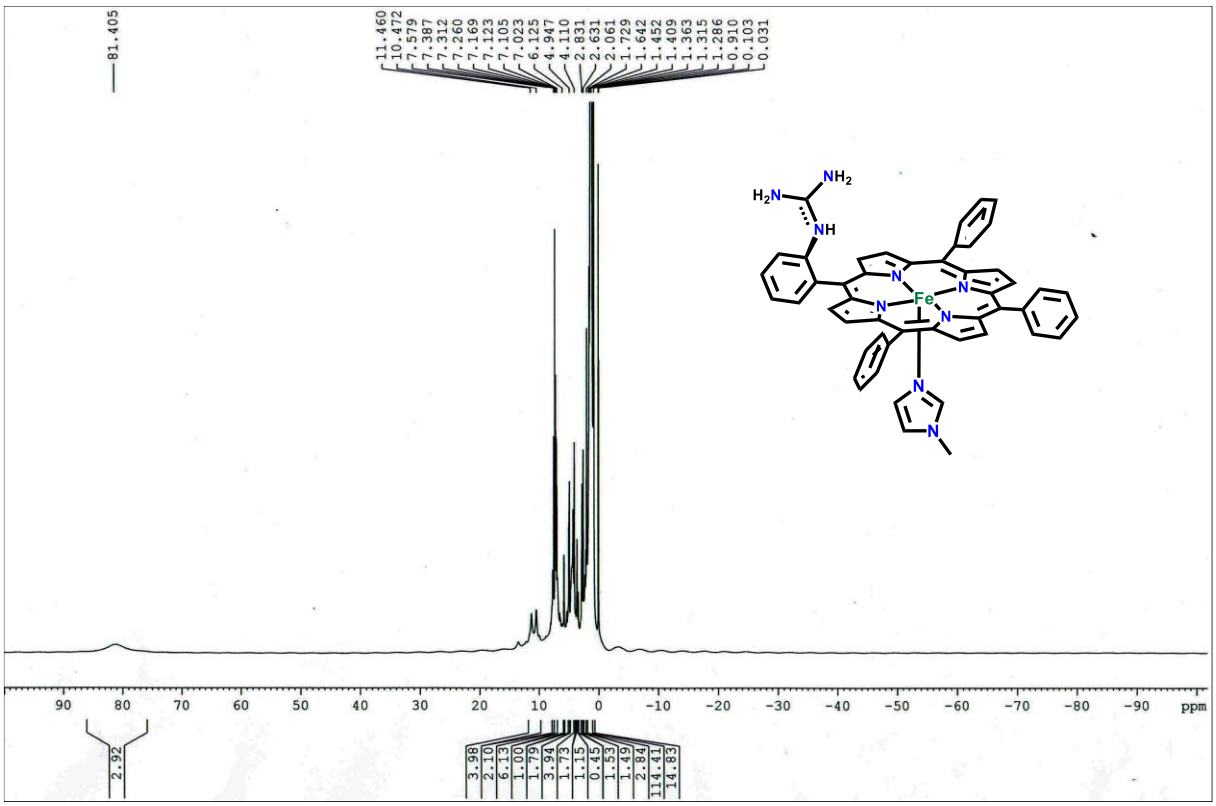
4.2.1. ^{1}H NMR ($CDCl_3$, 400 MHz) of free ligand MeMARG



4.2.2. 1H NMR (CDCl3, 400 MHz) of free ligand PhMARG



4.2.3. 1H NMR (CDCl3, 400 MHz) of Fe-MARG-N-MeImd



4.3. UV-Vis absorption spectra

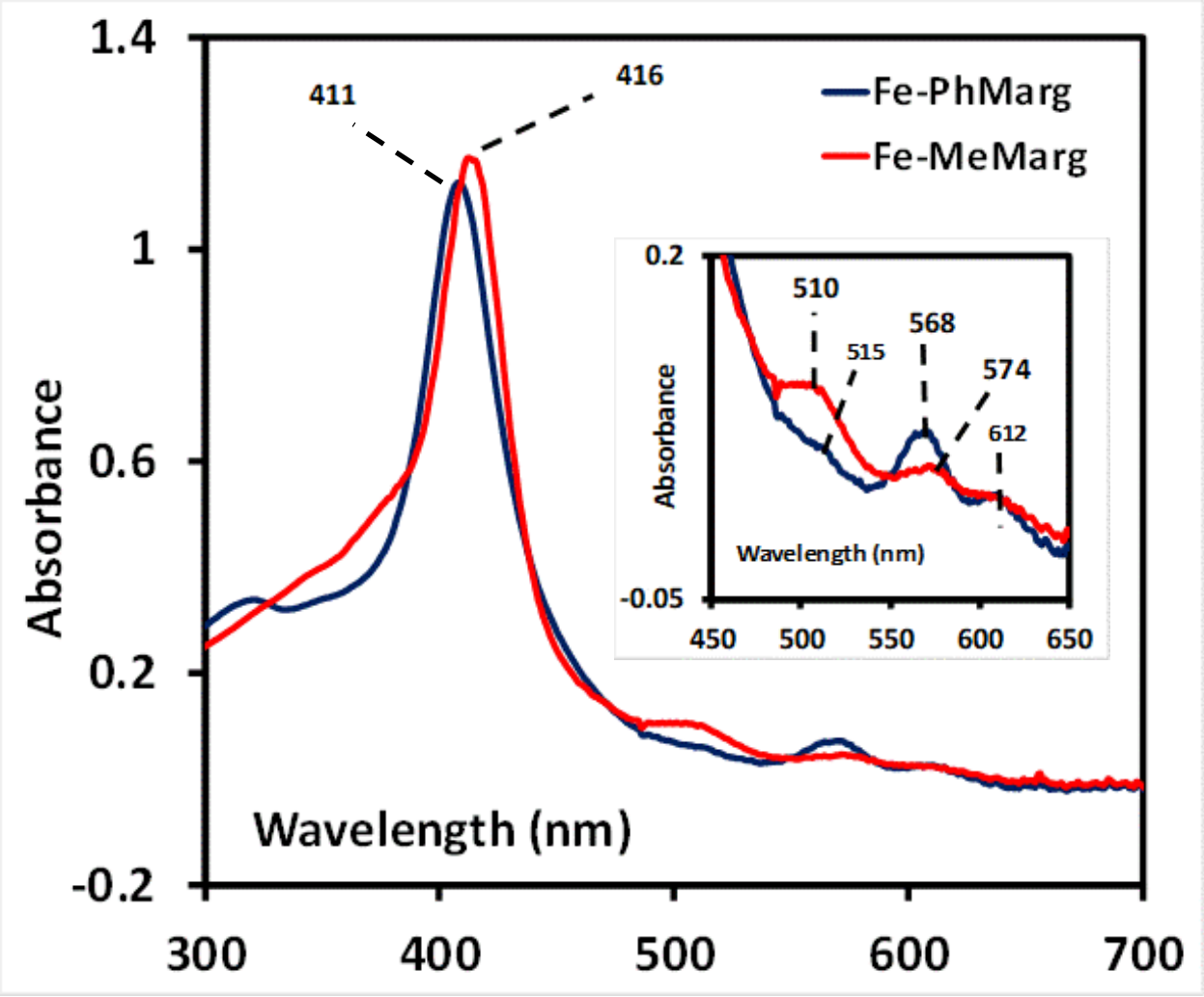


Figure S1. Absorption spectra in the UV-Visible region for $Fe^{III}Cl$-MeMarg (red) and $Fe^{III}Cl$-PhMarg (blue) complex in acetonitrile solvent. Inset shows the Q-band region of the complexes.

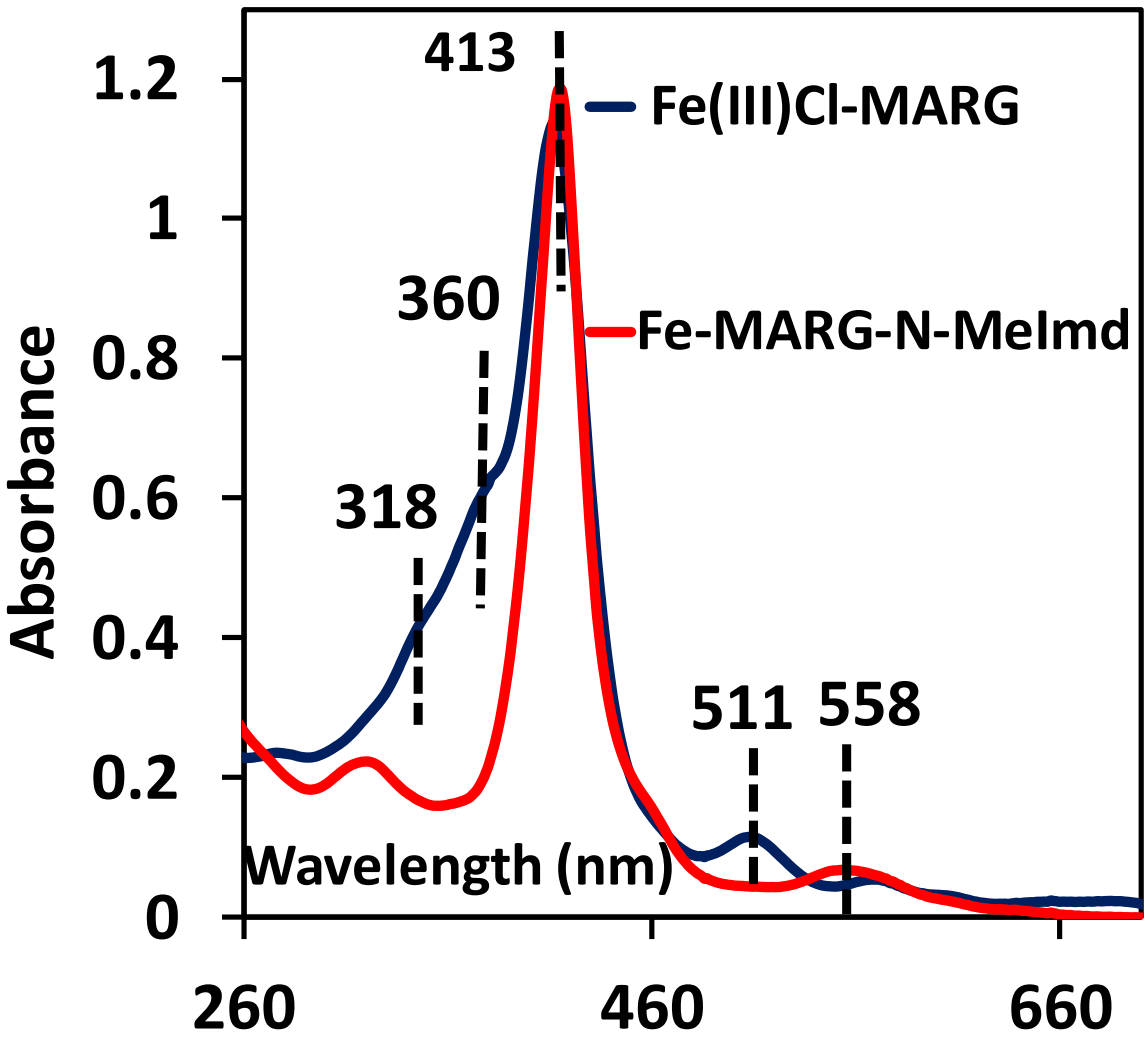


Figure S2. Absorption spectra in the UV-Visible region for Fe-Marg-N-MeImd (red) and Fe^{III}Cl-Marg (blue) complex in acetonitrile solvent.

4.4. Resonance Raman Spectra

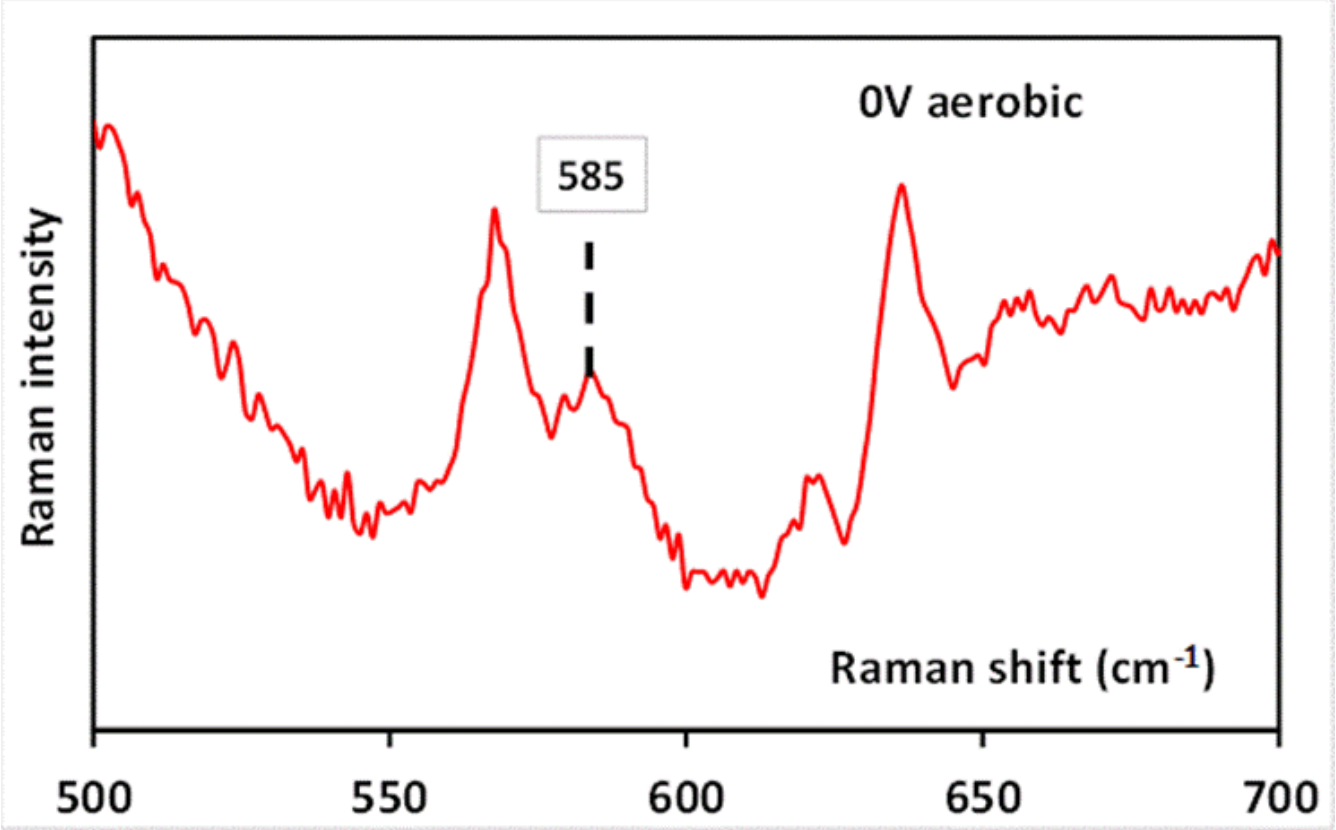


Figure S3. The metal-ligand region of the SERRS data of $Fe^{III}Cl$-MARG physiadsorbed on C8SH SAM modified Ag electrode at pH7 buffer with a constant rotation of 200 rpm.

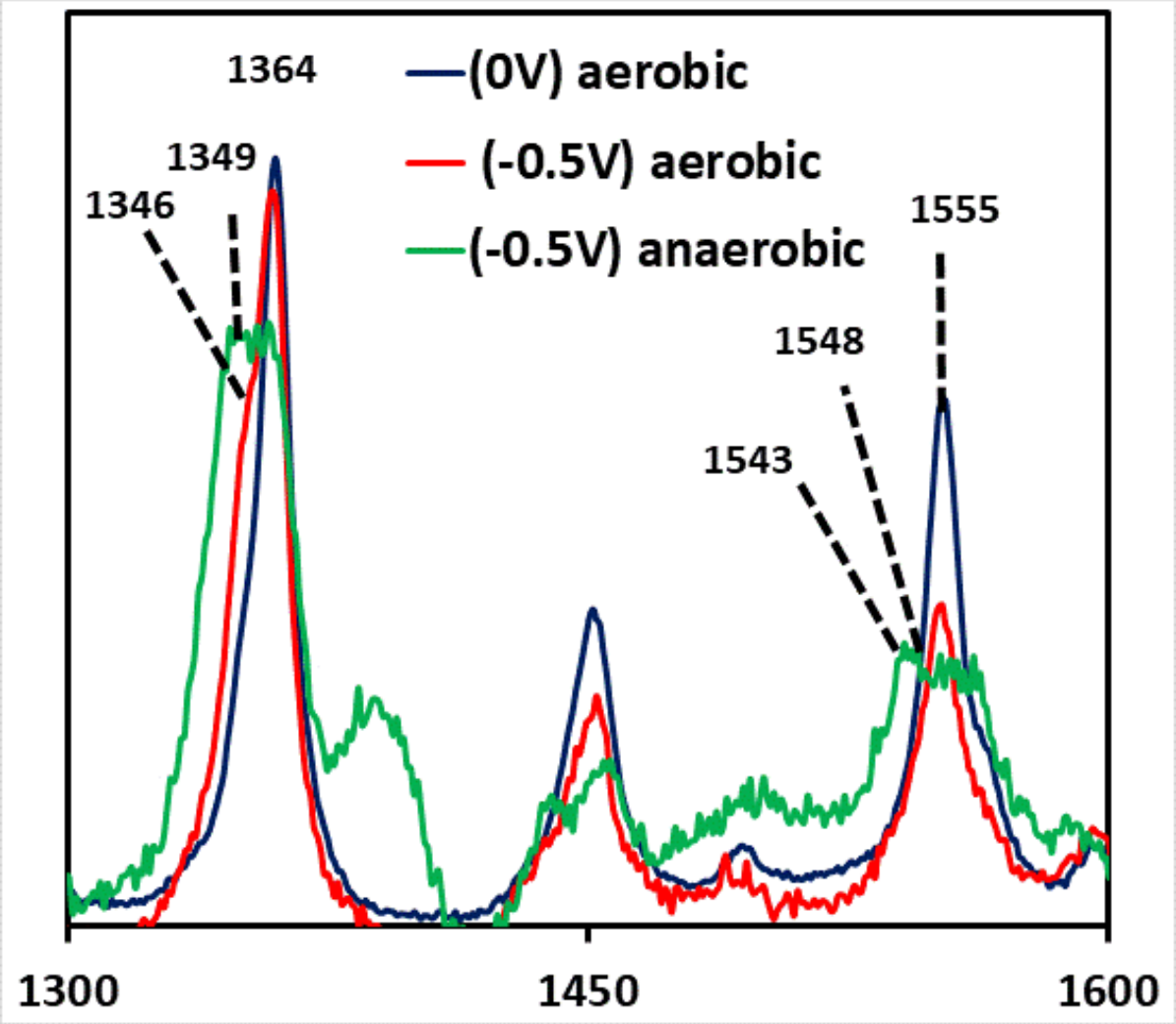


Fig.S4. SERRS-RDE data of $Fe^{III}Cl$-MARG physiadsorbed on a C_8SH modified Ag disc, under oxidising potential (0V, blue) and reducing potential (-0.5V, red) in pH7 phosphate buffer under aerobic condition and at reducing potential in pH7 phosphate buffer under anaerobic condition (green) at a constant rotation rate 200 rpm

5. Electrochemical Data

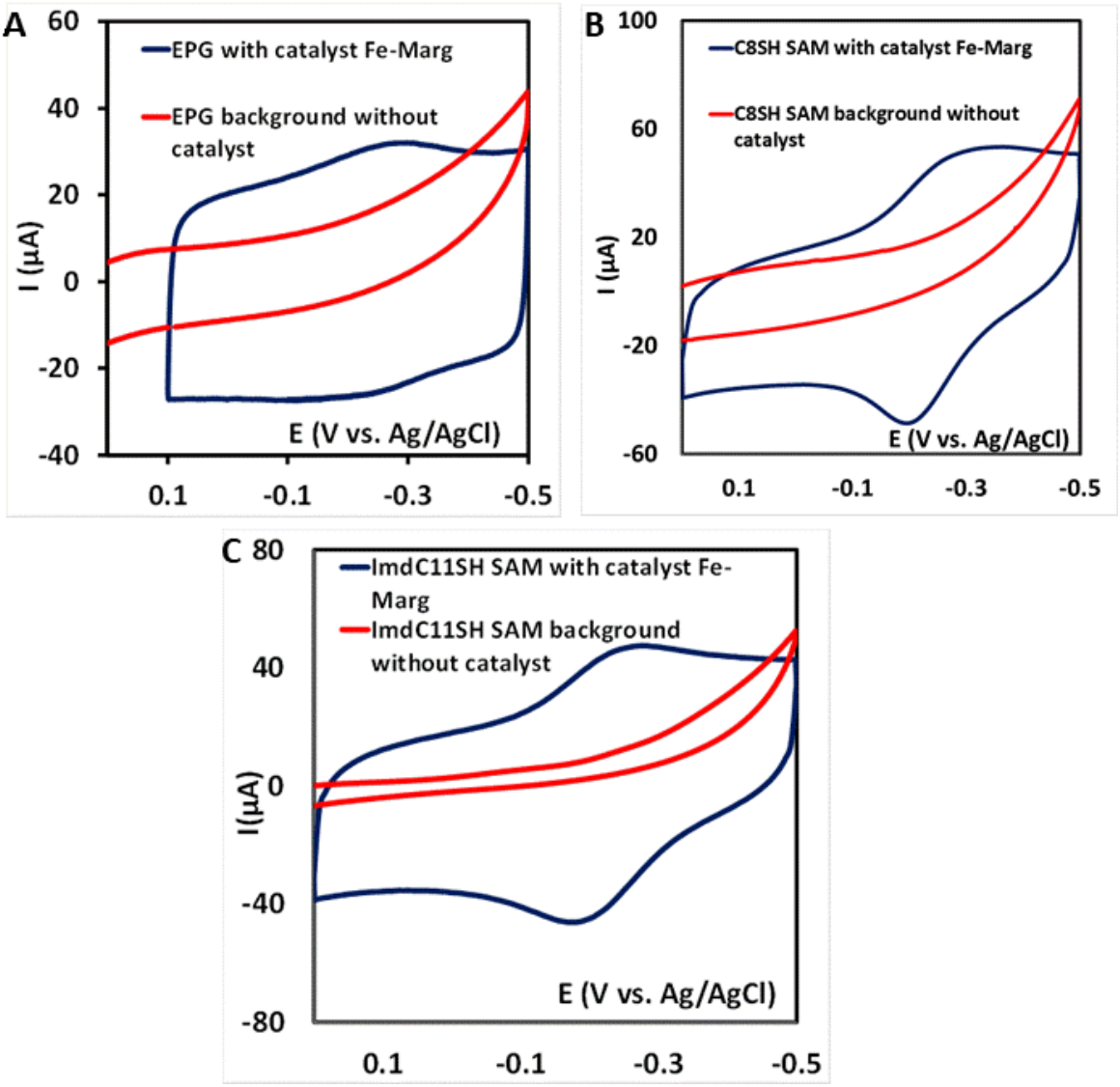


Figure S5. CV overlay of $Fe^{III}Cl$-MARG complex under heterogeneous condition in PH 7 buffer immobilizing the catalysts on A) EPG, B) C_8SH SAM covered Au electrode C) $ImdC_{11}SH$ SAM covered Au electrode along with their background without loading catalysts (blue line) using Pt counter electrode and Ag/AgCl (saturated KCl) as reference electrode.

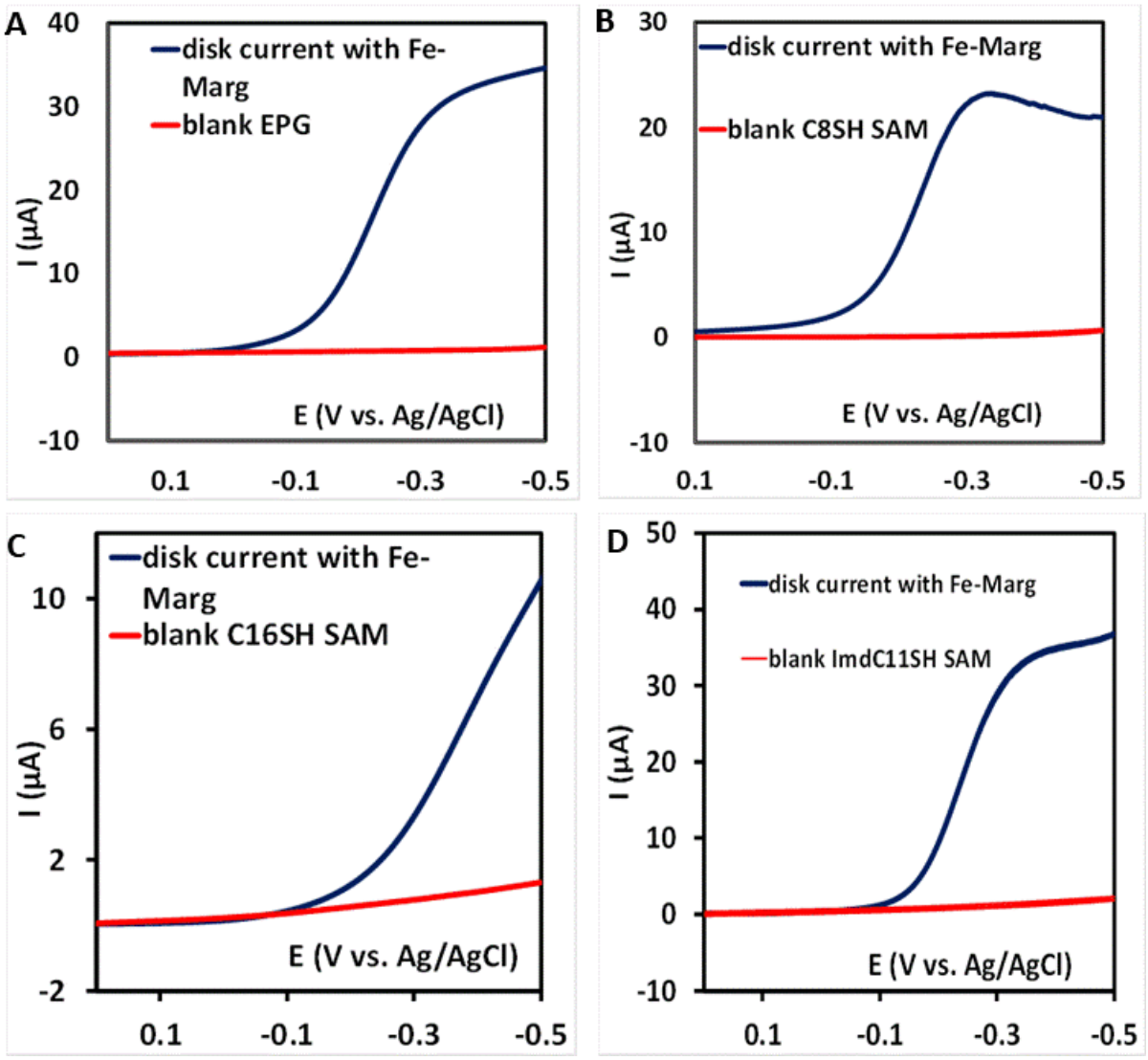


Figure S6. Disk current of complex $Fe^{III}Cl$-MARG immobilized on A) EPG B) C_8SH SAM C) $C_{16}SH$ SAM D) $ImdC_{11}SH$ SAM along with their corresponding background of the blank electrodes in aerobic PH 7 buffer at 10 mV/s scan rate using 300 rpm rotation, Pt as counter electrode and Ag/AgCl in sat. KCl reference electrode.

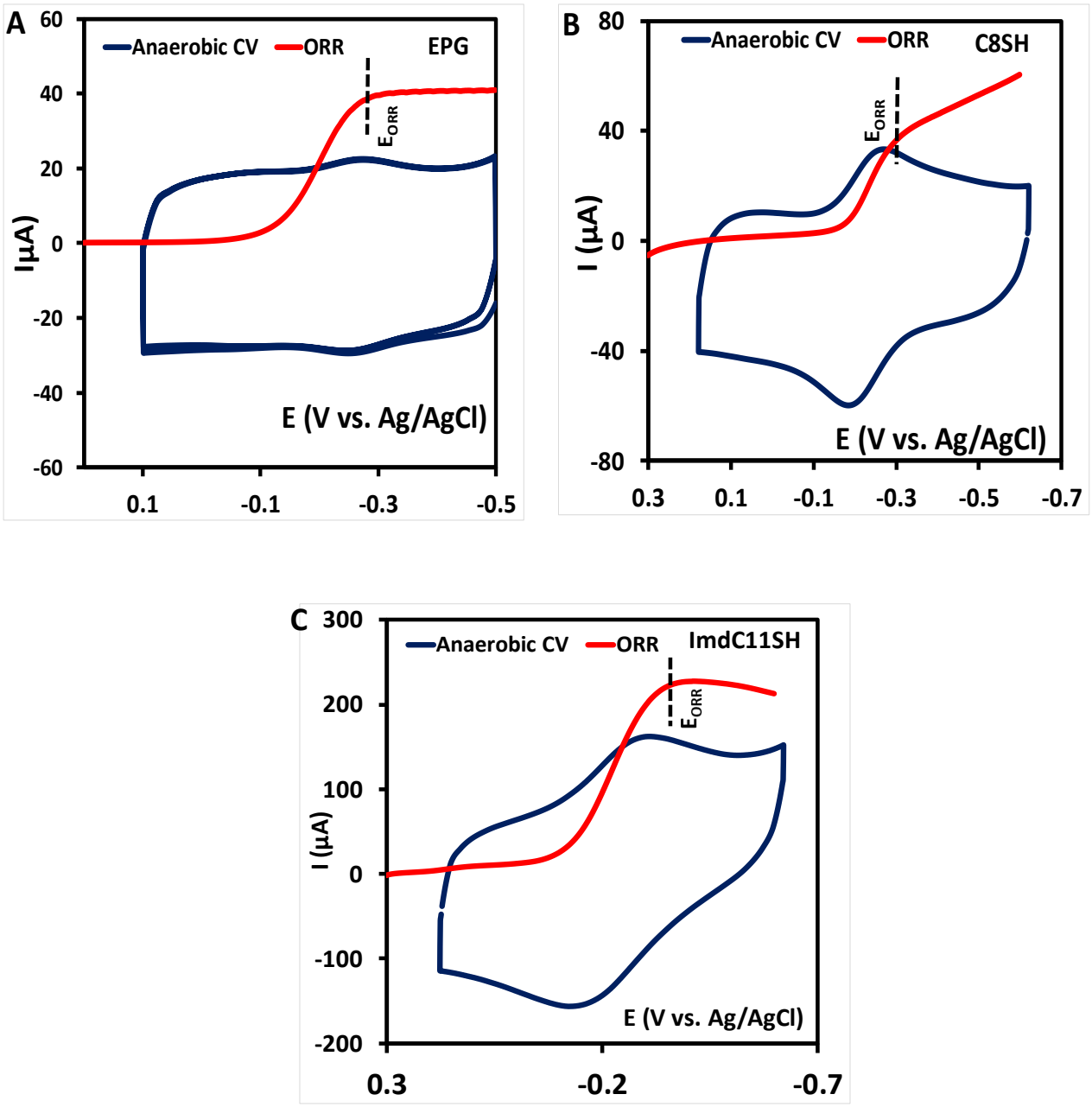


Figure S7. Comparison of Anaerobic CV data with the LSV of ORR for $Fe^{III}Cl$-MeMARG complex in (A) EPG, (B) C_8SH SAM and (C) $ImdC_{11}SH$ SAM modified Au electrode in pH7 phosphate buffer with KPF_6 supporting electrolyte using Pt as counter electrode and Ag/AgCl in sat. KCl reference electrode. CV data was collected at 1 V s^{-1} scan rate and LSV of ORR data was collected at 50 mV s^{-1}

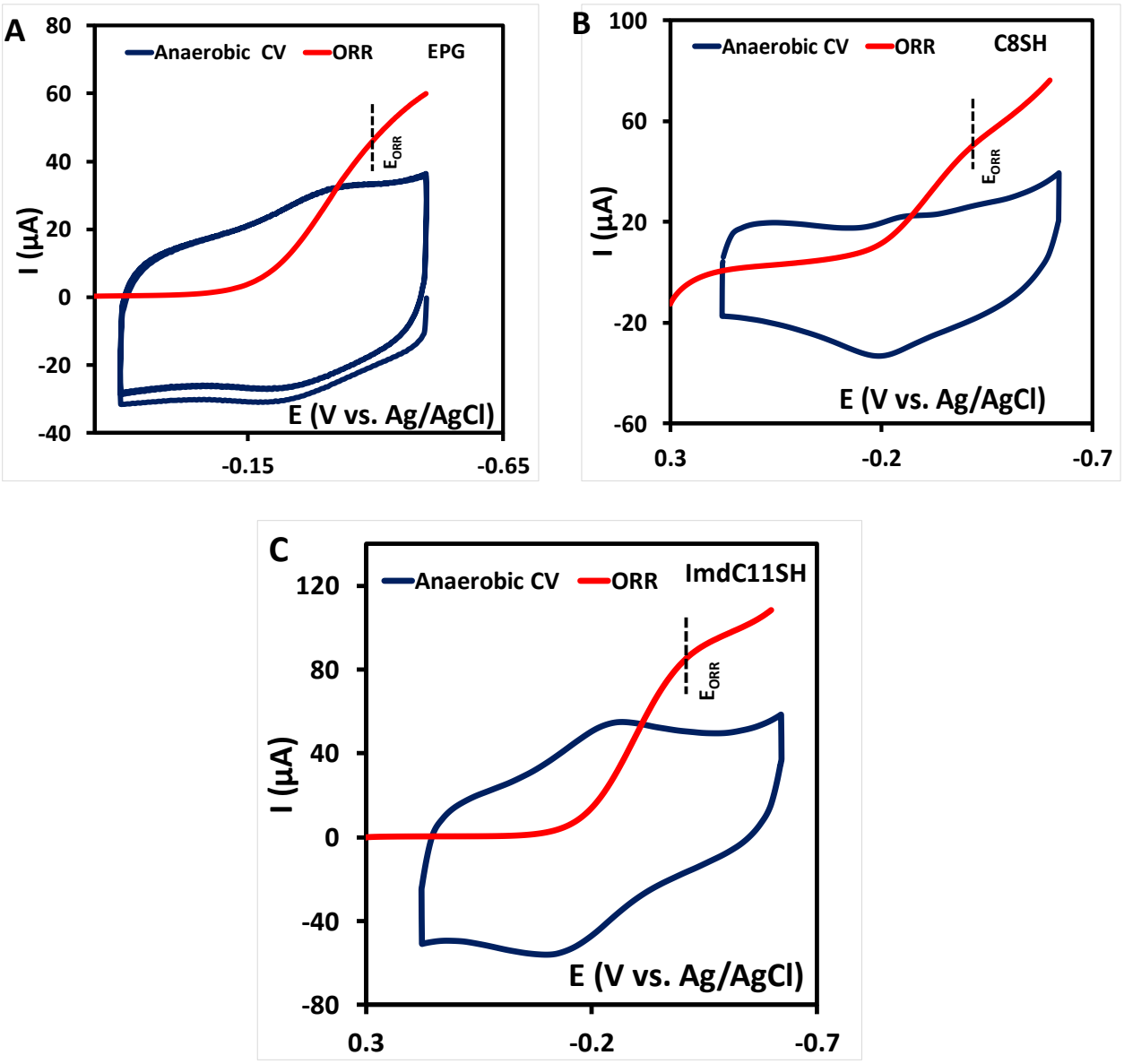


Figure. S8. Comparison of Anaerobic CV data with the LSV of ORR for $Fe^{III}Cl$-PhMARG complex on (A) EPG, (B) C_8SH SAM and (C) $ImdC_{11}SH$ SAM modified Au electrode in pH7 phosphate buffer with KPF_6 supporting electrolyte using Pt as counter electrode and Ag/AgCl in sat. KCl reference electrode. CV data was collected at 1 V s^{-1} scan rate and LSV of ORR data was collected at 50 mV s^{-1}

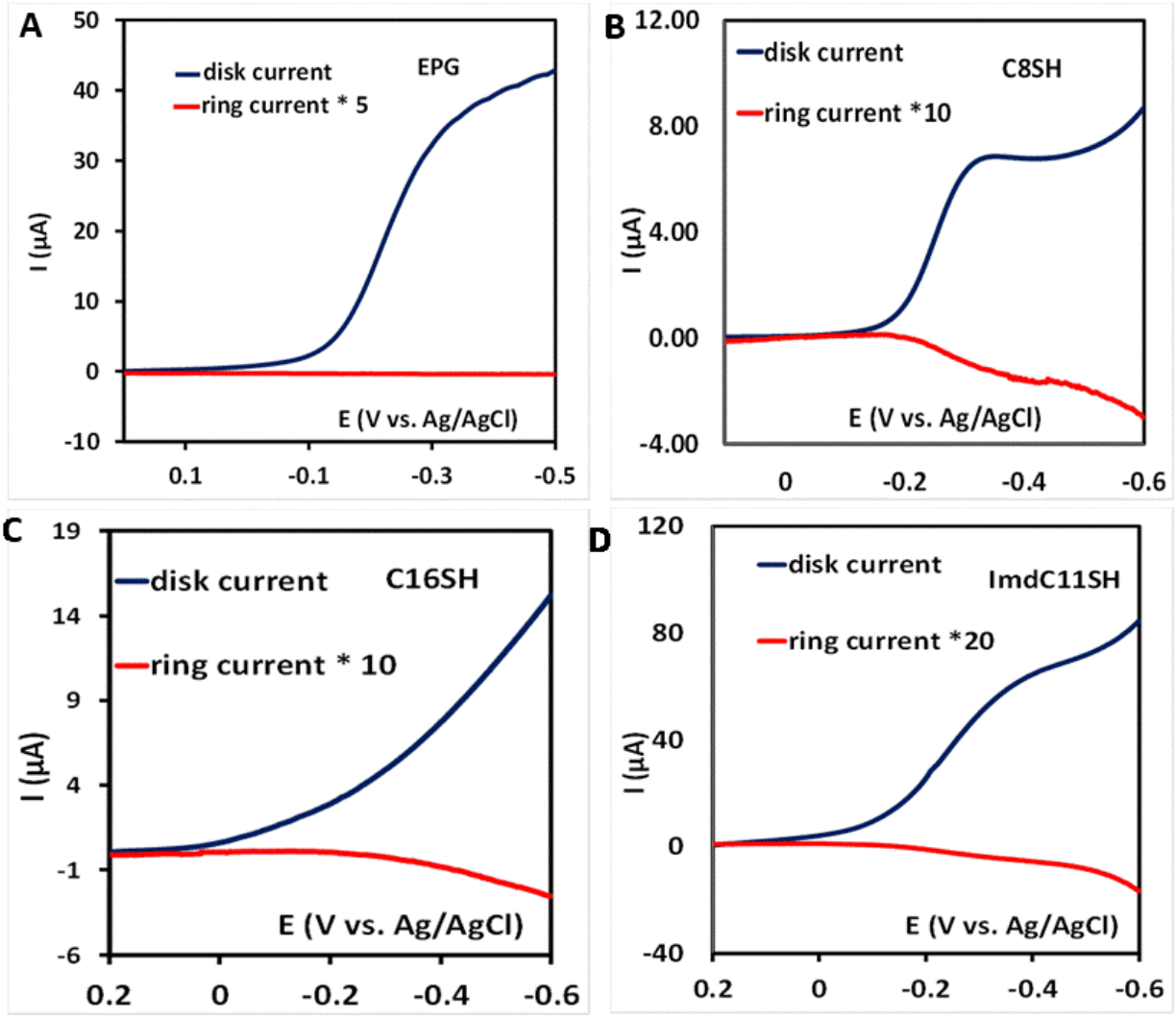


Figure. S9. RRDE data of the complex $Fe^{III}Cl$-MeMARG on (A) EPG, (B) C_8SH SAM modified Au electrode, (C) $C_{16}SH$ SAM modified Au electrode and (D)Imd$C_{11}SH$ SAM modified Au electrode at 10 mV/s scan rate, at 300 rpm using Pt counter electrode and Ag/AgCl (sat. KCl) as ref. electrode.

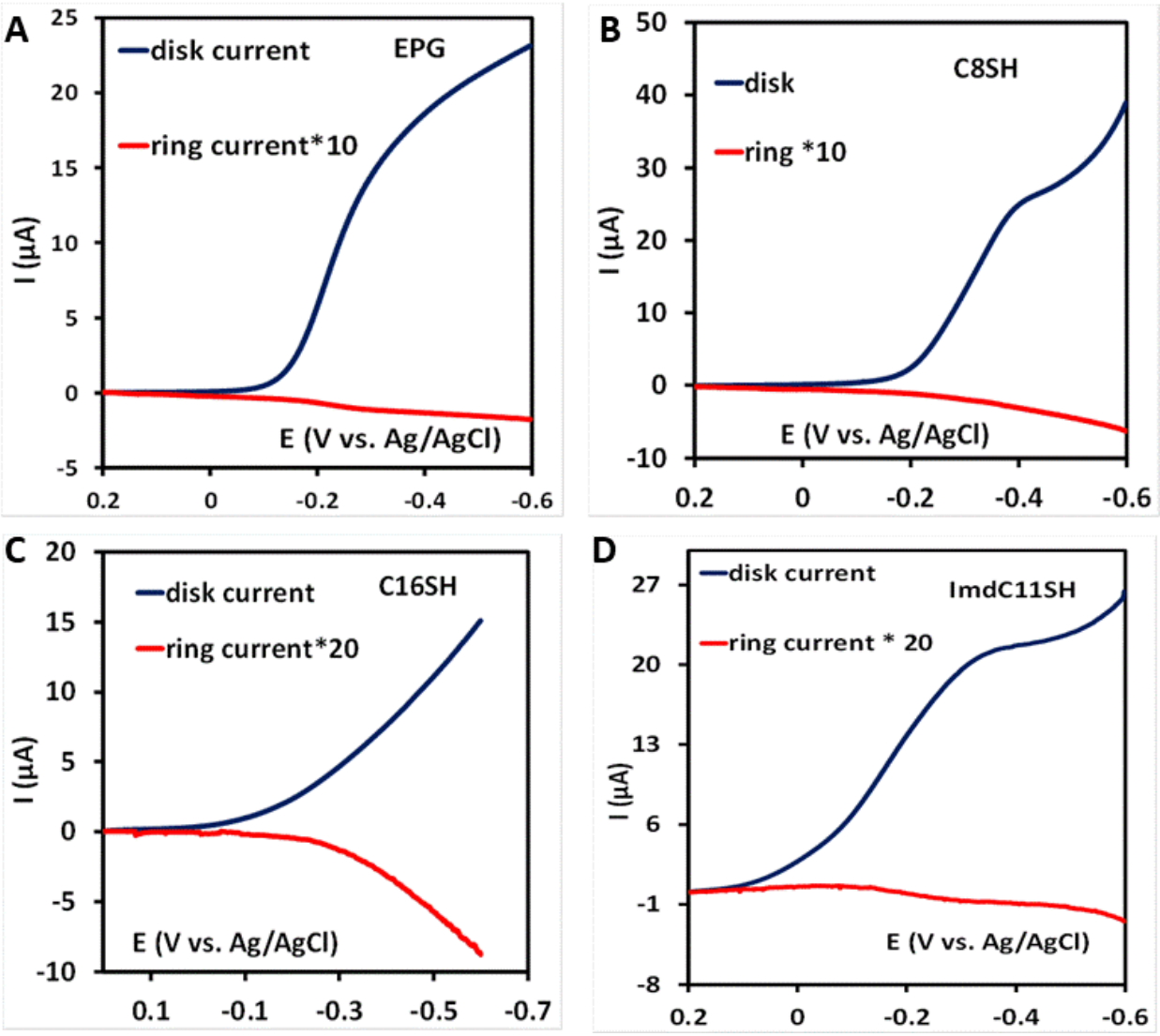


Figure S10. RRDE data of the complex $Fe^{III}Cl$-PhMARG on (A) EPG, (B) C_8SH SAM modified Au electrode, (C) $C_{16}SH$ SAM modified Au electrode and (D) $ImdC_{11}SH$ SAM modified Au electrode at 10 mV/s scan rate at 300 rpm using Pt counter electrode and Ag/AgCl (sat. KCl) as ref. electrode.

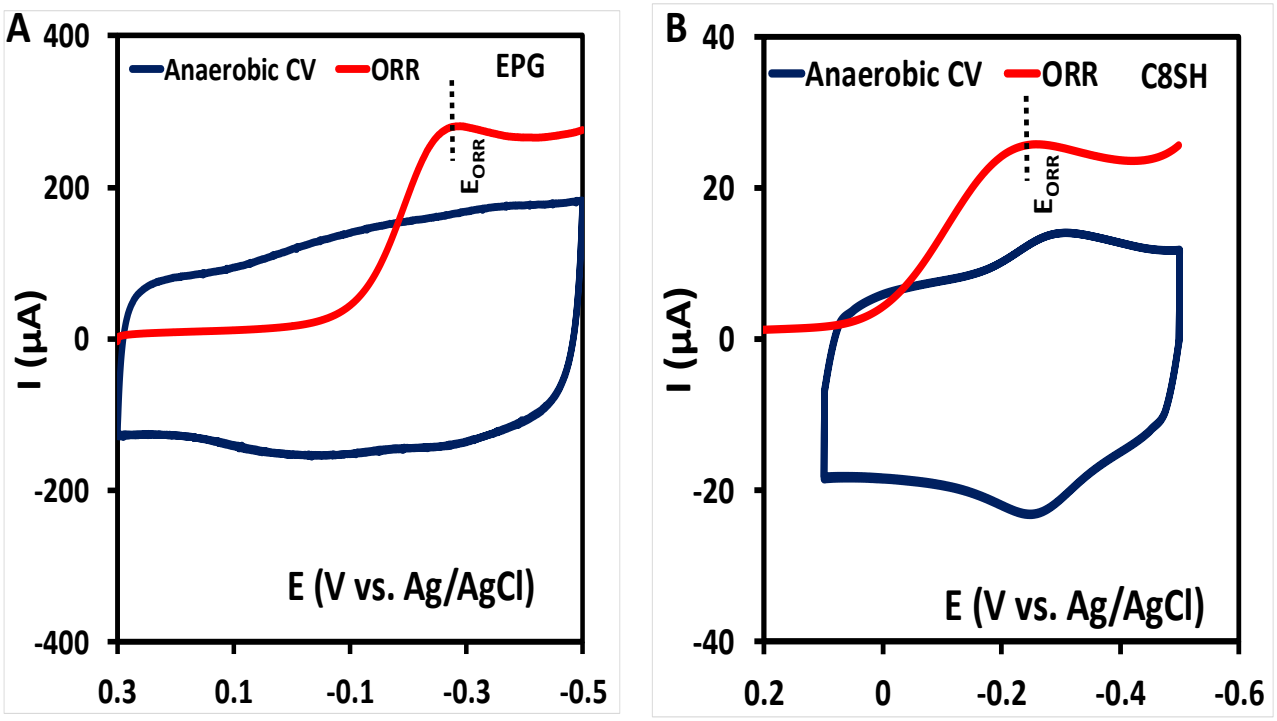


Figure S11. Comparison of Anaerobic CV data with the LSV of ORR for Fe-MARG-N-MeImd complex in (A) EPG and (B) C_8SH SAM modified Au electrode in pH7 phosphate buffer with KPF_6 supporting electrolyte using Pt as counter electrode and Ag/AgCl in sat. KCl reference electrode. CV data was collected at 1 V s^{-1} scan rate and LSV of ORR data was collected at 50 mV s^{-1}

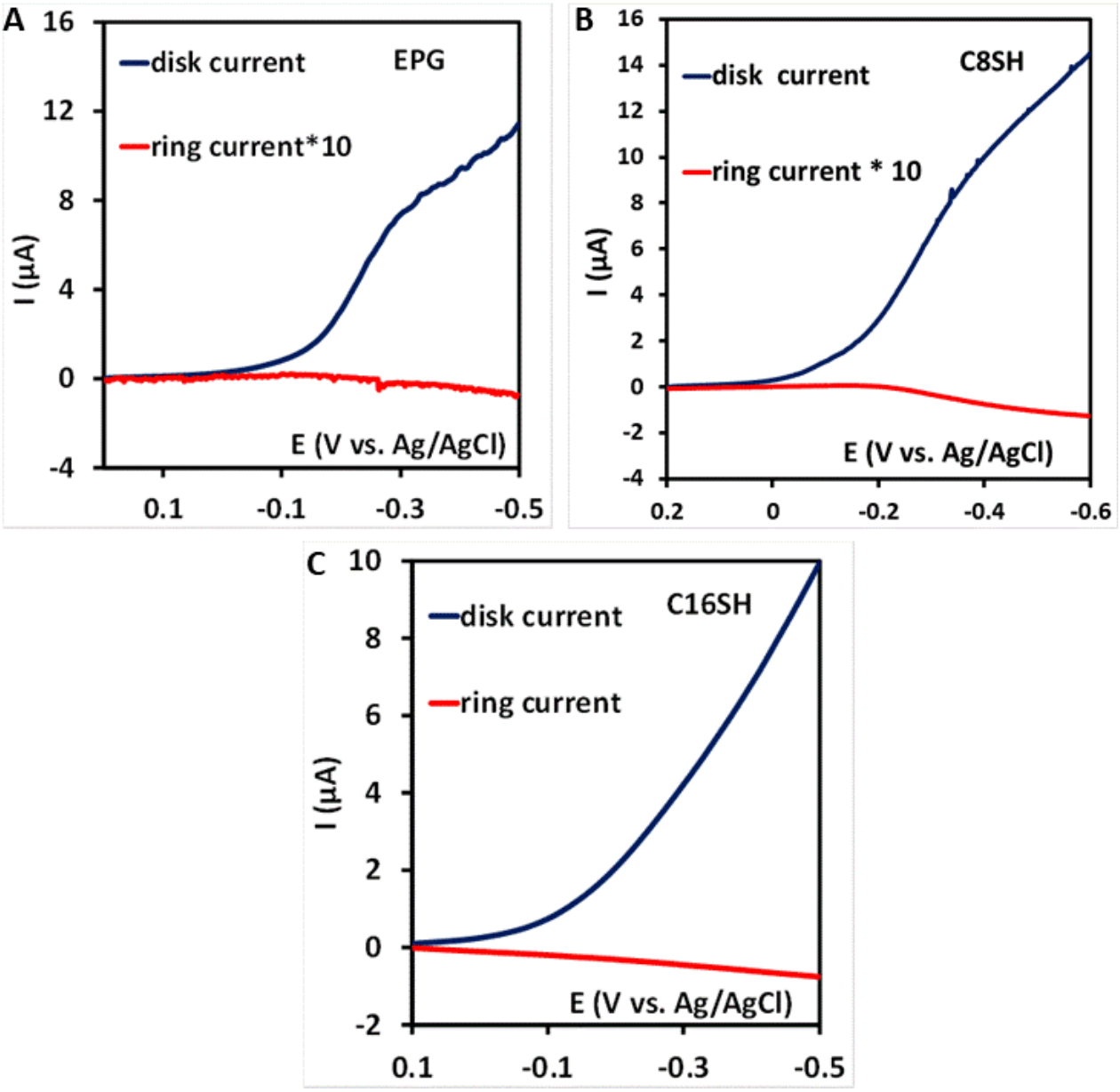


Figure S12. RRDE data of the complex Fe-MARG-N-MeImd on (A) EPG, (B) C_8SH SAM modified Au electrode and (C) C_{16}SH SAM modified Au electrode at 10 mV/s scan rate at 300 rpm using Pt counter electrode and Ag/AgCl (sat. KCl) as ref. electrode

6. DFT Optimized Structures.

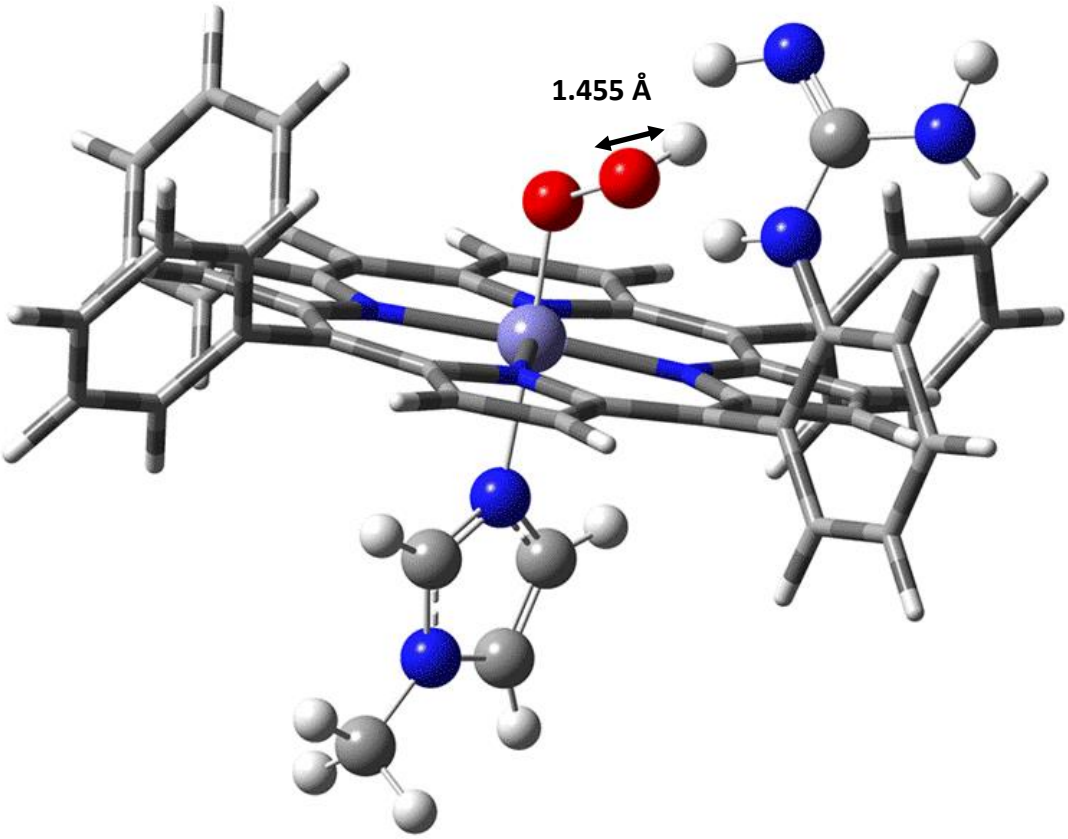


Figure S13. DFT optimized structure of N-Methylimidazole bound neutral Fe^{III}-MARG-hydroperoxide

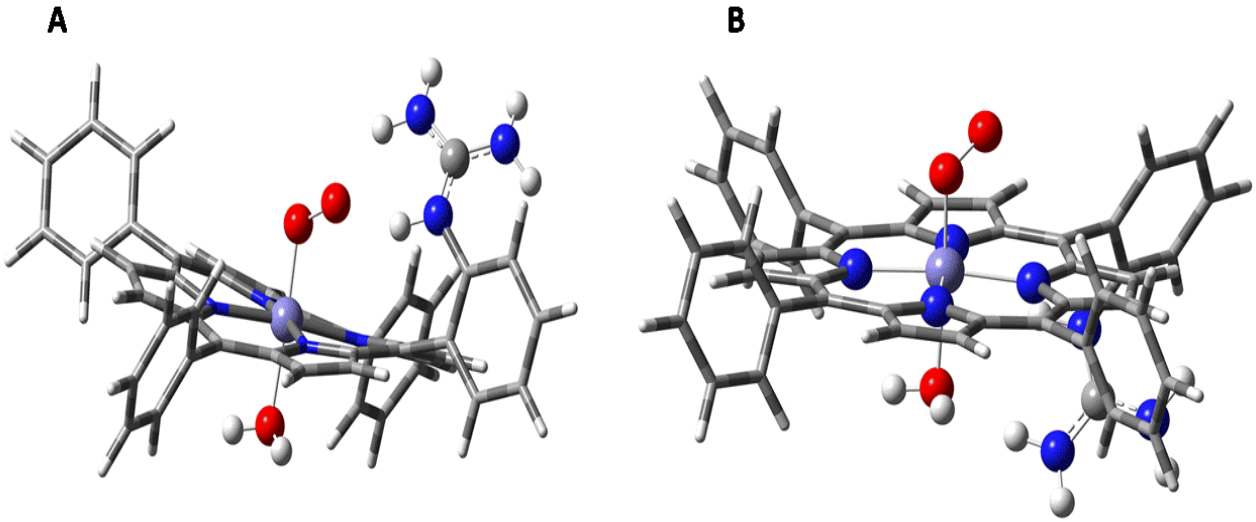


Figure S14. DFT optimized structure of water bound protonated Fe^{III}-MARG-superoxide (A) superoxide in the same side of guanidium (B) superoxide in the opposite site of guanidium

Optimized Coordinates.

Protonated Fe^{III}-MARG-N-MeImd-OOH.

	X	Y	Z
Fe	3.20683100	9.30397300	6.70143400
N	5.04298200	9.27322000	5.88853600
N	2.39679800	9.24062100	4.84151700
N	1.37592900	9.41583000	7.48185500
N	4.03475100	9.40550000	8.51933300
C	6.40484200	9.01138900	7.94186300
C	4.45197000	9.48984600	3.48511500
C	3.06339600	9.39189300	3.63935800
C	1.06107000	9.10567900	4.52226400
C	6.78812800	9.28185000	4.37612100
C	7.32911500	9.09257400	5.60825700
C	6.23670500	9.09542900	6.55128300
C	5.35804600	9.38186500	4.55340800
C	0.88603000	9.14515800	3.09385500
C	2.11752200	9.36170600	2.55099200
C	1.98023900	9.75077100	9.85976700
C	3.36505800	9.58406000	9.70452300
C	1.06553100	9.62684800	8.80672300

C	0.02135600	8.99983900	5.45477000
C	4.28672200	9.48026600	10.81343000
C	5.35184900	9.18508900	8.85111100
C	5.50922300	9.20935100	10.28771200
C	-0.91211300	9.31147600	7.77019400
C	-0.36791800	9.60616700	8.98093300
C	0.18323300	9.21400900	6.83332600
H	7.29934900	9.33209200	3.42619300
H	8.37074100	8.97381700	5.86718400
H	-0.06245600	9.06803700	2.58013900
H	2.37064000	9.48045800	1.50775800
H	4.01433700	9.56997700	11.85462000
H	6.43694300	9.03984600	10.81351900
H	-1.95900700	9.21109600	7.52135100
H	-0.88140600	9.77819500	9.91518500
C	7.78138800	8.75774000	8.47329600
C	8.48991500	9.75452400	9.16239600
C	8.39146800	7.50758700	8.28315100
C	9.77393100	9.50811200	9.65052000
H	8.03250500	10.72921900	9.31004300

C	9.67433900	7.26042300	8.77389100
H	7.84987500	6.72711800	7.75612600
C	10.36928000	8.25976700	9.45819800
H	10.30993900	10.29256500	10.17770600
H	10.12929200	6.28525300	8.62371800
H	11.36830100	8.06725000	9.83892000
C	-1.32280300	8.51825400	5.00146200
C	-2.33913300	9.37620700	4.57163800
C	-1.61063500	7.13593400	5.09100900
C	-3.61104300	8.89500500	4.24919800
H	-2.12482600	10.43851900	4.50269300
C	-2.90249000	6.65818900	4.83746500
C	-3.89511000	7.53951000	4.40105900
H	-4.38177800	9.58132800	3.91243000
H	-3.16034400	5.62334700	5.04159500
H	-4.89374800	7.16166500	4.20421500
C	1.45399200	9.99303100	11.24202800
C	0.78403000	8.98247900	11.94922400
C	1.63565600	11.24046600	11.85875600
C	0.30373400	9.21587000	13.23886400

H	0.65064400	8.00832500	11.48689700
C	1.15300100	11.47456600	13.14739300
H	2.15286100	12.02989200	11.32011500
C	0.48561000	10.46283200	13.84067100
H	-0.20770100	8.42124100	13.77515100
H	1.29764600	12.44763600	13.60875900
H	0.11185200	10.64412300	14.84444400
C	5.00814200	9.66004700	2.10460200
C	4.94943200	8.61978600	1.16380900
C	5.61130300	10.87095900	1.72990500
C	5.47658000	8.78680700	-0.11779900
H	4.49834600	7.67213100	1.44550800
C	6.13676000	11.03915600	0.44795000
H	5.66171300	11.68362900	2.44931800
C	6.07063100	9.99754900	-0.47972500
H	5.42869700	7.96862800	-0.83125400
H	6.59625400	11.98477600	0.17369000
H	6.48124300	10.12757200	-1.47698800
N	-0.55048800	6.27356100	5.51301800
H	0.20319000	6.72432500	6.04587000

C	-0.23463000	5.05302000	5.05314700
N	-1.03387600	4.38553200	4.19779900
N	0.89109900	4.47824100	5.49822900
H	-0.68354100	3.56026600	3.73262700
O	3.24958700	7.50140200	6.91654500
O	2.24564000	6.77986500	6.13321500
H	1.16596200	3.56602900	5.16479600
H	-1.78285100	4.88488600	3.73713900
H	1.59741700	5.06123700	5.96672500
H	2.41008500	7.16041900	5.24879400
N	3.24088400	11.35244500	6.59552400
C	4.21966500	12.13567400	7.02796300
C	2.27756600	12.18978600	6.07202500
H	5.13187300	11.79765100	7.49437300
C	2.69228800	13.48696400	6.19528100
H	1.36356800	11.80356100	5.65051800
H	2.23209800	14.42163700	5.91339600
N	3.93286300	13.43844200	6.80589200
C	4.77442600	14.57970800	7.14541600
H	4.24852600	15.24639600	7.83448700

H	5.68486000	14.21855500	7.62682200
H	5.04559100	15.13345500	6.24217500

Protonated Fe-TPP-N-Meimd-OOH.

	X	Y	Z
C	6.01193200	3.77161600	14.08533900
C	7.07258100	3.05115500	14.63665100
H	7.24023500	3.07724600	15.71024600
C	7.90950900	2.29316100	13.81498500
H	8.73507800	1.73176800	14.24437200
C	7.67606800	2.25786600	12.43869900
H	8.32206200	1.67073700	11.79090400
C	6.61440200	2.97778700	11.88867200
H	6.43565200	2.95049300	10.81729600
C	5.76804900	3.74843400	12.70235600
C	4.63207300	4.51711500	12.10331500
C	3.56729300	3.79482200	11.54566400
C	3.42468900	2.36169300	11.66361900
H	4.11829900	1.70835000	12.17194300
C	2.25292000	2.03257800	11.06164600

H	1.80101200	1.05559100	10.97566100
C	1.68665400	3.25894700	10.54670200
C	0.50486400	3.32089500	9.79469800
C	-0.23782700	2.04931400	9.52452600
C	0.30301000	1.05004500	8.69963300
H	1.27936400	1.20628500	8.24896600
C	-0.40028000	-0.12967400	8.45042800
H	0.03348600	-0.88976600	7.80564200
C	-1.65809000	-0.33056600	9.02275400
H	-2.20597400	-1.24915700	8.82990500
C	-2.20739600	0.65577800	9.84473600
H	-3.18361500	0.50594000	10.29852900
C	-1.50430200	1.83566300	10.09239700
H	-1.92868800	2.59918700	10.73801100
C	-0.01607100	4.50931000	9.26103600
C	-1.12645800	4.55576900	8.33545500
H	-1.67606700	3.69561400	7.98233400
C	-1.30491900	5.85961800	7.99844400
H	-2.03245900	6.27751600	7.31858400
C	-0.32282500	6.62065800	8.73743600

C	-0.24714500	8.01990700	8.73392200
C	-1.22008000	8.78721700	7.89351300
C	-0.77515500	9.52379900	6.78407100
H	0.28345500	9.52217000	6.53913500
C	-1.67415300	10.24495000	5.99673900
H	-1.31066200	10.80501700	5.13888700
C	-3.03552400	10.24456300	6.30733600
H	-3.73617200	10.80660800	5.69549400
C	-3.49080800	9.51928800	7.41050400
H	-4.54764700	9.51898700	7.66449000
C	-2.59126000	8.79725600	8.19657200
H	-2.94615700	8.24186000	9.06008300
C	0.65946800	8.74592600	9.51910000
C	0.60809500	10.18138700	9.67931200
H	-0.11080400	10.83342400	9.20548100
C	1.59307900	10.51525300	10.55245500
H	1.84092600	11.49568600	10.93136700
C	2.27033600	9.28846400	10.90981600
C	3.40432000	9.23185100	11.73309200
C	3.95180000	10.50982900	12.28863700

C	4.50436400	11.49155500	11.44981500
H	4.53136900	11.31710200	10.37765500
C	5.01838000	12.67757600	11.97625300
H	5.44434800	13.42310700	11.30962600
C	4.98993600	12.90419400	13.35384900
H	5.38901400	13.82782000	13.76455100
C	4.44446300	11.93650900	14.20008800
H	4.41279300	12.10577700	15.27323800
C	3.93196700	10.75059400	13.67222800
H	3.50144000	10.00291700	14.33232400
C	4.08229500	8.04105700	12.04455700
C	5.36272100	7.99169100	12.70776600
H	5.91181900	8.85244400	13.06064900
C	5.73009300	6.68179700	12.76960500
H	6.63593400	6.26638600	13.18597900
C	4.66658300	5.91738000	12.16774800
Fe	2.05158700	6.25940900	10.62121800
O	0.95144300	6.29398600	12.03668900
N	2.49646500	4.31889500	10.86695100
N	0.47175400	5.77450300	9.46992600

N	1.67082400	8.22233700	10.28401800
N	3.68046400	6.76637900	11.71089300
O	1.46109100	5.68805900	13.23507800
H	2.18282700	6.29353100	13.47781000
H	5.35551000	4.35045400	14.72878400
C	3.07501600	5.54149800	7.72443800
C	4.37865700	6.94703200	8.71531900
C	4.09051600	5.81561000	6.84828400
H	2.22627200	4.88700200	7.60298000
N	4.91723400	6.71698000	7.49204500
H	4.81823500	7.61613500	9.43975400
H	4.29947900	5.46316900	5.84954600
N	3.26827600	6.25413800	8.88640500
C	6.13839900	7.30438200	6.96390700
H	6.55926000	7.97769800	7.71316700
H	6.87198000	6.52427600	6.73819000
H	5.92671200	7.87454200	6.05410300

Neutral Fe^{III}-MARG-N-Meimd-OOH.

Fe	3.44028500	9.32623100	6.70026000

N	5.27197900	9.29696900	5.83527500
N	2.58456400	9.31856100	4.88378300
N	1.63658100	9.46243800	7.56928500
N	4.32537400	9.44069700	8.51997500
C	6.70664200	9.36482600	7.85078600
C	4.60046400	9.16322500	3.45432700
C	3.21659700	9.22359000	3.66513600
C	1.23799200	9.31433600	4.61254700
C	6.97230800	9.14566400	4.27437900
C	7.55857400	9.22454400	5.49656200
C	6.49307100	9.30343200	6.46838000
C	5.54479600	9.19948300	4.49008300
C	1.01452200	9.23957500	3.18905300
C	2.23850400	9.19621600	2.60097300
C	2.30670500	9.46365500	9.95417000
C	3.69228500	9.43008200	9.74030600
C	1.36298600	9.48407500	8.91753800
C	0.20606400	9.34781100	5.55650300
C	4.66701000	9.37850700	10.80655000
C	5.67251700	9.40737800	8.79307900

C	5.89145500	9.36972700	10.22053800
C	-0.65093500	9.49246200	7.90603300
C	-0.06617000	9.53177900	9.13132700
C	0.41694800	9.44552800	6.93596600
H	7.45161600	9.05912600	3.31039800
H	8.61287900	9.22233700	5.73021000
H	0.04284600	9.23877800	2.71650500
H	2.47106600	9.14932500	1.54718700
H	4.43316200	9.33749600	11.86006500
H	6.85864600	9.31999700	10.69852300
H	-1.70431200	9.50088300	7.66617200
H	-0.54751700	9.58045400	10.09694100
C	8.11887600	9.35281000	8.35223900
C	8.69242300	10.50701700	8.90776400
C	8.89654500	8.18632200	8.28019200
C	10.00766300	10.49708700	9.37571700
H	8.10084500	11.41662300	8.96639800
C	10.21171500	8.17538000	8.74794900
H	8.45969700	7.28473100	7.86003400
C	10.77174600	9.33105600	9.29656700

H	10.43598900	11.40200100	9.79919900
H	10.79679100	7.26139500	8.68741400
H	11.79564900	9.32266100	9.66078200
C	-1.18750200	9.06433700	5.08151100
C	-2.08495700	10.08094000	4.74791900
C	-1.59946300	7.70704000	4.98128900
C	-3.37894100	9.79255600	4.30801900
H	-1.75238900	11.11257900	4.83016400
C	-2.91195900	7.42429100	4.56285200
C	-3.78162600	8.45980300	4.22106400
H	-4.06077600	10.59620900	4.04538700
H	-3.24629500	6.39435200	4.52412100
H	-4.79073400	8.21513500	3.89896700
C	1.80606200	9.44510900	11.36637400
C	1.14697900	8.31424900	11.87498600
C	1.98554100	10.55012300	12.21338200
C	0.68069100	8.29070300	13.19033600
H	1.00967000	7.44932900	11.23234700
C	1.52003500	10.52792300	13.52918400
H	2.49471100	11.43214600	11.83365000

C	0.86526400	9.39741000	14.02181900
H	0.17720300	7.40398400	13.56640900
H	1.66678200	11.39517200	14.16792800
H	0.50277800	9.37847700	15.04614100
C	5.09634500	9.03170700	2.04562200
C	4.94186100	7.82540300	1.34425800
C	5.72556000	10.10556200	1.39676500
C	5.40230800	7.69705100	0.03283700
H	4.46292000	6.98401800	1.83720500
C	6.18715100	9.97868300	0.08541800
H	5.84997000	11.04624500	1.92658400
C	6.02637100	8.77346400	-0.60102700
H	5.27701800	6.75334300	-0.49162300
H	6.66917400	10.82319200	-0.40033200
H	6.38528600	8.67352800	-1.62190800
N	-0.68321300	6.71559300	5.36171700
H	0.12789700	7.05024900	5.87438000
C	-0.53190400	5.39219500	4.93841400
N	-1.37157300	4.97190300	3.90749600
N	0.30948700	4.56199800	5.44353200

H	-1.07020100	4.06395600	3.57166200
O	3.48589800	7.53983700	6.81899300
O	2.26889100	6.86081700	6.40105600
H	-1.50192100	5.64290700	3.15792300
H	2.59279000	6.38944700	5.61255700
N	3.49554000	11.42569800	6.61023300
C	3.05843000	12.25233800	7.54582300
C	3.97009200	12.21836900	5.58756200
H	2.61988500	11.95843200	8.48709700
C	3.81189700	13.53616900	5.92138000
H	4.38651600	11.78727300	4.69134500
H	4.05217900	14.44835400	5.39673100
N	3.22899200	13.54623100	7.17545600
C	2.86037800	14.72034100	7.95086200
H	2.12049200	15.31949900	7.41128000
H	2.42724500	14.39684700	8.89930600
H	3.74147900	15.33599800	8.15616700
H	0.76654500	4.95405300	6.26896700

Fe^{III}-MARG-superoxide (Fig. S13 A).

	X	Y	Z
Fe	3.26325900	9.31169000	6.66862700
N	5.07638000	9.22712100	5.84293000
N	2.41777000	9.32084700	4.86956600
N	1.46038600	9.57641700	7.49699400
N	4.13164500	9.46302900	8.46724200
C	6.46981000	8.91156600	7.86563000
C	4.44718400	9.46439000	3.45672400
C	3.06319400	9.40412600	3.65213400
C	1.08119800	9.17603200	4.58288300
C	6.79401200	9.20357100	4.29857900
C	7.35164600	8.98333800	5.51833000
C	6.27884400	9.00806400	6.48051200
C	5.37210100	9.33715100	4.50226900
C	0.87608100	9.16277400	3.15814000
C	2.09693900	9.34569700	2.58362600
C	2.12692900	9.94846900	9.85575200
C	3.49599200	9.70077000	9.66978400
C	1.18506100	9.84417100	8.82605400
C	0.04700600	9.13160100	5.52517400

C	4.43051600	9.55615200	10.75621500
C	5.44423400	9.15898200	8.78552400
C	5.62369500	9.19352300	10.21257300
C	-0.82580100	9.57200700	7.84169300
C	-0.24184400	9.89377100	9.02790500
C	0.23715700	9.39664600	6.88604900
H	7.28846800	9.25787900	3.34006700
H	8.39419500	8.83822700	5.75905200
H	-0.08562100	9.08749900	2.66971700
H	2.33336100	9.42689700	1.53298500
H	4.18666000	9.68272700	11.80053000
H	6.54782100	8.97410000	10.72590100
H	-1.88120900	9.49917500	7.62117300
H	-0.72623000	10.12215100	9.96555800
C	7.83967700	8.58728800	8.37241400
C	8.60773300	9.54508600	9.05344500
C	8.38411900	7.31052800	8.16149900
C	9.88688600	9.23193800	9.51529500
H	8.20360100	10.54138400	9.21047300
C	9.66168700	6.99723700	8.62747200

H	7.79663900	6.56121900	7.63821600
C	10.41625300	7.95688400	9.30541600
H	10.47106400	9.98622600	10.03501100
H	10.06589800	6.00239800	8.46238500
H	11.41136000	7.71339800	9.66652000
C	-1.30022500	8.65093100	5.08279700
C	-2.36779300	9.50171600	4.78161000
C	-1.51885100	7.25591900	5.01674800
C	-3.62035900	8.99350700	4.42592600
H	-2.20750300	10.57485000	4.82634500
C	-2.78405700	6.74130600	4.71235400
C	-3.82883400	7.61550800	4.40161000
H	-4.43273500	9.67319000	4.18809500
H	-2.97382400	5.67369700	4.77321900
H	-4.80855600	7.21273300	4.16360700
C	1.65149900	10.26061200	11.24216300
C	0.92215800	9.32113400	11.98778700
C	1.94502300	11.50302000	11.82531600
C	0.49288600	9.62020100	13.28182700
H	0.70319100	8.34960300	11.55343100

C	1.51331800	11.80282700	13.11830000
H	2.51096200	12.23832100	11.25947200
C	0.78566600	10.86200200	13.84967300
H	-0.06534900	8.87992300	13.84818700
H	1.74511900	12.77128200	13.55263100
H	0.45122000	11.09387300	14.85677700
C	4.97358100	9.60756100	2.06127400
C	4.91372500	8.54229900	1.14954100
C	5.54991100	10.81858300	1.64801700
C	5.41516100	8.68563700	-0.14523800
H	4.48207500	7.59571500	1.46370000
C	6.04929500	10.96210300	0.35253600
H	5.60034800	11.64982100	2.34583400
C	5.98305400	9.89636800	-0.54726600
H	5.36749100	7.84963400	-0.83770100
H	6.48871400	11.90743700	0.04673600
H	6.37361000	10.00778800	-1.55473900
N	-0.41559700	6.41001400	5.34976100
H	0.28735900	6.83779300	5.96118700
C	0.00928000	5.31470100	4.70124800

N	-0.70656700	4.77117200	3.69850100
N	1.14707200	4.73453500	5.10190100
H	-0.30368700	4.04008200	3.13044200
O	3.26073400	7.46649400	6.79284800
O	2.14272100	6.82601900	6.62998300
H	1.51143800	3.92726000	4.61808000
H	-1.46660800	5.30215600	3.29461200
H	1.75702000	5.22039400	5.77055100
O	3.38464300	11.37680100	6.55603700
H	4.00957600	11.66309300	7.24513300
H	2.51269900	11.72580500	6.81163100

Fe^{III}-MARG-superoxide (Fig. S13 B).

	X	Y	Z
Fe	3.42549100	9.25417700	6.62241900
N	5.27354600	9.16117100	5.81498700
N	2.61546900	9.05313100	4.79906300
N	1.60081900	9.15792100	7.44958500
N	4.26191800	9.25525000	8.45920900
C	6.66512200	9.37647100	7.85523800

C	4.67193400	9.00094000	3.41529400
C	3.28478000	8.97108700	3.59742800
C	1.27636100	9.06431300	4.48134200
C	7.01189700	9.20980000	4.28431600
C	7.56544700	9.33767100	5.51789400
C	6.48401400	9.29770500	6.47047500
C	5.58458900	9.11920000	4.47020700
C	1.10096400	8.95358200	3.05198100
C	2.34301200	8.89957900	2.50587800
C	2.21249500	9.22159800	9.85504800
C	3.59971600	9.24500600	9.67318500
C	1.29638100	9.20841600	8.79394200
C	0.22346400	9.15505300	5.39639100
C	4.54937300	9.26440100	10.75797000
C	5.60550200	9.32901600	8.77159800
C	5.78731900	9.32309200	10.20119100
C	-0.68856800	9.30224900	7.73342300
C	-0.12866200	9.29116600	8.97699800
C	0.39799700	9.21130700	6.78672800
H	7.51354000	9.19018400	3.32822200

H	8.60921400	9.44676700	5.77124200
H	0.15260500	8.94148800	2.53436400
H	2.61125800	8.83341600	1.46188800
H	4.29293100	9.23429000	11.80644800
H	6.74273500	9.34805200	10.70347300
H	-1.73300300	9.44064700	7.48512500
H	-0.62734600	9.37534200	9.93130100
C	8.05710300	9.52023400	8.38939000
C	8.46980400	10.72789300	8.97411800
C	8.97069500	8.45705500	8.31836900
C	9.76555800	10.86855300	9.47305100
H	7.77255100	11.55933500	9.02730100
C	10.26533900	8.59743600	8.82068500
H	8.66134000	7.51519100	7.87301200
C	10.66614400	9.80387700	9.39839900
H	10.07166700	11.81188300	9.91658100
H	10.95917500	7.76334500	8.76258000
H	11.67436000	9.91378000	9.78754700
C	-1.17332000	9.16261400	4.86021200
C	-1.67397400	10.25605700	4.13727400

C	-2.04047400	8.06918300	5.05421300
C	-2.96971700	10.25128900	3.61838700
H	-1.02825200	11.11573600	3.98833500
C	-3.34779700	8.06078100	4.55727200
C	-3.80878600	9.15367800	3.82326100
H	-3.32880900	11.11241100	3.06291500
H	-3.99834300	7.21536400	4.76317600
H	-4.82240900	9.15455100	3.43490600
C	1.67694700	9.24947000	11.25411600
C	1.06768500	8.11524000	11.81256200
C	1.77372000	10.41416100	12.03181200
C	0.57058900	8.14232100	13.11672700
H	0.99501300	7.20487100	11.22300300
C	1.27393100	10.44215900	13.33466400
H	2.23622800	11.30056400	11.60697200
C	0.67229200	9.30643900	13.88100900
H	0.10905500	7.25295800	13.53723500
H	1.35276500	11.35311500	13.92133300
H	0.28585700	9.32830100	14.89597600
C	5.20599500	8.93686700	2.01506100

C	5.24462000	7.71950700	1.31884300
C	5.67246400	10.09595900	1.37622100
C	5.73941900	7.66095500	0.01457800
H	4.88970100	6.81499900	1.80613900
C	6.16682400	10.03717000	0.07202500
H	5.64153800	11.04478000	1.90460900
C	6.20195300	8.81999900	-0.61176700
H	5.76743100	6.70954200	-0.50963900
H	6.52215400	10.94374000	-0.40986500
H	6.58804200	8.77509700	-1.62616000
N	-1.57306900	6.94565800	5.83048500
H	-1.17461800	7.18420200	6.73820700
C	-1.28816700	5.74256700	5.32777000
N	-1.44600200	5.48907400	4.02315000
N	-0.86745600	4.75864800	6.14606200
H	-1.44339100	4.54547400	3.66443100
H	-0.38317800	3.95599100	5.76916200
H	-1.73837300	6.23612500	3.40659000
H	-0.72157800	4.94906200	7.12801600
O	3.58139500	7.03016000	6.76899300

H	4.35991300	6.89932100	6.19929900
H	3.93825500	6.97737900	7.67340200
O	3.44357300	11.11636000	6.55985900
O	2.40350100	11.70736700	6.12837000

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