SUPPORTING INFORMATION

for

Skeletal Substituents and Distal Environment Determine Spin state of Natural and Synthetic Iron porphyrins: Role in O₂ Reduction Reaction

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EXPERMENTAL DETAILS

Materials and methods. All reagents used are of the highest grade commercially available. 1-(11-Mercaptoundecyl)imidazole, Octanethiol, Heme b, Cobaltocene and Potassium hexafluorophosphate (KPF₆) were purchased from Sigma-Aldrich. All solvents, deuterium oxide (D₂O), Imidazole, Disodium hydrogen phosphate dihydrate (Na₂HPO₄·2H₂O) were purchased from Merck and used without further purification. Fe(III) 2,4-Diacetyl deuteroporphyrin IX chloride was purchased from Frontier Scientific. 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). Solvents were distilled, dried, and deoxygenated pursuant to established protocols for use in the glovebox. Preparation and handling of air-sensitive materials were carried out under an inert atmosphere in the glovebox. Unless otherwise mentioned, all reactions were performed at room temperature. The meso-tetra(α_4 -o-pivaloylamidophenyl) porphyrin (Fe-picket fence), Iron tetraphenyl porphyrin (FeTPP), Iron diester porphyrin (FeDEsP) and Iron tetra ester porphyrin (FeTEsP) were synthesized and characterized following past literature reports.¹⁻³

Electron Paramagnetic Resonance. The Fe-porphyrin (FeDEsP or FeTEsP) complexes were dissolved in dry and degassed dichloromethane (DCM) so that the concentration of the solution is 1mM. It was then reduced to ferrous form by adding 1 equivalent of cobaltocene (20mM stock solution in THF) under inert atmosphere. For low spin bis-imidazole samples, 10 equivalent of imidazole solution in THF was added to the high spin ferric and ferrous iron porphyrin complexes under similar conditions. A 200 μ L portion of the stock solution of the reduced porphyrin is then taken in a sample tube. CW electron paramagnetic resonance (EPR) spectra were collected using an X-band JEOL spectrometer. Samples were kept frozen and immersed in a cold liquid N₂ finger dewar (77K) during EPR data collection.

Resonance Raman. The sample concentration and preparation methods for rR are similar to EPR sample preparation. rR data were collected at 77K using 413.1nm laser equipped with Trivista 555 spectrograph (Princeton Instruments) (gratings used in the three stages were 900, 900, and 1800/2400 grooves/mm) fitted with an electronically cooled Pixis CCD (camera) detector (Princeton Instruments).

UV-Vis. The sample preparation procedure is similar to that of EPR experiments except the iron porphyrins concentration were $30 \mu m$. $2ml 30 \mu m$ of these complexes were taken into the 1cm path length quartz cell cuvette with tight screw cap for maintaining the inert atmosphere during measurements. Data were collected at room temperature (298 K).

Electrochemical Measurements. All electrochemical experiments were carried out using CH instruments (model CHI700E, CHI720D Electrochemical Analyzer). Bipotentiostat, reference electrodes, Teflon plate material evaluating cell (ALS Japan) were purchased from CH Instruments. The RDE set up from Pine Research Instrumentation (E6 series Change Disk tips with AFE6M rotor) was used to obtain the RDE data.

Formation of Self-Assembled Monolayer (SAM). Au wafers and disks were cleaned electrochemically by sweeping several times between 1.5 V to -0.3 V (vs. Ag/AgCl) in 0.5 M H_2SO_4 . Ag disks were cleaned in alumina (size: 1, 0.3 and 0.05µm) and then roughened in 0.1 M KCl solution as described in literature.⁴ SAM solutions were prepared in ethanol using 0.4 mM concentration of the C₈SH alkanethiol. Mixed SAM solution is prepared by mixing the 1-(11-Mercaptoundecyl)imidazole and Octanethiol in 1:9 mole fraction ratio. This ratio was chosen following a literature report to obtain a

perfectly distributed ImdC₁₁SH SAM surface which binds porphyrin axially without any steric hindrance.⁵ Total thiol concentration was kept 0.4 mM. Freshly cleaned Au wafers, disks and freshly roughened Ag disks were initially rinsed with tripled distilled water, ethanol, purged with N₂ gas and then immersed in the depositing solution of SAM in ethanol for 48 h. SAM formation is confirmed by recording the Cyclic voltammetry and XPS as previously reported (Fig. S1).

Attachment of Catalysts on SAM Modified Ag and Au Electrode. The SAM modified Au and roughened Ag disks were taken out of the depositing solutions, rinsed with ethanol and copious amount of water and then mounted on the RRDE set-up. Heme b and diacetyl heme were attached by incubating the modified Au/Ag electrodes in the respective DMSO or DMF solutions for at least 2 h. After this, the electrode surfaces were rinsed with copious amount of DMSO/DMF and water respectively to remove any excess heme from the surface. In case of iron porphyrin complexes (FeTPP, FePf, FeDEsP and FeTEsP), chloroform solution of these complexes was drop-casted evenly on the electrode for 30 min for complete loading. After each respective loading, the surfaces were thoroughly rinsed with chloroform, ethanol and triply distilled water before carrying out electrochemical or SERRS/SERRS-RDE experiments. Cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS) were performed to characterize the catalyst attached to the SAM coated gold electrode as previously reported (Fig S2).

Electrochemical Experiments. All electrochemical experiments were carried out in pH 7 buffer (unless otherwise mentioned) containing 100 mM Na₂HPO₄.2H₂O and 100 mM KPF₆ (supporting electrolyte) using Pt wire as the counter electrode and double layer Ag/AgCl as the reference electrode. For the formation of bis-imidazole complexes, 100mM imidazole added pH 7 buffer were used. This is to be noted that presence of any excess imidazole in the buffer can reduce the porphyrin complexes to ferrous oxidation state especially in case of FeDEsP and FeTEsP, due to their relatively anodic Fe^{III/II} reduction potentials. pD 7 buffer was prepared by dissolving the required amount of electrolyte in D₂O and adjusted the pH to 6.6 in pHmeter as noted in literature.⁶ All electrochemical data were plotted following polarographic convention. A 3-neck glass cell fitted with PTFE stoppers from Pine research was used for all electrochemical experiments unless otherwise mentioned. Separation of the WE compartment separated from CE compartment didn't result in any difference in the data output. All experiments were carried out at 25°C. Applied voltages were corrected for IR compensation by running the IR compensation test in the electrochemical workstation. For anaerobic experiments the electrolyte was purged by UHP grade Argon gas at 10mL/min flow rate. Initial direction of the scan was cathodic. Electrochemical stability and purity of the catalyst at electrode surface during electrochemical experiments were verified by taking CV before and after the experiments where no visible changes were encountered (Fig. S28). The possibility of platinum cross contamination from the Counter electrode was checked by changing it to gold and glassy carbon electrode respectively. No change was observed in voltammogram (Fig. S29). LSV data for SAM modified Au electrode was checked where no electrocatalytic current was present as expected (Fig. S30). The effective diameter of Au and Ag electrode is 5mm.

Coverage Calculation. The surface coverage for a particular redox couple is estimated by taking the average of the integrated area under the corresponding oxidation and reduction currents of the respective species obtained from their reversible voltammogram. The value can be obtained from the equation: $\Gamma = Q/nFA$ [where Q = integrated area under the reduction/oxidation current in coulomb, n = no of electron involved in the process (n = 1), F =96500 C, and A = microscopic area of the disk

(0.196 cm²)]. The experiments were repeated three times and an average value with standard deviation has been presented.

Table S1: Surface coverage calculation of different complexes when attached to ImdC ₁₁ SH SAM surface			
calculated from Fe ^{III/II} redox couple CV area in pH7 buffer in absence of O ₂ and ORR current density			
normalized w.r.t. surface coverage (by taking ratio of $\Gamma_{FeTPP} / \Gamma_{cat}$ and multiplying the current (I _{cat}) at			
E_{ORR} by this factor for other catalysts to obtain I_{max}) in air saturated pH7 buffer.			
Complex	Surface Coverage (Γ_{cat}) (mol/cm ²)	I_{cat} at E_{ORR} (μA)	
FeTPP	$12.76 \pm 0.95 \times 10^{-12}$	10.94 ± 1.43	
FePf	$9.93 \pm 1.12 \times 10^{-12}$	52.18 ± 2.32	
FeDEsP	$8.80 \pm 0.67 \times 10^{-12}$	34.44 ± 1.68	
FeTEsP	$5.36 \pm 0.67 \times 10^{-12}$	43.45 ± 1.84	
Heme b	$9.45 \pm 1.27 \times 10^{-12}$	13.52 ± 1.37	
Diacetyl heme	$10.67 \pm 0.45 \times 10^{-12}$	39.18 ± 2.78	

Rotating Ring Disk Electrochemistry (RRDE). Partially Reduced Oxygen Species (PROS) Detection and Calculation. The platinum ring and the Au disk were both polished using alumina powder (grit sizes: 1, 0.5, and 0.03 μ m) and electrochemically cleaned and inserted into the RRDE tip which was then mounted on the rotor and immersed into a cylindrical glass cell equipped with Ag/AgCl reference and Pt counter electrodes. In this technique, the potential of the disk is swept from positive to negative and when O₂ is reduced, any H₂O₂, i.e., a 2e⁻ reduction product of O₂, produced in the working disk electrode is radially diffused to the encircling Pt ring, which is held at a constant potential and oxidizes the H₂O₂ back to O₂. The ratio of the 2e⁻/2H⁺ current (corrected for collection efficiency) at the ring and the catalytic current at the disk is expressed as PROS and it provides an insitu measure of the 2e⁻/2H⁺ reduction side reaction. The collection efficiency (CE) of the RRDE setup was measured in a 2 mM K₃[Fe^{III}(CN)₆] and 0.1 M KNO₃ solution at a 10 mV/s scan rate and 300 rpm rotation speed. A 17 ± 1.2% CE was generally recorded during these experiments (Fig. S26). The potential at which the ring was held at pH 7 for detecting H₂O₂ was obtained from literature.⁷

Surface Enhanced Resonance Raman Spectroscopy Coupled with Rotating Disk electrochemistry (SERRS-RDE). SERRS-RDE data were collected using a Trivista 555 spectrograph (Princeton Instruments) (gratings used in the three stages were 900, 900, and 1800/2400 grooves/mm) fitted with an electronically cooled Pixis CCD (camera) detector (Princeton Instruments) and 413.1 nm excitation from a Kr⁺ laser (Coherent Innova Sabre SBRC-DBW-K), rotating the electrode at 200 rpm unless noted otherwise.

Ag disks were cleaned using Alumina powder (grit size 1, 0.3, and 0.05 μ m) and then roughened in a 0.1 M KCl solution using reported procedures and then immersed in SAM solutions. The catalysts were loaded as mentioned earlier. The roughened modified Ag disks were then inserted into the RRDE setup for the collection of SERRS-RDE data. The disks were held at 0 V vs Ag/AgCl to obtain the oxidized spectra and at Fe^{III/II} E_{1/2} potentials (from CV) vs Ag/AgCl to obtain the reduced spectra and the spectra under steady state conditions under anaerobic and aerobic conditions, respectively. Experiments were done using an excitation wavelength 413.1 nm and the power used at the electrode surface was 8-10 mW. All the SERRS spectra have been normalized using the characteristic buffer peaks which appear at 742 cm⁻¹ (coming from electrolyte KPF₆) and 951 cm⁻¹ (symmetric v_{P-0}). ORR current before and after these experiments remain the same, suggesting that most of the iron porphyrin are intact on the electrode surface (Fig. S27).

X ray Photoelectron Spectroscopy. XPS (XPS, Omicron, model: 1712-62-11) measurements were performed using a high-resolution monochromatic Mg–Kα radiation source at 1253.6 eV under 15 kV voltage and 5 mA current conditions. The ImdC₁₁SH SAM attached Au electrodes were used for XPS data collection. The ImdC₁₁SH SAM attached Au wafers were kept under Ar atm prior to data acquisition. FeTPP porphyrin was drop casted and was subsequently washed thoroughly to get a monolayer of iron porphyrin complex for XPS measurements (Fig. S1-2). XPS data of ImdC₁₁SH bound Au wafer clearly show the presence of N, S and C elements. The $4f_{7/2}$ and $4f_{5/2}$ binding energy peak for Au wafer appear at 83.8 eV and 87.8 eV, respectively. The high resolution N_{1s} spectra shows two peaks with binding energies 399.1 eV and 401.1 eV indicates two environments for N atoms in the $ImdC_{11}SH$ SAM, where one N is attached to carbon tail and the other being free to coordinate. The equal intensity of these two peaks further confirms both N's has equal population at the surface. The binding energies of S ($2p_{3/2}$ and $2p_{1/2}$ at 161.8 eV and 163.2 eV respectively) and C (1s at 285.2 eV) are in agreement with reported data for such constructs. Upon covalent attachment of FeTPP to ImdC₁₁SH SAM, 3p_{3/2}, 2p_{3/2} and 2p_{1/2} binding energy peak for the Fe^{III} appear at 55.8 eV, 711.3 eV and 724.1 eV, respectively. In the N_{1s} region, a new peak at 398.7 eV with higher intensity appears. This peak corresponds to 4 nitrogen atoms of the iron porphyrin complex. Other elements binding energy remains same which ensure the integrity of the SAM at the electrode surface when attached to the iron porphyrin complex. The C_{1s} peak becomes broad since it contains contribution from different types of C atoms (aromatic, aliphatic etc.).



Figure S1. High resolution X-ray photoelectron spectra for $ImdC_{11}SH$ attached Au electrode. (A) N $1s_{1/2}$ (B) S $2p_{3/2}$ and $2p_{1/2}$ (C) C $1s_{1/2}$ (D) Au $4f_{7/2}$ and $4f_{5/2}$.



Figure S2. High resolution X-ray photoelectron spectra for FeTPP covalently attached to ImdC₁₁SH modified Au electrode. (A) Fe $3p_{3/2}$ (B)Fe $2p_{3/2}$ and $2p_{1/2}$ (C) N $1s_{1/2}$ (D) C $1s_{1/2}$ (E) S $2p_{3/2}$ and $2p_{1/2}$



Figure S3. Lorentzian fit of the SERRS-RDE v_4 region showing high spin and low spin components when attached to different SAM modified electrode surfaces for ferric and ferrous heme b in pH buffer. The ration of low spin to high spin heme b in ferric and ferrous state are 2.91 and 3.22 respectively.



Figure S4. Lorentzian fit of the SERRS-RDE v_2 region showing high spin and low spin components when attached to different SAM modified electrode surfaces for ferric and ferrous heme b in pH7 buffer.



Figure S5. Lorentzian fit of the SERRS-RDE v_4 region showing high spin and low spin components when attached to different SAM modified electrode surfaces for ferric and ferrous diacetyl heme in pH7 buffer. The ratio of high spin to low spin diacetyl heme in ferric and ferrous state are 4.25 and 3.86 respectively.



Figure S6. SERRS-RDE data of diacetyl heme attached to different SAM modified Ag electrode surface indicating the acetyl carbonyl($v_{C=0}$) stretches in both ferric and ferrous states.



Figure S7. Lorentzian fit of the SERRS-RDE v_4 and v_2 region showing high spin and low spin components when FeTPP attached to ImdC₁₁SH SAM modified electrode surfaces for ferric and ferrous states in pH7 buffer. The ratio of low spin to high spin FeTPP in ferric and ferrous state are 5.72 and 3.63 respectively. Purple traces in Fe^{II} samples are from residual ferric FeTPP.



Figure S8. Uv-Vis absorption spectra of 50µM Fe^{III}DEsP (high spin) and Fe^{II}DEsP (high spin) in dichloromethane solution at room temperature. Zoomed in Q-band region is shown in inset.



Figure S9. Uv-Vis absorption spectra of 50µM Fe^{III}DEsP-(Imd)₂ (low spin) and Fe^{III}DEsP-(Imd)₂ (low spin) in dichloromethane solution at room temperature formed by adding 10 equivalent imidazole to the Fe^{III}DEsP and Fe^{III}DEsP respectively.



Figure S10. X-band EPR data of FeDEsP complex in both ferric and ferrous states with and without imidazole added showing low spin and high spin states respectively. The EPR data were recorded at 77K in liq. N_2 .



Figure S11. Resonance raman data in the high frequency region (excitation 413.1 nm, laser power 6-8 mW at sample) of the ferric and ferrous FeDEsP in both high spin and low spin states in dichloromethane solution at room temp (Details in experimental section).



Figure S12. Lorentzian fit of the SERRS-RDE v_4 and v_2 region showing high spin and low spin components when FeDEsP attached to ImdC₁₁SH SAM modified electrode surface for ferric and ferrous FeDEsP in pH7 buffer. The ratio of low spin to high spin FeDEsP in ferric and ferrous state are 0.47 and 1.24 respectively.



Figure S13. SERRS-RDE data of A) FeDEsP and B) FeTEsP attached to different SAM modified Ag electrode surface indicating the ester carbonyl stretches in both ferric and ferrous states. The higher intensity of the ester group in FeTEsP compared to FeDEsP reflects increase in number of ester functional groups.



Figure S14. Resonance raman data in the high frequency region (excitation 413.1 nm, laser power 6-8 mW at sample) of the ferric and ferrous FeTEsP in both high spin and low spin states in dichloromethane solution at room temp (Details in experimental section).



Figure S15. Uv-Vis absorption spectra of 50μ M Fe^{III}TEsP (high spin) and Fe^{II}TEsP (high spin) in dichloromethane solution at room temperature.



Figure S16. Uv-Vis absorption spectra of 50μ M Fe^{III}TEsP-(Imd)₂ (low spin) and Fe^{III}TEsP-(Imd)₂ (low spin) in dichloromethane solution at room temperature formed by adding 10 equivalent imidazole to the Fe^{III}TEsP and Fe^{III}TEsP respectively.



Figure S17. X-band EPR data of FeDEsP complex in both ferric and ferrous states with and without imidazole added showing low spin and high spin states. The EPR data were recorded at 77K in liq. N_2 .



Figure S18. Lorentzian fit of the SERRS-RDE v₄ and v₂ region showing high spin and low spin components when FePf attached to ImdC₁₁SH SAM modified electrode surfaces for ferric and ferrous FePf in pH7 buffer. The ratio of low spin to high spin FePf in ferric and ferrous state are and 7.62 and 7.93 respectively.



Figure S19. Low region SERRS-RDE spectra of (A) Heme b (B) FeTPP showing Fe^{III}-OH stretching frequency and their secondary isotope shifts upon deuterium labelling when attached to ImdC₁₁SH SAM modified surface pH7/pD7 buffer medium. This indicates the 6th axial position of ferric Heme b and FeTPP remains occupied by water derived ⁻OH ligand in physiological conditions.



Figure S20. Low region SERRS-RDE spectra of $Fe^{III}Pf$ when attached to ImdC₁₁SH SAM modified surface pH7/pD7 buffer medium. No Fe^{III} -OH(D) bands were observed in this region which shifts upon deuterium labelling. This indicates the 6th axial position of ferric FePf remains unoccupied in physiological conditions.



Figure 21. CV data of (A) Heme b (B) Diacetyl heme on C₈SH (green trace), ImdC₁₁SH SAM modified Au electrode (red trace) and ImdC₁₁SH SAM modified Au electrode with 100mM imidazole (blue trace) in absence of O₂ in pH7 phosphate buffer with KPF₆ supporting electrolyte at a scan rate of 1V s⁻¹.



Figure 22. CV data of (A) FeTPP (B) FeDEsP and (C) FeTEsP on C_8SH (green trace), ImdC₁₁SH SAM modified Au electrode (red trace) and ImdC₁₁SH SAM modified Au electrode with 100mM imidazole (blue trace) in absence of O_2 in pH7 phosphate buffer with KPF₆ supporting electrolyte at a scan rate of 1V s⁻¹.



Figure 23. RRDE data of (A) Heme b and (B) Diacetyl heme attached to ImdC₁₁SH SAM modified Au electrode in air saturated pH7 buffer at a scan rate of 10 mV s⁻¹ at 300 rpm using a Pt counter electrode and an Ag/AgCl (satd. KCl) reference electrode.



Figure 24. RRDE data of (A) FeTPP (B) FeDEsP and (C) FeTEsP attached to ImdC₁₁SH SAM modified Au electrode in air saturated pH7 buffer at a scan rate of 10 mV s⁻¹ at 300 rpm using a Pt counter electrode and an Ag/AgCl (satd. KCl) reference electrode.



Figure 25. Low region SERRS-RDE data of Heme b when attached to C_8SH (blue) and ImdC₁₁SH (red) SAM modified electrode under reduced conditions in CO saturated pH7 buffer medium. The Fe-C stretch of Fe²⁺-CO adduct is shown.



Figure 26. RRDE data for the detection of collection efficiency using 2 mM K_3 [Fe^{III} (CN)₆] and 0.1 M KNO₃ solution at a 10 mV/s scan rate and 300 rpm rotation. Here the ring is held at a constant potential of 0.6V vs. Ag/AgCl.



Figure 27. LSV data of ImdC₁₁SH modified FePf complex in pH 7 buffer before and after SERRS-RDE experiment respectively.



Figure 28. 10 cycles of cyclic voltammogram at 5V/s scan rate for FePf over ImdC₁₁SH modified Au electrode where peak current remains stable showing stability of the catalyst under experimental condition.



Figure 29. LSV data Fe-picket fence over ImdC₁₁SH modified Au electrode at pH 7 phosphate buffer using Pt counter (blue trace), glassy carbon counter (red trace) and Au counter (green trace) respectively.



Figure 30. Overlay of disc current containing the electroactive species during LSV along with the blank background current of the electrode over $ImdC_{11}SH$ modified Au electrode at 100 mV/s scan rate in air saturated pH7 phosphate buffer.

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