In this chapter, an iron porphyrin catalyst with four electron donor groups is reported. The porphyrin ligand bears a distal hydrogen bonding pocket which inverts the normal axial ligand binding selectivity exhibited by porphyrins bearing sterically crowded distal structures. This catalyst specifically reduces $\text{O}_2$ by four electrons under both fast and slow electron flux at pH 7.

### 1.1 INTRODUCTION

Metalloporphyrin containing active sites are ubiquitous in nature. These enzymes are involved in fundamental reactions, e.g. $\text{O}_2$ transport (globins), $\text{O}_2$ reduction (cytochrome c oxidase), substrate oxidation (cytochrome P450), small molecule reduction (Nitrite Reductase etc.) and electron transfer (cytochrome c), which forms the basis of life and the ecology around it. \(^1\,^2\,^3\)

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**Chapter 1**

**SELECTIVE FOUR ELECTRON REDUCTION OF O$_2$ BY AN IRON PORPHYRRIN ELECTROCATALYST UNDER FAST AND SLOW ELECTRON FLUXES.**
Although the basic backbone of most of the enzymes are same but depending on the active site environment and geometrical configurations, reactivities are different. Mimicking the diverse reactivities of these active sites has been a long term goal of inorganic chemists. Several scientists have been working in the field of bio-inorganic chemistry containing heme cofactor as there are several enzyme active sites that does tremendous catalytic activity. One of these is the O$_2$ reduction reaction. Generally O$_2$ reduction is done by Pt as the electrocatalyst for the fuel cell.

$$\text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad \text{......... (1.1)}$$

The Oxygen reduction reaction is a key component of many fuel cells which promises excellent efficiency in the conservation of chemical to electrical energy using Pt as electrocatalyst. But for cost and scarcity, there is a great interest in the catalysts that do not require precious metals like Pt. the new catalyst should be working rapidly at moderate over-potential and also selective for O$_2$ reduction. In biological system there are several peptides that show the proton donating ability, also some electron storage proteins which are the key factors for the redox reaction. Mimicking these activities in the daily life is the long challenging.

Recently porphyrins have major role in electrocatalytic Oxygen reduction. Several groups have been involved in synthesizing meso-tetraaryl porphyrin derived catalysts where substituents on the aryl ring are used to include additional chemical functionalities by introducing specific distal super-structures.$^{4, 5}$ Most of the cases, these distal environments are important for the selectivity of the active sites to be exposed in the aerial atmosphere. It may be co-ordination site or electron donating site (this chapter). These distal sites are responsible for extra electron donation. Here we are able to synthesize an iron porphyrin containing four electron donating ferrocene on the distal position (same side). These are responsible for electron donation for the Oxygen reduction. The catalyst reduces O$_2$ in both slow and fast SAM in buffer medium

**1.2 MATERIALS & METHODS.**

Tetramethyilsilylazide is purchased from AVRA Pvt. Ltd, t-Butyl nitrite is purchased from MERCK and all other reagents e.g. Ethynyl Ferrocene, 2-Nitrobenzaldehyde, Pyrrole, Na-ascorbate were purchased from Aldrich chemical company. t-Butanol, Acetonitrile, Dichloromethane, Na$_2$SO$_4$, CuSO$_4$ were from MERCK, and used without any further
purification. Unless otherwise mentioned all reactions were performed at room temperature and the column chromatography were performed on SiO\textsubscript{2} (60-100 mesh). Au (III) wafers were bought from Platypus Technologies (1000Å of Au on 50 Å of Ti adhesion layer on top of a Si (III) surface. Au discs and Edge Plane Graphite (EPG) discs were purchased from Pine Instruments. The absorption spectra are measured in the SHIMDZU spectrograph (UV-2100). The FT-IR data are measured on the Shimadzu FT-IR 8400S instrument. All the NMR spectra were recorded on the Bruker DPX-300 or DPX-500 spectrometer at room temperature. The EPR spectrum is recorded on a JEOL instrument. The mass spectra are recorded by QTOF Micro YA263 instrument. X-ray single crystal data was collected at 120 K using radiation on a SMART APEX diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution refinement were carried out using the software package of APEX II. The structure was solved by direct method and refined in a routine manner. The non-hydrogen atoms were treated anisotropically. All the hydrogen atoms were located on a difference Fourier map and refined.

**ELECTROCHEMICAL MEASUREMENTS**

**Cyclic Voltammetry**

The cyclic voltammograms are recorded on a PAR instrument potentiostat/galvanostat model 237A. A 2 mm diameter Pt electrode was used as a working electrode. A Pt wire was used as a counter electrode. The measurements were made against an Ag/AgCl aqueous reference electrode with scan rates varying from 50mvs to 500mvs.

**FABRICATION OF THE $\alpha$-FeFC PHYSIADOSORBED ELECTRODES:**

a. **On Edge Plane Graphite (EPG):** 50 uL of a dilute solution (1mM) of the catalyst (in CHCl\textsubscript{3}) was uniformly distributed on the disc. After the CHCl\textsubscript{3} has evaporated, the surface was sonicated in ethanol and washed with triple distilled water.

b. **On Alkyl thiol Self Assembled Monolayer (SAM):** On freshly cleaned Au disc self-assembled monolayer of C\textsubscript{16}SH were made. 50 mL of a dilute solution (1 mM) of the catalyst (in CHCl\textsubscript{3}) was uniformly distributed on the alkyl thiol SAM. After the CHCl\textsubscript{3} has evaporated, the surface was sonicated with ethanol and washed with triple distilled water.

**Rotating Disc Electrochemistry:** The RDE measurements were performed on a CHI 700D Bi-potentiostat with a Pine Instrument Modulated speed rotor fitted with an E6 series Changedisc tip. The graphite surface was cleaned by polishing it uniformly on a Silicon
The complex was physiadsorbed on the disc as described above. The Koutecky-Levich experiment was done at different rotations 100 rpm, 200 rpm, 300 rpm, 500 rpm, 800 rpm.

### 1.3 RESULTS

**Scheme 1.1:** General scheme for the synthesis of clicked porphyrins

Here we are started with tetraaminophenyl porphyrin (TAPP) which is first prepared by Professor James P. Collmann. We are using TAPP to be our basic scaffolds for this catalyst. All the amino functional groups are protected by pivolyl chlorides. Synthesis of most of these heme types of catalysts require use of acid chlorides (amides) or elevated temperatures (Michael addition). These techniques have been widely used and have been very successful in synthesizing porphyrin ligands with and without covalently attached arms bearing additional co-ordinating ligands. Several remarkable porphyrin catalysts have been reported using these techniques. These include the cytochrome c oxidase, nitric oxide reductase and cytochrome P450 models. Porphyrins bearing distal functional groups have been used to synthesize a series of pacman porphyrins which show remarkable O₂ and H⁺
reduction properties.\textsuperscript{19, 20} Lately the PCET process involved in O\textsubscript{2} reduction has been elucidated by an Iron porphyrin bearing a covalently attached carboxylic acid residue.\textsuperscript{21}

The use of acid chloride in the synthesis of porphyrin ligands bearing distal functionalities may sometimes limit the choice of functional groups that can be introduced and the use of elevated temperatures during Michael addition may lead to generation of a mixture of atropisomers. The 1,3-cycloaddition of azides to alkynes (known as the “click” reaction) is a benign alternative for attachment of most functional groups.\textsuperscript{22} It can be performed in various solvents at room temperatures with high yields.\textsuperscript{23, 24} It has extensively been used to attach electrocatalysts to electrodes.\textsuperscript{25-28} A synthetic method exploring this mode of attachment to generate distal super-structures bearing porphyrins is explored in this study.

![Figure 1.1: Molecular structure of $\alpha_4$-ZnFc\textsubscript{4} complex C (black), Fe (orange), N (blue), Zn (pink) and O (red). H atoms and CH\textsubscript{2}Cl\textsubscript{2} solvent molecules are omitted for clarity.](image)

The general synthetic methodology (Scheme: 1.1) utilizes the $\alpha_4$-meso-tetra-o-aminophenylporphyrin (1) which is synthesized by known methods.\textsuperscript{29} This is then converted to $\alpha_4$-meso-tetra-o-azidophenylporphyrin (2) using tert-butyl nitrite and trimethylsilylazide.\textsuperscript{30} Metallation with Zn(OAc)\textsubscript{2} yields $\alpha_4$-meso-tetra(2-azidophenyl)porphyrinatoZn(II) (3). This is followed by attachment of the terminal alkyne containing functionality using click
The metallation by Zn is required for structural characterization and to avoid partial Cu incorporation into the porphyrin ring during the cycloaddition reaction.

The $\alpha_4$-meso-tetra-(2-(4-ferrocenyltriazole)-phenyl)-porphyrinato Zn(II) ($\alpha_4$-ZnFc$_4$) compound crystallizes from a CH$_2$Cl$_2$/MeOH solvent with a P2(1)/n point group. The structure (Fig. 1.1) shows the four ferrocene groups on the distal side of the porphyrin ring. These are attached to the phenyl substituents via the 1, 2, 3-triazole ring formed after the cycloaddition reaction. A MeOH solvent molecule is bound to the Zn. There is a H$_2$O molecule hydrogen bonded to the MeOH (O --- O = 2.61 Å) and to the N$_3$ moiety of two triazoles (N --- O = 2.8 Å). Interestingly the axial ligand MeOH is in the crowded distal pocket and not in the open proximal side of the complex. This is very different from picket fence type porphyrins where axial ligands bind the open proximal face of the macrocycle to avoid steric congestion. This unusual axial ligand binding is due to the presence of a hydrogen bonding cavity, provided by the distal triazole rings, which overcomes the steric hindrance.

Demetallation of the porphyrin bound Zn is performed by acidification and the free ligand, $\alpha_4$-meso-tetra(2-(4-ferrocenyltriazol)phenyl)porphyrin ($\alpha_4$-Fc$_4$), is obtained which is followed by metallation with FeBr$_2$ under inert atmosphere to yield $\alpha_4$-meso-tetra(2-(4-ferrocenyltriazol)phenyl)porphyrinato Fe(II) ($\alpha_4$-FeFc$_4$). The Zn and Fe bound complexes are characterized by very different optical properties (SI).

1.4 SYNTHESIS

1. $\alpha_4$-meso-o-azidophenyl-porphyrin (TAzPP)

To a solution of TAPP (100 mg, 0.1482 mmol) in 15 ml acetonitrile, t-butyl-nitrite was (106 µl, 6 eq.) added followed by the addition of TMS-azide (94 µl, 4.8 eq.) and the reaction was stirred for 4 hours. To the reaction mixture DCM and water were added and after workup the organic layer was collected, dried over anhydrous Na$_2$SO$_4$ and was purified by column chromatography with 70% DCM- hexane mixture as eluent.

Yield : 95% (101 mg).

($^1$H NMR,CDCl$_3$) -2.73 (s, 2H), 7.42 (m, 4H), 7.64 (m, 4H), 7.74 (d, 4H, $J = 5.0$ Hz), 7.93 (d, 4H, $J = 5.0$ Hz), 8.60 (s, 8H). IR spectra (cm$^{-1}$) – 2123, 2090 for (N$_3$) stretch. ESI-MS (+ve ion mode, acetonitrile) m/z = 779.11 (100%), [MH]$^+$. 
2. α₄-ZnTAzPP: To a solution of TAzPP (460 mg, 0.635 mmol) in 25 ml THF, Zn(OAc)$_2$.2H$_2$O (154 mg, 1.1 eq.) was added and the reaction was stirred for 3 hours. The reaction was quenched with water, DCM was added and the organic layer was collected. It was dried over anhydrous Na$_2$SO$_4$ and was purified by column chromatography using 85% DCM-hexane mixture. Yield = 497 mg (93%) ($^1$H NMR, CDCl$_3$) 7.51 (t, 4H, $J=7.5$ Hz), 7.58 (d, 4H, $J= 8$ Hz), (t, 4H, $J= 7.5$Hz), 8.77 (s, 8H). IR spectra (cm$^{-1}$) - 2088, 2123 (for N$_3$- stretch). ESI-MS - (+ve ion mode, acetonitrile) m/z = 841.0704 (32%, [MH]$^+$), 907.9606 (100%, [M+ acetonitrile+ Na$^+$]).

3. α₄-tetra-(3-ferrocenyl-1,2,3-triazolyl)-phenylporphinato zinc (α₄-ZnFc$_4$) To a solution of ZnTAzPP (50 mg, 0.059 mmol) in 30 ml t-butyl alcohol, ethynyl ferrocene (124 mg, 10 eq.) was added followed by the addition of CuSO$_4$/sodium ascorbate. The reaction was stirred overnight. To it water was added followed by the addition of DCM. The organic layer was collected, dried over anhydrous Na$_2$SO$_4$ and was purified by column chromatography using (9:1) DCM-methanol mixture as eluent. Yield = 80 mg (80%). ESI-MS (+ve ion mode, acetonitrile) m/z = 1682.0502 (100%, [MH]$^+$). IR Spectra (cm$^{-1}$) 995, 1627, 3436.

4. α₄-tetra-2-(3-ferrocenyl-1,2,3-triazolyl)-phenylporphyrin (α₄-Fc$_4$): To a solution of α₄-ZnFc4 (50 mg product in 15 ml DCM solution, 10 ml 6(M) HCl was added and the reaction was stirred for 45 mins. The reaction was neutralized by aq. NH$_3$ solution, followed by the addition of DCM and water. The organic layer was collected, dried over anhydrous Na$_2$SO$_4$ and was purified by flash column chromatography using (99:1) DCM-MeOH solvent mixture. The demetallation of Zn was confirmed by Absorption spectroscopy and Mass Spectroscopy. Yield = 95%, $\lambda_{max}$=425, 517, 547, 547, 590, 648 nm, ESI-MS (+ve ion mode, acetonitrile) m/z = 1619.1897 (100%, [MH]$^+$), 1642.1045(68%, [M+Na]$^+$).

5. α₄-tetra-2-(3-ferrocenyl-1,2,3-triazolyl)-phenylporphinato iron (III) bromide ([α₄-FeFc$_4$]Br) To a solution of the demetallated product (230 mg, 0.142 mmol) in 15 ml dry degased THF, 2,4,6-collidine (37 µl, 2 eq.) was added, followed by addition of FeBr$_2$ (123 mg, 4 eq.) into
the solution. The solution was stirred overnight in a glove box. The reaction mixture was quenched by water followed by the addition of DCM. The organic layer was washed with brine solution and was collected. It was dried over anhydrous Na₂SO₄ and was purified by column chromatography using (99: 1) dry DCM–MeOH mixture in nitrogen atmosphere. The two fractions of comparable polarities were separated. They gave same molecular ion peak in the mass spectroscopy but different elemental analysis and FTIR data.

Yield = 92%. ESI-MS (+ve ion mode, acetonitrile) m/z = 1672.7169(100%, [M]+), λ_max (CHCl₃)= 421, 521, 572 nm.

Calc.value: ([α₄FeFc₄]Br. H₂O. MeOH) (more polar fraction): C (61.96), H (3.91) and N (12.43). Experimental value: C (62.15), H (3.64) and N (12.23).

Calc.value: ([α₄FeFc₄]Br. THF) (less polar fraction): C (63.33), H (3.76), N (12.31). Experimental value: C (63.79), H (3.77), N (12.04).

1.5 ELECTROCHEMISTRY

Cyclic Voltammogram of the α₄-ZnFc₄ complex in CH₂Cl₂ shows two oxidation reduction processes (Fig. 1.2, blue). The quasi-reversible wave with E_{1/2} of 0.54 V represents four Fe₃/II processes for the four ferrocene groups in the distal pocket of the α₄-ZnFc₄ complex. There is also an irreversible one electron process at 0.92 V. This represents the oxidation of the porphyrin ring (P) to a cation radical species (P⁺). For the α₄-FeFc₄ complex the quasi-reversible Fc/Fc⁺ couple is observed at 0.83 V and the one electron P/P⁺ couple is observed at 1.09 V (Fig. 1.2, red), consistent with previous reports on analogous complexes. Additionally, there is another one electron quasi-reversible wave at 0.34 V which represents the Fe³/II couple. Note that the Fc/Fc⁺ redox waves show no evidence for Fc-Fc interaction. This is due to ~7 Å separation between the Fc rings and is different from the results obtained on several ferrocene functionalized Zn porphyrin complexes. Thus the fully reduced α₄-FeFc₄ complex can in principle donate six electrons and act as an O₂ reduction catalyst.
Figure 1.2: CV of the $\alpha_4$-ZnFc$_4$ (blue) and the $\alpha_4$-FeFc$_4$ (red) complexes in CH$_2$Cl$_2$ solvent having 100 mM tetra-n-butyl-ammonium perchlorate as supporting electrolyte with Pt working electrode (2 mm diameter), Pt counter electrode and Ag/AgCl non-aqueous reference electrode at 50 mV/s scan rate. The individual redox processes are indicated in text.

The $\alpha_4$-FeFc$_4$ catalyst was deposited on an edge-plane graphite (EPG) disc electrode and its electrocatalytic $\text{O}_2$ reduction was investigated in pH 7 buffer. Linear sweep voltammetry (LSV) of this catalyst shows a substrate diffusion limited catalytic $\text{O}_2$ reduction current below -0.1 V (Fig. 1.3A). The Fc$^+/\text{Fc}$ reductive process is observed at 0.305 V under aqueous conditions which is ~0.5 V lower relative to its value in an organic medium and is consistent with previous reports. $^{37}$ Similarly the Fe$^{\text{III}}$/Fe$^{\text{II}}$ redox process (as indicated by the onset of the $\text{O}_2$ reduction current) is observed at -0.1 V in an aqueous medium relative to 0.34 V in CH$_2$Cl$_2$ i.e. ~ -0.45 V shift. The $\text{O}_2$ reduction current increases with increasing rotation rates following the Koutecky-Levich equation. $^{38}$

$$I^{-1} = i_k(E)^{-1} + i_L^{-1}, \quad \text{...............(1.2)}$$
Where $i_K(E)$ is the potential dependent kinetic current and $i_L$ is the Levich current. $i_L$ is expressed as

$$i_L = 0.62nFA[O_2](D_{O_2})^{2/3} \omega^{1/2} \nu^{-1/6}, \ldots (1.3)$$

where $n$ is the number of electrons transferred to the substrate, $A$ is the macroscopic area of the disc (0.096 cm$^2$), $[O_2]$ is the concentration of O$_2$ in an air saturated buffer (0.26 mM) at 25$^0$C, $D_{O_2}$ is the diffusion coefficient of O$_2$ (1.8x10$^{-5}$ cm$^2$s$^{-1}$) at 25$^0$C, $\omega$ is the angular velocity of the disc and $\nu$ is the kinematic viscosity of the solution (0.009 cm$^2$s$^{-1}$) at 25$^0$C. $^{39,40}$
**Figure 1.3:** (A) LSV of α₄-FeFc₄ deposited on EPG surface at multiple rotations in pH 7 buffer, using 100 mM KPF₆ as the supporting electrolyte and Pt and Ag/AgCl as counter and reference electrodes, respectively (inset) K-L plot of the α₄-FeFc₄ catalyst (black bold line). The theoretical plots for 4e⁻ and 2e⁻ processed are indicated by the dashed and the dotted lines, respectively. (B) RRDE data of α₄-FeFc₄ immobilized on hexadecanethiol, at pH 7, at 50 mV/s scan speed, 300 rpm rotation rate using Pt counter electrode and Ag/AgCl reference electrode. Plot of I¹ at multiple rotation rates with the inverse square root of the angular rotation rate (ω⁻¹/²) is linear. The slope obtained from the experimental data is almost identical to that predicted for a 4e⁻ process (n=4 line in Fig. 1.3A, inset) and very different from that predicted for a 2e⁻ process (n=2 line in Fig. 1.3A, inset). The experimentally obtained slope indicates an n=3.88 for the process, i.e. 97% of O₂ is reduced to H₂O. Thus a 4e⁻ reduction of O₂ to H₂O is facilitated by the α₄-FeFc₄ catalyst in a buffered aqueous medium.⁴¹ Note that non-ferrocene containing Fe porphyrins also show significant 4e⁻ reduction on EPG electrodes (i.e. under fast electron transfer conditions).⁴ So the electrocatalytic O₂ reduction under slow electron transfer rates were investigated.
The electrocatalytic O\textsubscript{2} reduction by the α\textsubscript{4}-FeFc\textsubscript{4} catalyst is also evaluated using rotating ring disc electrochemistry (RRDE) under slow electron flux.\textsuperscript{12} The catalyst, physiabsorbed on an Au disc electrode with a hexadecanethiol self assembled monolayer (SAM) reduces O\textsubscript{2} in air saturated pH 7 buffer (Fig. 1.3B). It has been demonstrated that the rate of electron transfer (ET) from the electrode is very slow for this long chain thiol monolayer (~ 5 s\textsuperscript{-1}) for both absorbed and covalently attached redox active species.\textsuperscript{37, 42} We assume similar k\textsubscript{ET} on these surfaces. K-L analysis, however, could not be performed on this dilute monolayer. Alternatively, RRDE can be used to evaluate the selectivity for 4e\textsuperscript{-}/4H\textsuperscript{+} O\textsubscript{2} reduction, as it can measure any partially reduced oxygen species (PROS) produced due to incomplete O\textsubscript{2} reduction \textit{in situ}.\textsuperscript{38, 43, 44, 45} The amount of PROS produced by the α\textsubscript{4}FeFc\textsubscript{4} catalyst absorbed on SAM, is only 9±1% i.e. 91±1\% of O\textsubscript{2} is converted to H\textsubscript{2}O. Note that an unfunctionalized iron porphyrin produces much greater amount of PROS under these conditions which leads to its rapid degradation.\textsuperscript{17} In fact, an analogous complex, bearing four triazole groups but no ferrocenes, produce quantitative PROS on the hexadecanethiol SAM bearing electrodes. Thus, the extra redox centers present in the distal pocket (the ferrocenes) facilitate complete reduction of O\textsubscript{2} to H\textsubscript{2}O even under slow ET. The effect of additional redox centers (ferrocenes) and possible proton relay sites (triazoles) observed here is resonant of those observed in several reported Fe and Co porphyrins and may result from a proton coupled electron transfer step involved in the 4e\textsuperscript{-}/4H\textsuperscript{+} reduction of O\textsubscript{2}.\textsuperscript{12, 17, 21, 46-48}

\textbf{1.6 ABSORPTION SPECTROSCOPY}

The absorption spectra of the α\textsubscript{4}-ZnFc\textsubscript{4} complex (Fig. 1.4, blue) in chloroform shows soret band at 427nm and Q band absorption at 552 nm. When the complex was demetalated α\textsubscript{4}-Fc\textsubscript{4} (Black), the band shifted to blue shift region at 425 nm and four other peaks arises at the Q band region which support that the α\textsubscript{4}-ZnFc\textsubscript{4} was completely demetalated. Again when the free base porphyrin α\textsubscript{4}-Fc\textsubscript{4} complex was metalated α\textsubscript{4}-FeFc\textsubscript{4} (Fig. 1.4, Red), then the soret band again shifted to blue region at 422 nm and Q bands appeared at 532 nm, 570nm which confirmed that Iron metal was inserted into the cavity of the Porphyrin.
Figure 1.4: Absorption spectra in the UV-Visible region for the free ligand (black) and the Zn(II) (blue) and the Fe(III) (red) complexes in CHCl₃

1.7 CONCLUSION

In summary, we report a “click chemistry” based approach to synthesize porphyrin catalysts with distal super-structures. This approach allows functionalization of the porphyrin catalyst using most functional groups. Using this strategy we have synthesized ferrocene functionalized Zn and Fe porphyrins which have several uncoupled redox centers. The latter is a good O₂ reduction electrocatalyst showing selective 4e⁻ reduction under both fast (>97%) and slow (>90%) electron flux at pH 7.

1.8 REFERENCES


36. However, as reduction of O₂ requires only four electrons, we think the P⁺/P couple, being the most unfavorable one, will possibly not be involved in the process.


41. At pH 7 no detectable decay is observed even after 1000 turnovers.


1.9 SUPPORTING INFORMATION

TAzPP

$^1$H NMR (CDCl$_3$)
IR spectra

ESI-MS
\( \alpha_4\text{-ZnTAzPP} \)

\(^1\text{H-NMR (CDCl}_3\text{)}\)
IR spectra
ESI-MS

KSIC-ZNNJ-GB
KSIC-ZNNJ 6 (0.112) Sb (1,40.00); Sn (Mn, 10±5.00); Cm (3:12)

TOF MS ES+ 5.67

841.0704
843.0216
840.3412
847.0242
843.0331
863.0337
865.0117
863.3283
907.9506
908.9558
909.9590
910.9550
925.9000
926.9598
935.9998
946.9550
957.9590
968.9500
979.9500
990.9500

m/z
α₄-tetra-2-(3-ferrocenyl-1,2,3-triazolyl)-phenylporphyrinato zinc (α₄-ZnFc₄)

¹H NMR (CDCl₃): The pyrrole H’s and the aromatic H’s can be assigned but detailed assignment of the ferrocene H’s and the triazole H’s are complicated because of the shifts resulting from the diamagnetic ring current and is beyond the scope of this study.
IR spectra
Simulated ESI-MS

α₄-tetra-2-(3-ferrocenyl-1,2,3-triazolyl)-phenylporphyrin (α₄-Fc₄)
\( \alpha_4\text{-tetra-2-(3-ferrocenyl-1,2,3-troazolyl)-phenylporphyrinato iron (III) bromide} \)

\( ([\alpha_4\text{-FeFc}_4]\text{Br}) \)
ESI-MS

Simulated (in red) ESI-MS
\(^1\)H NMR in CDCl\(_3\)

Pyrrole C-H’s (broad peak at 80 ppm), meso-phenyl-\(m\)-protons (12-14 ppm)

*J. Am. Chem. Soc.* **1984**, *106*, 4945-4950. Note that the complex is not symmetric (the triazole orientations are different in the crystal structure of the Zn complex). Thus the meso-phenyl-\(m\)-protons in the \(^1\)H NMR data do not show same resonance.
FTIR