Supporting Information for

A Hydrogen Bond Scaffold Supported Synthetic Heme Fe^{III}-O_2^- Adduct

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Experimental details

Materials

Tetramethylsilylazide (TMS-N_3) was purchased from AVRA pvt. Ltd, t-butyl nitrite (^{t}buONO) was purchased from MERCK, sodium sulphide nonahydrate ($Na_2S.9H_2O$) was from RANKEM and all other reagents e.g. methyl propiolate, ethynyl ferrocene, 2-nitrobenzaldehyde, pyrrole, sodium-L-ascorbate, ferrous bromide ($FeBr_2$), 2,4,6-collidine, methanol-d_4 (99.8%) were purchased from Aldrich chemical company. The $^{18}O_2$ isotope (99%) was purchased from ISOTEC. t-Butanol (^{t}-BuOH), tetrahydrofuran (THF), acetonitrile (CH_3CN), dichloromethane (DCM), Na_2SO_4, $CuSO_4$ were from MERCK, and used without any further purification. Unless otherwise stated all chemicals were used as purchased and reactions were performed at room temperature.

Instrumentation

UV-Vis absorption data were taken in Agilent technologies spectrophotometer model 8453 fitted with a diode-array detector. All the NMR spectra were recorded on a Bruker DPX-300 or DPX-500 spectrometer at room temperature. The EPR spectra were recorded on a JEOL instrument. The mass spectra were recorded by QTOF Micro YA263 instrument. Resonance Raman (rR) data ware collected using 413.1 nm excitation wavelength from a Kr^+ ion source (Coherent, Sabre Innova SBRC-DBW-K) and a Trivista 555 triple spectrophotometer (gratings used in the three stages were 900, 900 and 1800 grooves/mm) fitted with a Pixis CCD camera (Princeton Instruments). The optics (e.g. plano – convex lenses, mirrors etc.) for the collection of rR data were purchased from Sigma – koki, Japan.

Synthesis and Spectral Characterizations

1. Synthesis of α_4-*meso*-*o*-tetraazidophenylporphyrin (TAzPP)

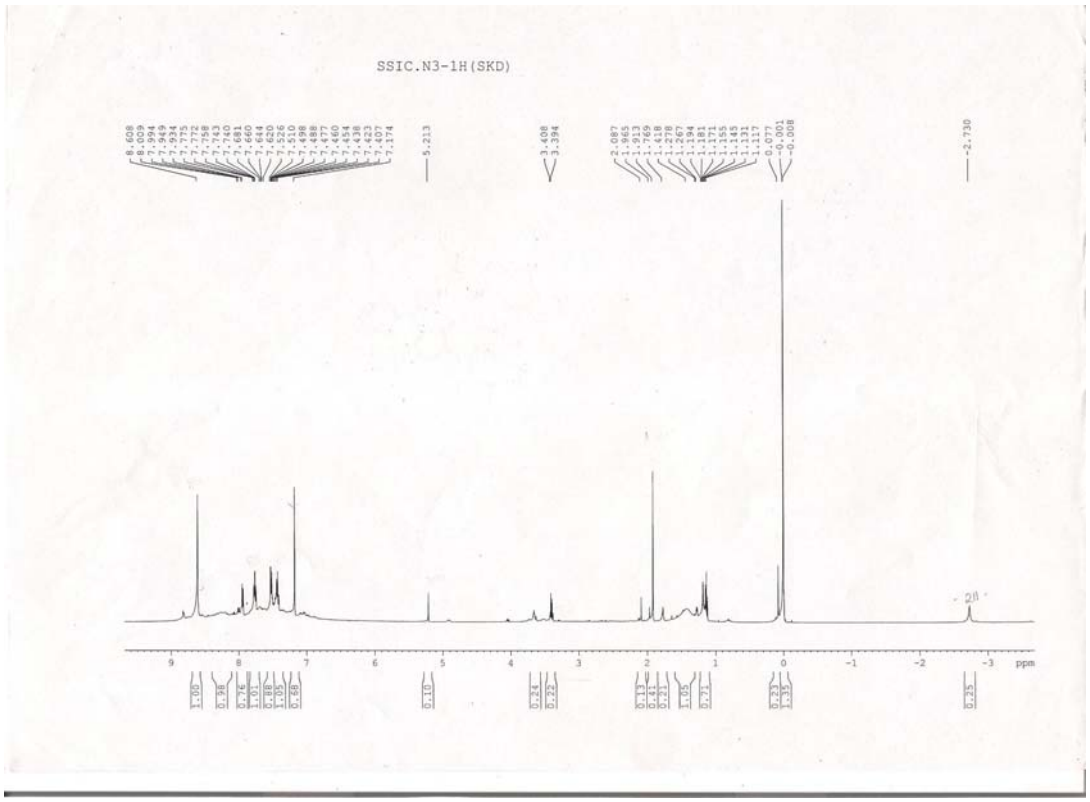
To a solution of α_4-*meso*-*o*-tetraaminophenylporphyrin (TAPP) (100 mg, 0.1482 mmoL) in 15 mL acetonitrile, t-butyl-nitrite was (106 µL, 6 eq.) added followed by the addition of TMS-azide (94 µL, 4.8 eq.) and the reaction was stirred for 4 hours. To the reaction mixture DCM and water were added and after workup the organic layer was collected, dried over anhydrous Na_2SO_4 and was purified by column chromatography with 70% DCM- hexane mixture as eluent.

Yield : 95% (101 mg).

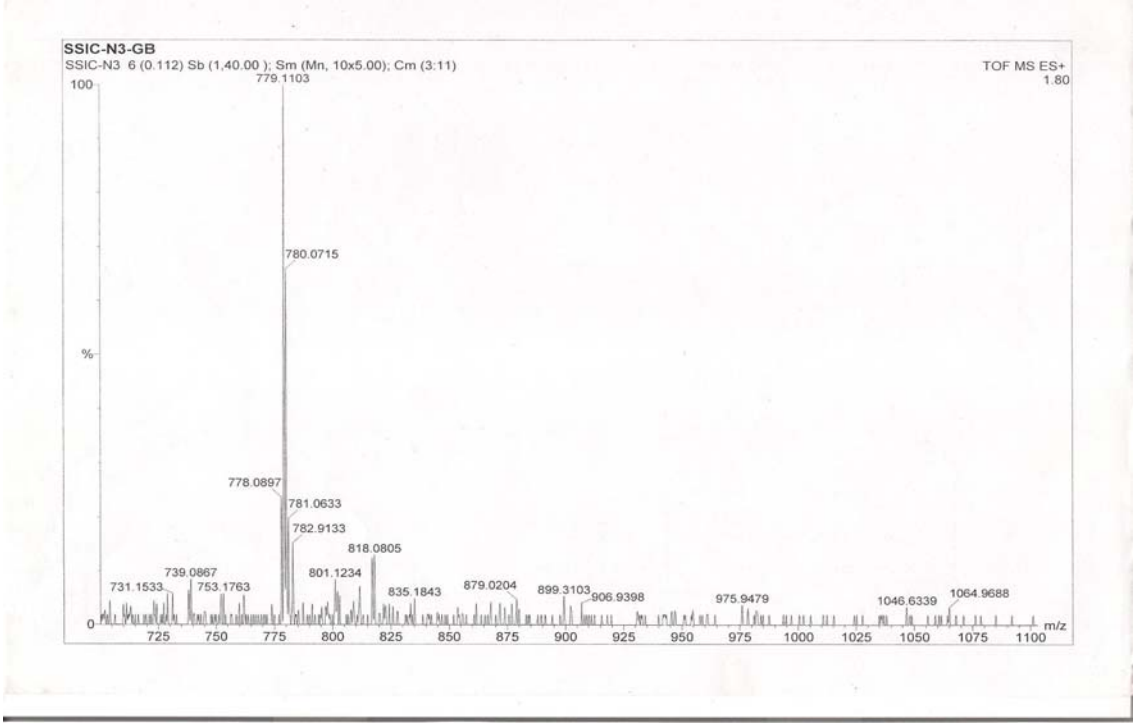
(^{1}H NMR,$CDCl_3$) -2.73 (s, 2H), 7.42 (m, 4H), 7.64 (m, 4H), 7.74 (d, 4H, J = 5.0 Hz), 7.93 (d, 4H, J = 5.0 Hz), 8.60 (s, 8H). IR spectra (cm^{-1}) – 2123, 2090 for (N_3^-) stretch. ESI-MS (+ve ion mode, acetonitrile) m/z = 779.11 (100%), $[MH]^+$

TAzPP

^{1}H NMR ($CDCl_3$)



ESI-MS



2. Synthesis of α_4-*meso*-*o*-tetraazidophenylporphyrinato zinc (α_4-ZnTAzPP):

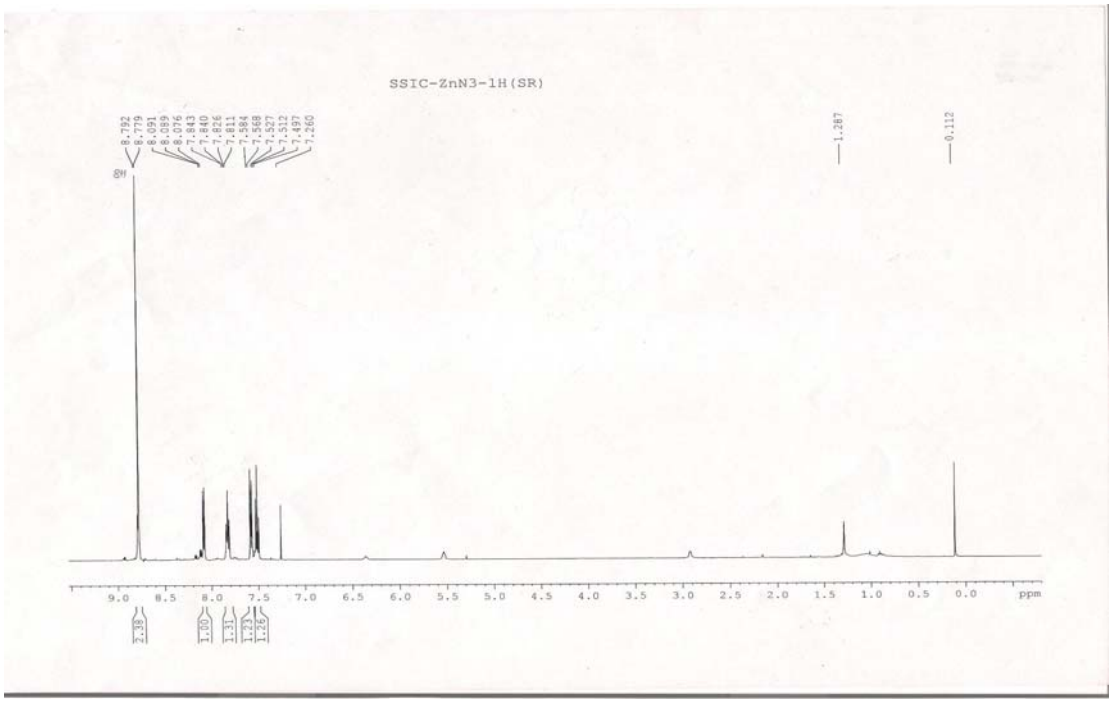
To a solution of TAzPP (460 mg, 0.635 mmoL) in 25 mL THF, $Zn(OAc)_2.2H_2O$ (154 mg, 1.1 eq.) was added and the reaction was stirred for 3 hours. The reaction was quenched with water, DCM was added and the organic layer was collected. It was dried over anhydrous Na_2SO_4 and was purified by column chromatography using 85% DCM-hexane mixture.

Yield = 497 mg (93%)

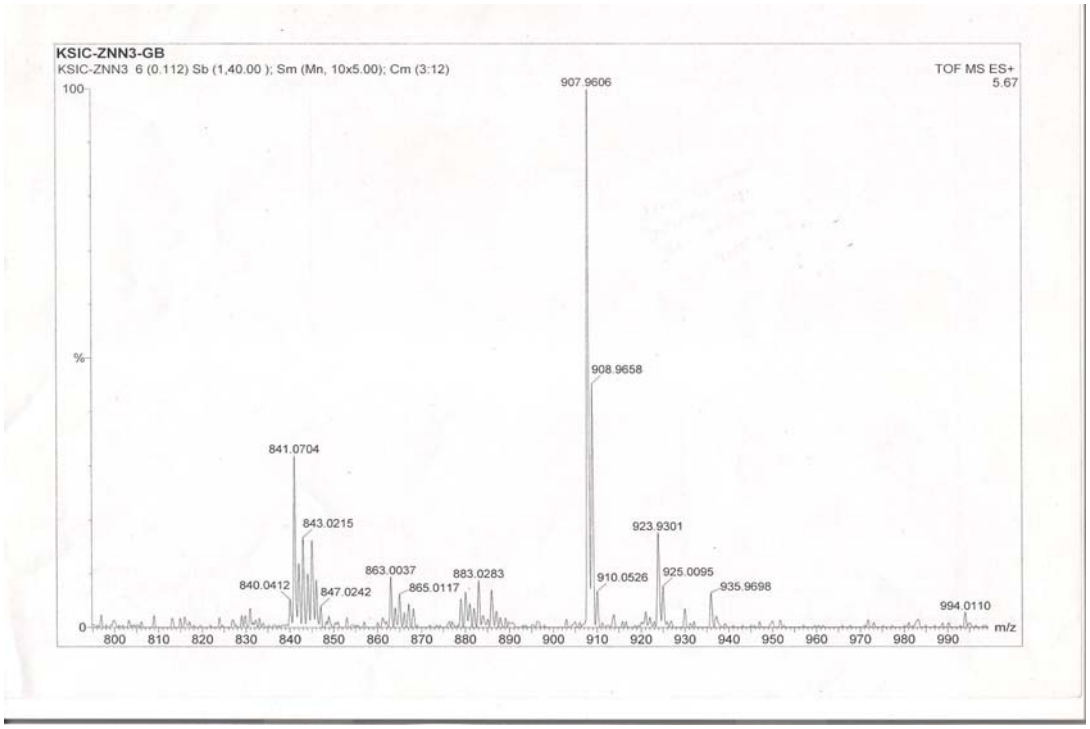
(^{1}H NMR, $CDCl_3$) 7.51 (t, 4H, *J*=7.5 Hz), 7.58 (d, 4H, *J*= 8 Hz), (t, 4H, *J*= 7.5Hz), 8.77 (s, 8H). ESI-MS - (+ve ion mode, acetonitrile) m/z = 841.0704 (32%, $[MH]^+$), 907.9606 (100%, [M+ acetonitrile+ Na^+]).

α_4-ZnTAzPP

^{1}H-NMR ($CDCl_3$)



ESI-MS



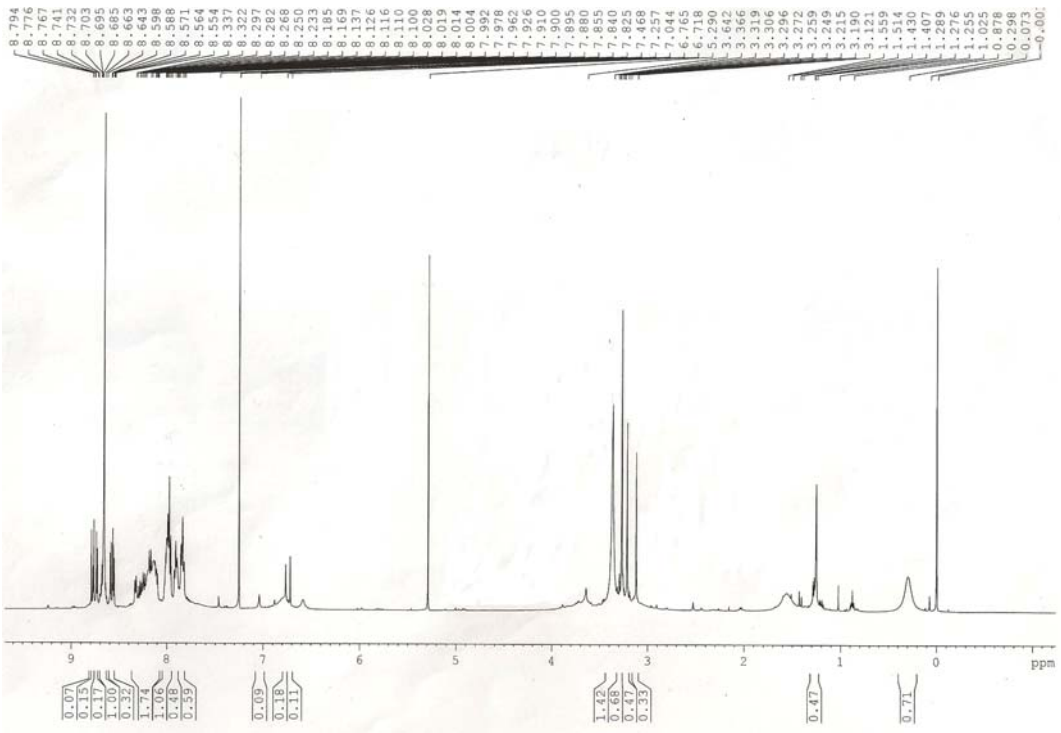
3. Synthesis of α_4-tetra-2-(4-carboxymethyl-1,2,3-triazolyl)-phenylporphyrinato zinc (α_4-ZnEs$_4$) :

To a solution of ZnTAzPP (50 mg, 0.059 mmoL) in 30 mL t-butyl alcohol, methyl propiolate (50 µL, 10 eq.) was added followed by the addition of $CuSO_4$/sodium-L-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_2SO_4 and was purified by column chromatography using (9:1) DCM-methanol mixture as eluent.

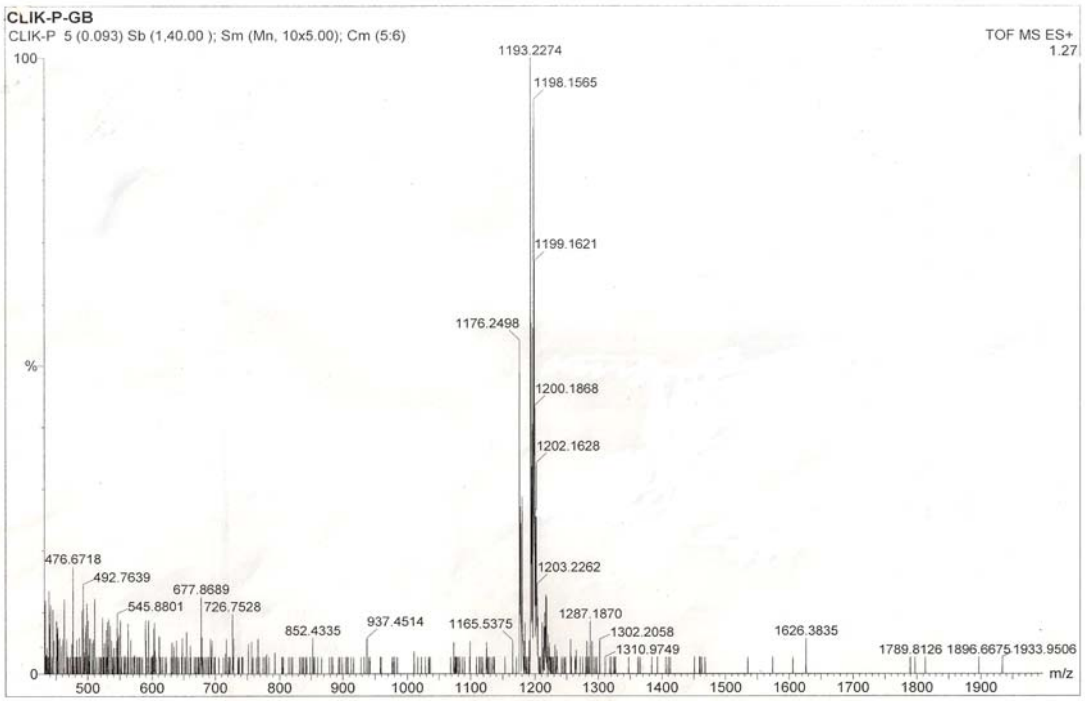
Yield = 74%.

(^{1}H NMR, $CDCl_3$) 3.12 (s,3H), 3.19 (s,3H), 3.29 (s, 6H), 7.8-8.1 (m, 16H, aromatic), 8.5 (d, 2H, triazole), 8.6 (s, 8H, pyrole), 8.7 (d, 2H, triazole). ESI-MS (+ve ion mode, acetonitrile) m/z = 1176.2498 (52% $[M]^+$), 1199.1621(67%, $[M+Na]^+$), 1193.2274 (100%, $[M+H_2O]^+$).

^{1}H-NMR ($CDCl_3$)



ESI-MS

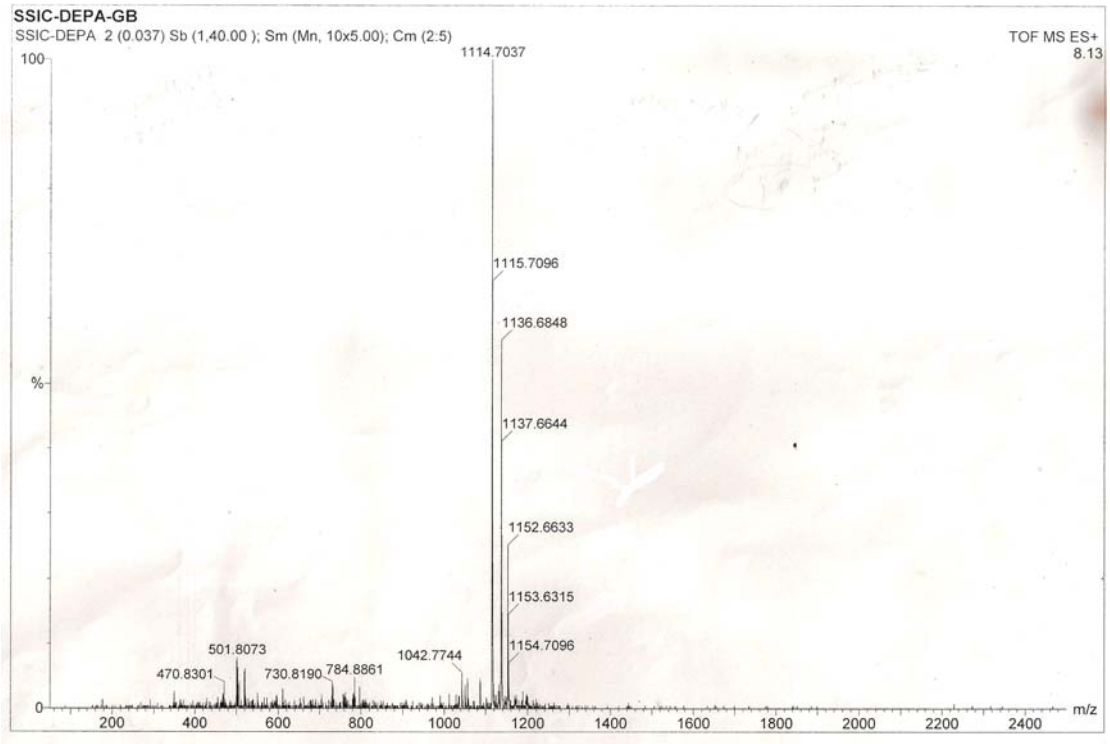


4. Synthesis of α_4-tetra-2-(4-carboxymethyl-1,2,3-triazolyl)-phenylporphyrin (α_4-Es$_4$): To a solution of α_4-ZnEs4 (50 mg) in 15 mL DCM solution, 10 mL 6(M) HCl was added and the reaction was stirred for 45 mins. The reaction was neutralized by aq. NH_3 solution, followed by the addition of DCM and water. The organic layer was collected, dried over anhydrous Na_2SO_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%.

ESI-MS (+ve ion mode, acetonitrile) m/z = 1114.7037 (100%, $[M]^+$), 1136.6848 (54%, $[M+Na]^+$), 1152.6633 (22%, $[M+K]^+$)

ESI-MS



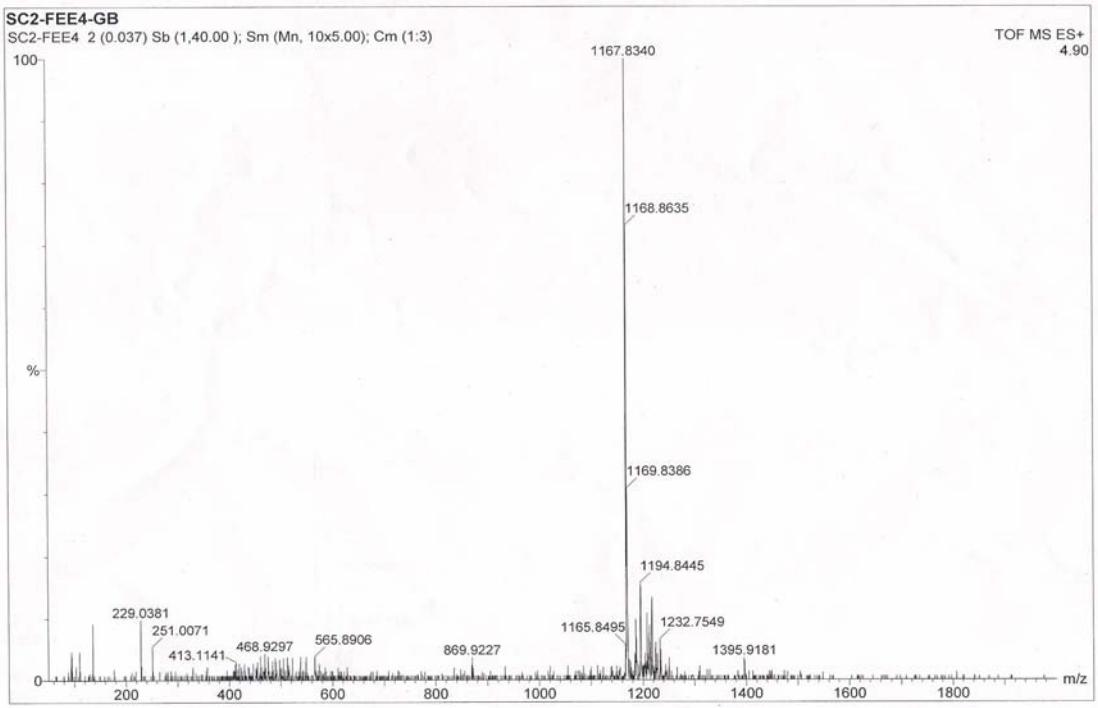
5. Synthesis of α_4-tetra-2-(4-carboxymethyl-1,2,3-troazolyl)-phenylporphyrinato iron (III) bromide ([α_4-FeEs$_4$]Br) :

To a solution of the demetallated product (230 mg, 0.206 mmoL) in 15 mL dry degased THF, 2,4,6-collidine (54 µL, 2 eq.) was added, followed by addition of $FeBr_2$ (177 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 Na_2SO_4 and was purified by column chromatography using (98:2) dry DCM–MeOH mixture in nitrogen atmosphere. The metallation with iron of metal-free ligand was confirmed by Absorption spectroscopy and Mass Spectroscopy.

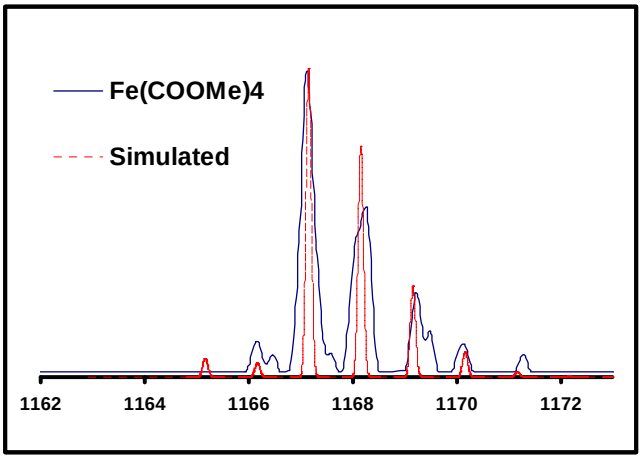
Yield = 91%.

ESI-MS (+ve ion mode, methanol) m/z = 1167.8340 (100%, $[M]^+$).

ESI-MS



Simulated ESI-MS



Crystal structure of analogous α_4-tetra-2-(3-ferrocenyl-1,2,3-triazolyl)-phenylporphyrinato zinc (α_4-Znfc$_4$) :

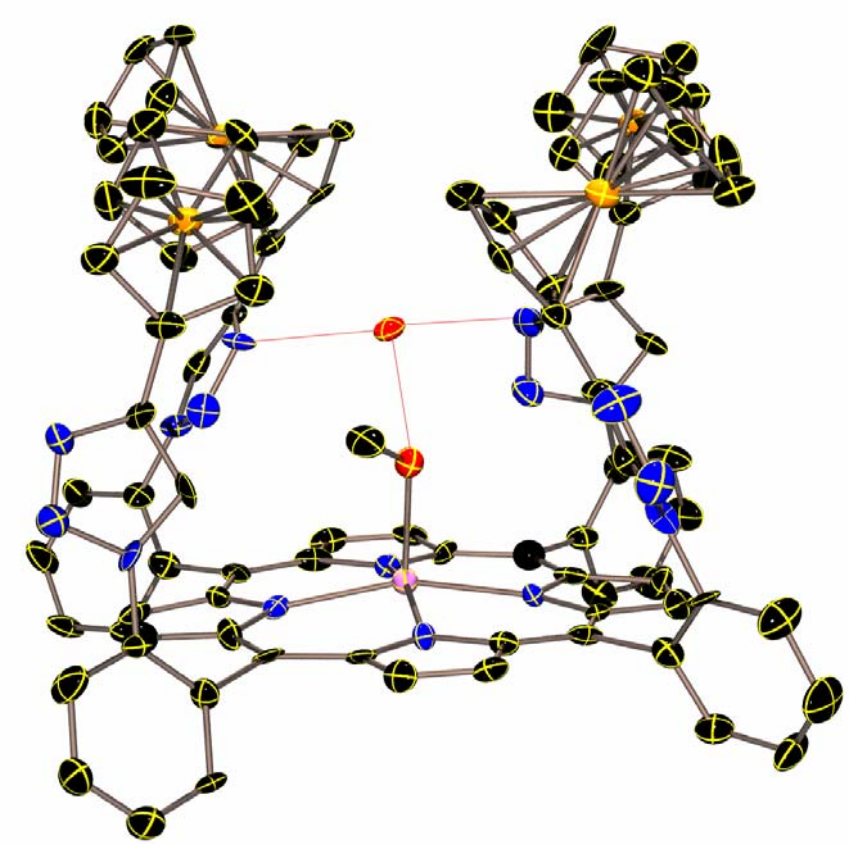


Fig S1. Crystal structure of the α_4-Znfc$_4$ complex. Carbon atom is shown in black, nitrogen in blue, iron in orange, Zinc in pink, oxygen in red. H atoms are omitted. Hydrogen bonding interactions are indicated by pink lines.

Sample preparation and Spectral characterization:

Complex **1** was dissolved in dry and degassed THF to make 1mM solution. Then 10 mM methanolic (dry and degassed) solution of $Na_2S.9H_2O$ was prepared and 0.5 eq. of it was added to reduce the Fe(III) centre to Fe(II). After complete reduction the resulting solution was cooled to -80^{o}C bath for several minutes. Maintaining the temperature at -80^{o}C the solution was oxygenated. Then the oxygenated sample was made to react for about 5 minutes at -80^{o}C and then it was frozen in liquid nitrogen. In case of isotopic study the $Na_2S.9H_2O$ was prepared in methanol-d_4 instead of methanol and $^{18}O_2$ was used to oxygenate the sample instead of $^{16}O_2$.

1. Absorption spectroscopy :

20 μM solution of **1** was prepared in dry and degassed THF. UV-Vis absorption spectra of oxidised, reduced and oxy adduct were taken at -80°C maintaining the anaerobic condition.

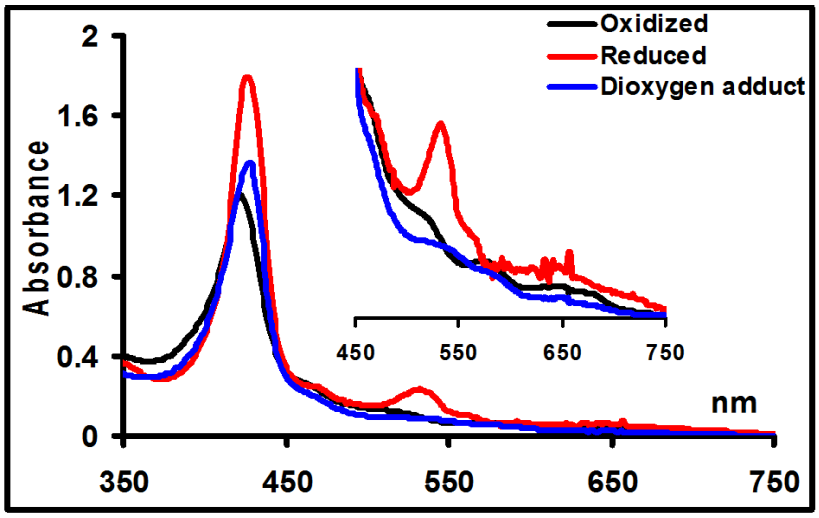


Fig S2: Absorption data in the visible range for oxidized (black), reduced (red) and O_2 adduct (blue) of the $Fe(COOMe)_4$ complex.

2. Electron Paramagnetic Resonance (EPR) Spectroscopy :

The sample concentration used for the EPR spectra was 1 mM. All the oxidised, reduced and oxygenated samples were prepared likewise as mentioned above. The data were collected at 77 K. Power at the sample was 10 mW and gain was $1x10^4$.

3. Resonance Raman (rR) spectroscopy:

The rR spectra were taken for the same samples that had been used for EPR spectroscopy. The laser excitation wavelength was 413.1 nm and the irradiation power at the sample was limited between 7-10 mW to avoid photo-reduction and sample degradation. Data were collected at low temperature (77 K) for 400 seconds using a Trivista 555 triple spectrophotometer from Princeton Instruments fitted with a Pixis CCD camera.

3A. Resonance raman data of oxygenation of α_4-Fefc$_4$:

The samples for rR spectroscopy of α_4-FeFc$_4$, analogous to α_4-FeEs$_4$, were prepared in the same procedure and under the same experimental condition.

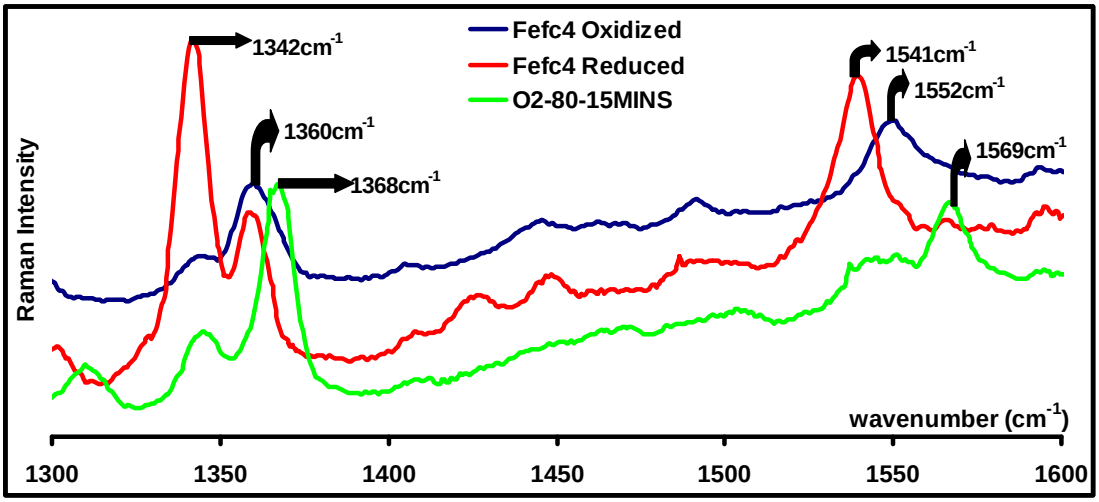


Fig S3. rR spectra of the range 1300 – 1600 cm^{-1}, showing oxidized α_4-Fefc$_4$ in blue, reduced α_4-Fefc$_4$ in red and the corresponding oxy-adduct in green. Laser wavelength= 413.1nm, Laser power on sample= 7-10 mW. All spectra were recorded at 77 K.

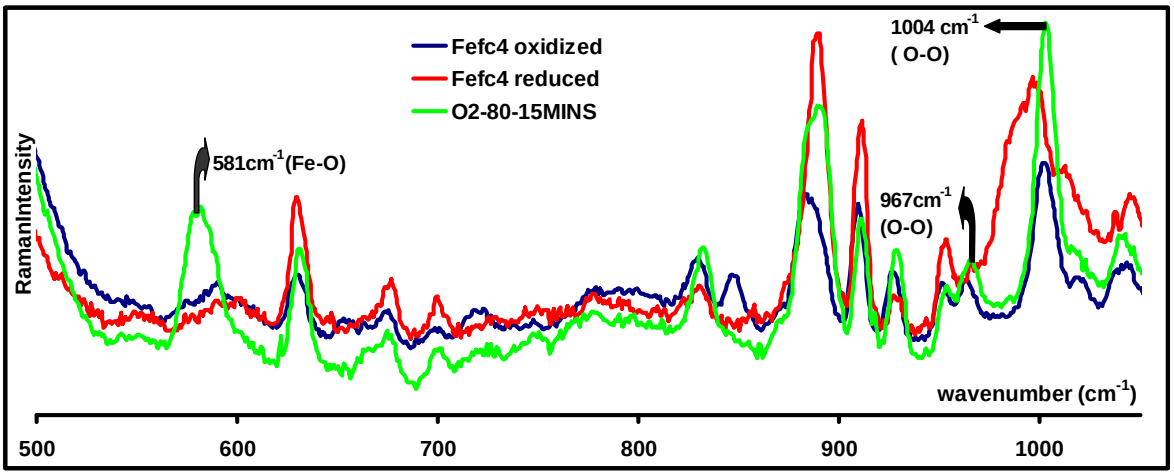


Fig S4. rR spectra of the range 1300 – 1600 cm^{-1}, showing oxidized α_4-Fefc$_4$ in blue, reduced α_4-Fefc$_4$ in red and the corresponding oxy-adduct in green. Laser wavelength= 413.1nm, Laser power on sample= 7-10 mW. All spectra were recorded at 77 K

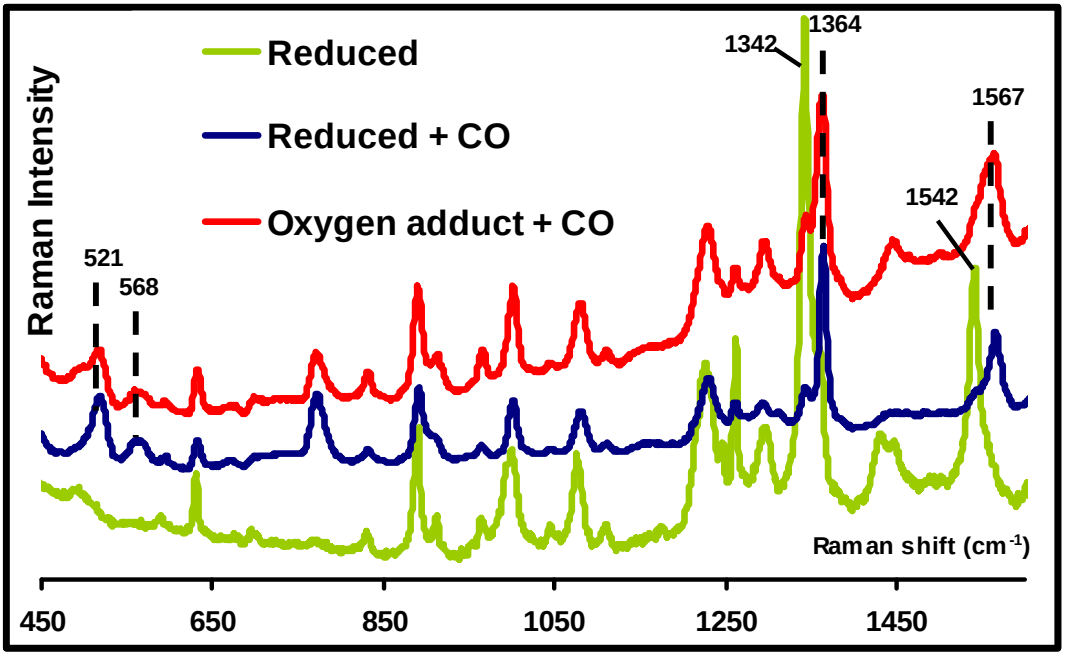


Fig S5. rR data of α4-Fe(II)(COOMe)4 (green), CO adduct of α4-Fe(II)(COOMe)4 (blue) and the species formed after the addition of CO to the Fe-O2 species (red).

DFT Calculations

The broken symmetry geometry optimization of the $FeEs_4$-O_2 complex was carried out using 6-31g* basis set on all atoms. For the smaller complexes a split basis set (6-311g* on Fe, O and N and 6-31g* on C and H atoms) were used. The final electronic structure calculations were carried out using 6-311+g* basis set on all atoms. The frequencies were calculated on the optimized structures. Since BP86 functional was used no scaling of the vibrational frequencies were necessary (A.P.Scott and L.Radom *J. Phys. Chem.* **1996,** *100,* 16502-16513)

To obtain the broken symmetry ground state of the Fe-O_2 adducts, first the triplet wave function was obtained. Then using the triplet wave function as an initial guess a single point calculation of the singlet ground state was performed. This approach generally always yielded the broken symmetry singlet ground state. The geometries were then optimized by vertically shifting the occupied & the unoccupied orbital using the $V_{shift} = 500$ keyword.

The spin density on Fe is 1.2 i.e. different from O_2^-, because the Fe has covalent interaction with the O_2^- as well as the porphyrin ligand while the O_2^- only interacts with the Fe. The α orbitals and the β orbitals of the S= ½ Fe centre are inequivalent in energy due to exchange interaction. Hence there are differences in the overlap of α and β orbitals of the Fe with the donor orbitals of the porphyrin ligand. The excess 0.2 spin density on Fe reflects better covalent spin delocalization of the β spin of Fe (leading to excess α spin density in Fe) into the porphyrin ligand relative to the α spin orbitals. Hence the porphyrin ring bears a total electron spin density of -0.2. For this reason spin densities having opposite sign but unequal magnitude is previously reported in several heme-oxy adducts. (1. Keiji Morokuma, J. Am. Chem. Soc., 2008, 130, 12299-12309 2. U. Ryde J. Biol. Chem., 2004, 279, 14561-14569 and 3) D. L. Harris, J. Am. Chem. Soc., 1998, 120, 8941-8948.)

TABLE S1:

		Fe-O		O-O		Δ E (Kcal) end-on - side-on
		Bond length	frequency	Bond length	frequency	
Fe-O_2	End-on	1.77	545	1.28	1211	-21.13
	Side-on	1.89	521 (sym)	1.37	1040	
Fe-O_2 + $2H_2O$	End-on	1.73	572	1.31	1140	-15.8
	Side-on	1.89	530 (sym)	1.39	1019	

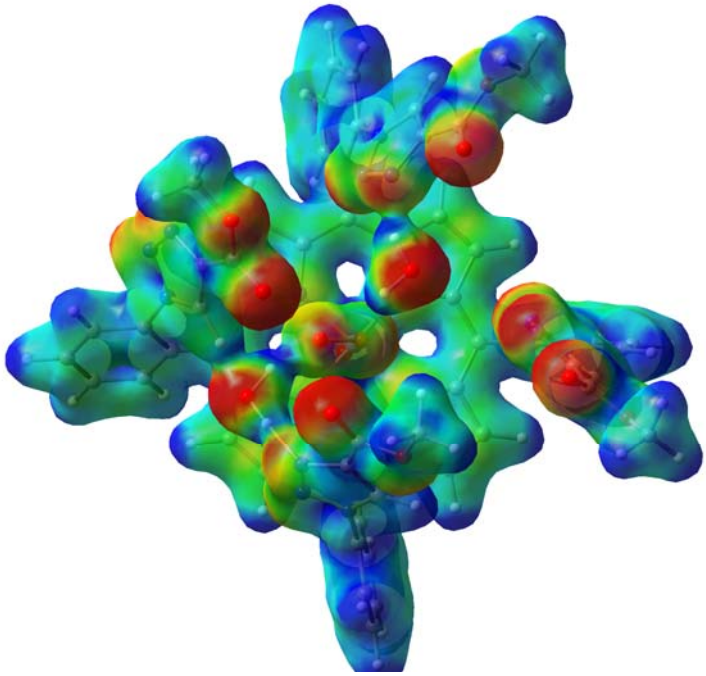


Fig S6. Electrostatic potential map of the optimized Fe^{II}-O_2 complex. The H_2O dipoles polarize negative charge density on the O_2 unit making this a Fe^{III}-O_2^- species.

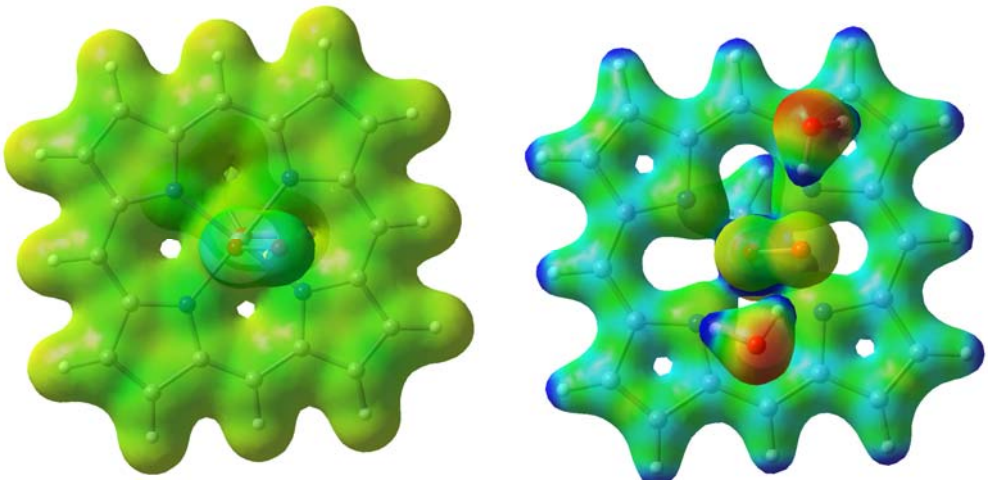


Fig S7: Electrostatic potential map of the smaller porphyrin models without hydrogen bonding (left) & with hydrogen bonding (right). As is evident from the figures presence of hydrogen bonding interactions (positive dipoles) induces complementary negative dipoles on the iron bound oxygen atom.

Optimized Geometry

$FeEs_4$-O_2

Fe	-0.27526500	-0.43377700	-1.57407700
N	-0.48771300	-2.43164900	-1.45275800
N	-2.27679700	-0.24768400	-1.59003200
N	-0.07707700	1.53345900	-1.90953800
N	1.70847200	-0.65750500	-1.83902000
C	1.88894500	-3.10501200	-1.50493700
C	-2.95602500	-2.60555500	-1.21682300
C	-3.22024700	-1.23894800	-1.38292300
C	-2.99469200	0.92977900	-1.69337800
C	-1.35620400	-4.53830900	-1.02800800
C	-0.01156700	-4.67237300	-1.11442300
C	0.52838000	-3.35927500	-1.35730400
C	-1.65552000	-3.14101400	-1.23303200
C	-4.40503300	0.66228100	-1.57583700
C	-4.54480500	-0.67388300	-1.39412700
C	2.37412600	1.69617300	-2.19325400
C	2.64005300	0.33147000	-2.07748300
C	1.09059500	2.24333700	-2.07540900
C	-2.45464900	2.20837800	-1.88435600
C	3.48351600	2.62633700	-2.59565800
C	-3.41930100	3.33281400	-2.13933600
C	-4.06483400	3.35520700	-3.38880300
C	-4.29509500	-4.47023100	-2.15750200
C	-4.11617900	-3.55840500	-1.10117100
C	3.95495500	-0.24008500	-2.19172600
C	2.42364800	-1.83061400	-1.75210900
C	3.82725500	-1.57505400	-1.97100900
C	3.42579600	3.11938300	-3.91290800
C	-0.53539800	3.78787900	-2.13792800
C	0.80758900	3.65191000	-2.19833600
C	-1.08318800	2.46932900	-1.94909100
C	-3.74180300	4.36703600	-1.23812600
C	-4.67573400	5.35539600	-1.57938400
C	-4.97976700	4.34557600	-3.74210300

C	-5.28885100	5.35343700	-2.82856400
C	3.39984400	-4.72702600	-0.21234600
C	2.86308100	-4.24513600	-1.41898500
N	-3.12817700	4.47310800	0.04446700
N	-2.25897500	3.79551300	1.88357800
N	-2.82492500	3.37562700	0.79841000
C	-2.73555900	5.60184900	0.68790100
C	-2.18683700	5.15814400	1.86748800
N	2.91886500	-4.24706900	1.04812000
C	3.45068200	-3.35039700	1.91856000
C	2.52866000	-3.28148700	2.94393100
N	1.73537700	-4.72195600	1.51615100
N	1.50740900	-4.13834200	2.65037000
N	4.81789600	2.57026000	-0.48880600
N	4.39477000	2.12094700	1.57366000
N	3.83381500	2.50569800	0.47302400
C	4.58807000	3.02827600	-1.81656300
C	6.01225100	2.22084400	0.04506800
C	5.73696800	1.93577100	1.36236200
N	-5.06675000	-2.71700100	1.06362900
N	-6.04105900	-1.30808200	2.36340100
N	-6.21594000	-1.98622200	1.27558200
C	-4.80531300	-1.57833000	2.87586200
C	-4.17160100	-2.49129200	2.05110500
C	5.47422600	4.35540600	-3.65147200
C	5.55950400	3.89290000	-2.34229800
O	-0.04368700	-0.24877100	0.22806200
O	-0.88667500	-0.87656400	0.97139600
C	-5.05807600	-3.61862800	-0.04398200
C	-5.33842200	-5.39091500	-2.18231500
C	-6.25492900	-5.42676400	-1.13260400
C	-6.11052600	-4.54079000	-0.06956200
C	4.39533000	3.96490600	-4.44387800
C	4.88661000	-6.22579500	-1.39149500
C	4.40128000	-5.69721400	-0.19470800
C	3.35940900	-4.80608400	-2.60880600
C	4.35307500	-5.78306800	-2.60246300

O	0.01406900	2.06223400	2.01145200
H	-0.84826000	2.42725800	2.28405300
H	-0.17304700	1.14834700	1.76725900
C	2.52757500	-2.46387200	4.18408400
C	6.67598900	1.49212500	2.40996000
C	-1.57725000	5.93490900	2.96544500
C	-4.18948900	-1.02073900	4.10485500
O	-1.58275800	7.26156300	2.65976400
O	-1.13967600	5.47679500	3.99504700
O	-3.01756100	-1.26058000	4.37660500
O	-4.91309500	-0.24146300	4.93732500
O	3.67428300	-1.75497300	4.29239300
O	1.61167700	-2.43101600	4.97590100
O	7.94866900	1.45372100	1.91841000
O	6.39065000	1.19564800	3.56323100
C	8.95187400	1.03746200	2.85756400
C	-6.30608500	-0.00241600	4.76040400
C	3.70779700	-0.81957000	5.39304700
C	-1.01008400	8.11311500	3.66477500
H	-2.08287900	-5.30283000	-0.80988600
H	0.57534400	-5.56773800	-0.98615700
H	-5.18458600	1.40645800	-1.60940600
H	-5.46118500	-1.22233000	-1.24911000
H	-3.82418700	2.56997200	-4.09735200
H	-3.59064400	-4.43912300	-2.98171500
H	4.85747300	0.31226100	-2.40292900
H	4.60369500	-2.32340300	-1.97693600
H	2.58621200	2.81485000	-4.52795400
H	-1.11313300	4.69620700	-2.21564200
H	1.54714400	4.42628100	-2.32284000
H	-4.93546900	6.11182100	-0.84757700
H	-5.44935500	4.32475400	-4.72012500
H	-6.01120600	6.12417800	-3.07512600
H	-2.85030200	6.58847300	0.27566300
H	4.37590800	-2.82947800	1.74063800
H	6.92416100	2.17653700	-0.52409300
H	-3.19222600	-2.95259800	2.10957200

H	6.23487000	5.02527800	-4.03857700
H	6.37479800	4.21493800	-1.70404800
H	-5.43686700	-6.07155800	-3.02212300
H	-7.07513000	-6.13719600	-1.13701400
H	-6.81187100	-4.54134700	0.75592700
H	4.30907200	4.31250000	-5.46807200
H	5.66148300	-6.98487300	-1.37377200
H	4.77803000	-6.04454300	0.76105900
H	2.95928800	-4.45058400	-3.55261400
H	4.71515000	-6.18974300	-3.54144600
H	9.89382000	1.07243700	2.31157300
H	8.74968700	0.02408900	3.21088000
H	8.97796400	1.71332700	3.71470300
H	-6.59030500	0.60219600	5.62196700
H	-6.87290700	-0.93538600	4.75717100
H	-6.50550000	0.53606000	3.83520900
H	4.67282400	-0.32684300	5.31948300
H	3.58964200	-1.35060500	6.33919800
H	2.90446500	-0.08873100	5.27907600
H	-1.09341200	9.12589400	3.27117800
H	0.03601300	7.85102400	3.83704200
H	-1.55783400	8.01856700	4.60506600
O	-0.56478300	-0.64280200	-3.75812200
C	-0.11932900	-1.76504300	-4.53930100
H	-0.39869100	-1.62737900	-5.58936000
H	-0.52611400	-2.70686700	-4.16133300
H	0.96607900	-1.78494300	-4.45554500
H	-1.53484600	-0.57633200	-3.79060000
O	-1.07219400	-3.37886400	2.09340300
H	-0.82844000	-2.45556000	1.93384400
H	-0.24167100	-3.75727500	2.42668900

Fe-O_2 end-on

Fe	0.00682100	0.04154200	-0.12277800
N	0.69642200	-1.83535600	-0.00136100
N	1.87887200	0.72791600	0.06497300
N	-0.70689200	1.92690800	-0.06021700
N	-1.89084100	-0.64192100	-0.13118500
C	-1.44217300	-3.06829500	-0.12905200
C	3.12635800	-1.40126900	0.07244000
C	3.05597100	-0.00973400	0.08460800
C	2.28116500	2.05410600	0.08997400
C	2.10433500	-3.69238400	0.00759900
C	0.81553700	-4.16027400	-0.04269800
C	-0.04998400	-3.00267000	-0.05646000
C	2.02098600	-2.25029800	0.02508100
C	3.72394900	2.14777300	0.13977000
C	4.20642800	0.86452100	0.13585500
C	-3.13108900	1.48950300	-0.17318700
C	-3.06127400	0.09753800	-0.18532600
C	-2.02677500	2.33830000	-0.10847900
C	1.42789100	3.15619100	0.06495300
C	-4.21612900	-0.77425500	-0.24660600
C	-2.29543400	-1.96612800	-0.16691600
C	-3.73907100	-2.05860100	-0.23502300
C	-0.82938100	4.25177300	-0.00616000
C	-2.11505700	3.78325000	-0.07580800
C	0.03651100	3.09097500	0.00181100
O	0.01375900	0.05451300	-1.89818500
O	1.04131600	-0.34228300	-2.55282700
H	3.03655700	-4.25966900	0.02541500
H	0.46646600	-5.19402800	-0.07789100
H	4.28197000	3.08559800	0.16689100
H	5.24290400	0.52364100	0.16252000
H	-5.25063100	-0.42924100	-0.29284700
H	-4.29863900	-2.99518700	-0.27209300
H	-3.04864500	4.34804800	-0.10150500
O	0.02477000	0.07673300	2.04150300
C	-0.90457500	-0.64563000	2.87434400

H	-0.67574400	-0.46074100	3.93975600
H	-0.88355800	-1.72977400	2.66086600
H	-1.90129100	-0.24855100	2.63923500
H	0.93839800	-0.20162700	2.25348400
H	-0.47995400	5.28514800	0.03457500
H	4.11964000	-1.86092100	0.09012700
H	-4.12367900	1.94920400	-0.21612500
H	-1.89846500	-4.06270500	-0.16967400
H	1.88652400	4.14982600	0.09578100

Fe-O_2 2H_2O end-on

Fe	-0.09404000	0.07803200	-0.18593600
N	1.75669600	-0.63315400	-0.41090900
N	-0.82592700	-1.74606300	-0.53343500
N	-1.95578500	0.83342700	-0.16224300
N	0.63106100	1.94927300	-0.04631600
C	3.04816400	1.45514900	-0.10247300
C	1.26984300	-3.04353200	-0.67163500
C	-0.11762300	-2.93829300	-0.65888800
C	-2.16305200	-2.12278500	-0.54338000
C	3.57925600	-2.08308900	-0.51735900
C	4.07881100	-0.81226600	-0.36328400
C	2.94444200	0.07705200	-0.28660500
C	2.14128200	-1.96381800	-0.53916200
C	-2.29018500	-3.55357200	-0.70280400
C	-1.01911800	-4.06084400	-0.77443700
C	-1.46713600	3.23464100	0.12752700
C	-0.07849700	3.13064200	0.10813800
C	-2.33866500	2.15537700	0.00231900
C	-3.24489000	-1.25639100	-0.41185600
C	0.82029600	4.25657900	0.25006600
C	1.96628200	2.32316800	0.01060700
C	2.09249200	3.75389300	0.18992500
C	-4.27991400	1.00679800	-0.12255500
C	-3.78010300	2.27348100	0.02657400
C	-3.14174300	0.12158700	-0.23791200
O	-0.07277300	-0.09795700	1.53756700

O	0.33459100	-1.21633900	2.08958000
O	-2.03134000	-1.18529300	3.83369300
H	-1.98367400	-0.22628100	4.01842800
H	-1.16361100	-1.35673600	3.40089600
H	4.12460200	-3.02412900	-0.60928100
H	5.12022600	-0.49291700	-0.29441000
H	-3.24098500	-4.08808600	-0.74014800
H	-0.70308900	-5.09928900	-0.88715400
H	0.49930000	5.29134400	0.38181800
H	3.04235800	4.28627700	0.26421700
H	-4.32209600	3.21346800	0.14427300
O	-0.17948700	0.24664700	-2.32240500
C	0.73724300	1.06929800	-3.08376500
H	0.55778700	0.91921300	-4.16288900
H	1.78699700	0.84135400	-2.83056900
H	0.51154100	2.10936800	-2.81445900
H	-0.04294500	-0.69300300	-2.57307700
H	-5.32134500	0.68160800	-0.15001400
H	1.70606100	-4.04251300	-0.77005300
H	-1.90287800	4.23022200	0.25788400
O	3.04261500	-0.70526600	3.02447900
H	2.06818800	-0.82856000	2.95738600
H	3.37003000	-1.23627400	2.27051000
H	4.05311100	1.88020200	-0.01893500
H	-4.24881500	-1.69126100	-0.43731700

Fe-O_2 side-on

Fe	0.03280300	0.02713700	-0.19128900
N	1.49323500	-1.35969800	0.18223800
N	1.42446700	1.46510200	-0.08687500
N	-1.42607900	1.39392000	0.08387000
N	-1.34801400	-1.42383000	-0.17343900
C	0.10923700	-3.40534000	0.02111600
C	3.47483000	0.09990800	-0.04550600
C	2.79604800	1.31492400	-0.12706500
C	1.20627900	2.82737900	-0.04497800
C	3.56697600	-2.40412900	0.14693300

C	2.61376200	-3.39368700	0.18837800
C	1.32841800	-2.74055000	0.15419600
C	2.86506900	-1.14577500	0.09875800
C	2.46391400	3.55065200	-0.09338500
C	3.45421100	2.60900000	-0.15196900
C	-3.39512500	-0.05885600	-0.23852300
C	-2.71584000	-1.27377100	-0.30515000
C	-2.78834700	1.18226500	-0.04037400
C	-0.03902400	3.43769100	0.08354000
C	-3.36626100	-2.56609000	-0.40541200
C	-1.12831100	-2.78888500	-0.16171800
C	-2.37884500	-3.50935500	-0.30869000
C	-2.54830800	3.42336300	0.14821700
C	-3.49801700	2.43928100	0.03386300
C	-1.26085900	2.76572300	0.13267400
O	-0.36829300	0.52743400	-1.96801500
O	0.55006900	-0.49405700	-1.93184400
H	4.65349200	-2.50666300	0.13197700
H	2.75694100	-4.47555600	0.20748200
H	2.55418100	4.63820000	-0.07334100
H	4.53550600	2.75361600	-0.18550200
H	-4.44234700	-2.71180900	-0.51548500
H	-2.46842400	-4.59704400	-0.32705800
H	-4.58391100	2.54015800	-0.00978300
O	0.09399000	0.04547500	1.90610200
C	-1.01115300	-0.38168300	2.73399500
H	-0.72567800	-0.26630400	3.79466000
H	-1.30112300	-1.42497600	2.52152700
H	-1.84788100	0.28980800	2.49976400
H	0.85139600	-0.57756100	2.00833300
H	-2.68952200	4.50369800	0.21250600
H	4.56830800	0.12399000	-0.09033400
H	-4.48510300	-0.07850400	-0.33820600
H	0.13384900	-4.49986000	0.01472900
H	-0.06587200	4.53157500	0.11831900

Fe-O_2 side-on $2H_2O$

Fe	0.03440300	-0.00117600	-0.07402200
N	-0.73428600	1.84735200	-0.50217300
N	1.88112900	0.77504000	-0.20166000
N	0.78207300	-1.85316000	-0.32913300
N	-1.82163200	-0.76403600	-0.08032700
C	-3.14409800	1.30378400	-0.31046200
C	1.34429700	3.17727300	-0.31106700
C	2.23487400	2.11037800	-0.20295400
C	3.07450800	0.08181200	-0.22714200
C	-0.95868300	4.15838900	-0.51222900
C	-2.22596600	3.62653700	-0.53195700
C	-2.08339600	2.19401100	-0.46881300
C	-0.03758000	3.05252600	-0.44606800
C	4.20047000	0.99513500	-0.20582100
C	3.67840500	2.25858800	-0.18701500
C	-1.28497800	-3.16429000	0.01130900
C	-2.17505600	-2.09369300	0.06351400
C	0.09119300	-3.04645800	-0.18540000
C	3.19293000	-1.30140100	-0.32869700
C	-3.61446400	-2.23264700	0.16247800
C	-3.01652400	-0.06855900	-0.10150500
C	-4.13785400	-0.97262000	0.05615700
C	2.26954400	-3.63253500	-0.35465800
C	1.00837000	-4.16087500	-0.23732300
C	2.12351200	-2.19548900	-0.36536300
O	0.31059200	-0.54593000	1.71336300
O	-0.21846400	0.73607200	1.64854200
O	2.80311300	0.09743400	3.03292500
H	2.02947800	-0.26692000	2.54034200
H	2.57098300	1.03575700	3.16395100
H	-0.66196700	5.20857900	-0.52068800
H	-3.18315800	4.15009000	-0.55291300
H	5.24669900	0.68609800	-0.20780500
H	4.20244300	3.21585400	-0.18115100
H	-4.13837900	-3.18246500	0.28291300
H	-5.18306900	-0.66105700	0.08149300

H	0.71056500	-5.20897100	-0.17591900
O	0.08288800	0.00774600	-2.17714300
C	-0.74292900	-0.86104000	-2.98674000
H	-0.52403600	-0.66367500	-4.05089300
H	-1.81630900	-0.71474000	-2.77722600
H	-0.45098700	-1.88845000	-2.73245200
H	-0.20251900	0.94473200	-2.29421700
H	3.22628800	-4.15486000	-0.40475500
H	1.75905800	4.19008500	-0.29581300
H	-1.69456700	-4.17334300	0.12196900
O	-2.71526200	0.44389700	3.08551000
H	-1.91703600	0.65095300	2.54259200
H	-2.54958400	-0.46104400	3.40980100
H	-4.15385300	1.72475500	-0.29443000
H	4.20212900	-1.72387600	-0.34419800