Supporting information

Role of Distal Arginine Residue in the Mechanism of heme Nitrite Reductases

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1. Materials and Methods

All reagents used are of the highest grade commercially available products. Hydrochloric acid, sulfuric acid and spectroscopic grade THF, methanol are purchased from Merck. Sodium sulphide (Na_2S, $9H_2O$), sodium nitrite, anhydrous tetra-butyl ammonium nitrite, 2,6-xylidine, potassium hydroxide are purchased from Sigma-Aldrich chemical company.

2. Instrumentation

The anaerobic cuvettes are purchased from Starna Scientific. The Fourier transform infrared (FTIR) data are measured on a Shimadzu FTIR 8400S instrument. The CaF_2 windows for FTIR spectroscopy are purchased from Sigma-Aldrich. The anaerobic setup for FTIR spectroscopy is purchased from PerkinElmer. All the EPR spectra are recorded on a X-band JEOL (JES FA200) instrument. Head-space gas is detected in GC instrument of model no. 7890B (G3440B), serial no. CN14333203 fitted with TCD. The porphyrins, tetra-butyl ammonium nitrite and 2,6-xylidininium chloride are dissolved in dry, deaerated THF to carry all these experiments.

UV-Vis Data Collection

All anaerobic absorption data are collected by taking the samples in tightly sealed anaerobic cuvettes at RT. The samples are prepared in a glove box under the pressure of Ar. The solvent background is corrected prior to the experiments with an identical amount of solvent mixture. Ferric porphyrins are reduced by 1 electron with required equivalent of Na_2S solution (half equivalent reductant for 1 equivalent ferric porphyrin). For H/D KIE experiments, we incubated $[Fe^{III}MARGH]Cl_2$ complex with methanol-d_4 for overnight and then reduced it with required Na_2S also dissolved in methanol-d_4. To prepare the deuterated 2,6-xylidininium chloride solution the salt was also incubated with for methanol-$d_4$overnight.

FTIR Data Collection

The CaF_2 windows are fitted in an anaerobic setup and sample solution is taken into it. The samples are prepared in a glove box under the pressure of Ar. Ferric porphyrins are reduced by 1 electron with required equivalent of Na_2S solution (half equivalent reductant for 1 equivalent ferric porphyrin).

X-band EPR Data

The samples (150 µL) are taken in EPR tubes and thoroughly sealed inside the glovebox under the pressure of Ar, brought from the box and frozen in liquid N_2. All the data are collected at 77 K. Ferric porphyrins are reduced by 1 electron with required equivalent of Na_2S solution (half equivalent reductant for 1 equivalent ferric porphyrin).

GC-TCD Data

400 µl head-space gas is syringe out by a gas tight syringe and injected into the inlet of the GC (fitted with TCD). The N_2O gas is detected in GC-TCD.

3. Synthesis of $[Fe^{III}MARGH]Cl_2$

The molecule is synthesised using the protocol reported in the reference 1.[1] Elemental analysis of C45H32N7Cl2Fe is calculated(%) to be: C 67.77, H 4.04, N 12.29 and found to be: C 67.50, H 4.10, N 12.20.

4. Synthesis of $Fe^{III}TPPCl$

The molecule is synthesised using the protocol of Alder et al.[2-3]

5. **Preparation of 2,6-xylidinium chloride salt and 2,6-xylidinium *p*-toluene sulfonate salt**

2,6-xylidine is dissolved in THF and 6N hydrochloric acid is added to it dropwise till white solids appear. Then the solid is dried under high vacuum to make it anhydrous powder and kept in glove box. The aliquot of 2,6-xylidinium chloride is made by dissolving required amount of the salt in dry, deaerated THF in glove box. 2,6-xylidinium *p*-toluene sulfonate salt is prepared with the same protocol.

6. **Preparation of NO complexes**

Dry, degassed NO is generated upon dropwise addition of a deaerated, saturated solution of sodium nitrite to a deaerated 3N sulfuric acid solution. The gas is passed through bubblers containing 4N KOH solution, followed by a bubbler containing concentrated sulfuric acid. The gas is purged through the samples as well as dry, deaerated THF solution taken in properly sealed, septa-attached anaerobic vials over a period of 10 minutes.

7. **DFT Calculation**

Density functional theory (DFT) optimized structures are obtained for the hypothetical models of high spin [Fe^{III}MARG**H**]-NO_2^-, Fe^{III}TPP-NO_2^-, [Fe^{III}MARG**H**]-Cl, Fe^{III}TPP-Cl, low spin $\{Fe(MARGH)NO\}^6$ complex of and $\{Fe(TPP)NO\}^6$ complex. The geometries are optimized using unrestricted BP86 functional with gradient correction with the help of the Gaussian 16 version (g16) in the gas phase. (Ref: https://gaussian.com/citation/). The 6-311G(d) basis set is used for the optimization of all of the atoms..[4] Frequency calculations are performed on the optimized geometry to confirm that the minimum energy is obtained and the absence of any imaginary modes in these models. All of the atoms are optimised using the 6-311+G(d) basis set in a polarizable continuum model with THF to determine the final energy of the models and the frequency convergence criterion of 10^{-10} Hartree.[5-7] The Gibbs free energies are calculated from the final optimized geometries and frequencies. The electrostatic potential plot in *figure 10* distributions was made using the cubegen utility of the GaussView 6 software (https://gaussian.com/citation/) with an isovalue of 0.0004.

8. Spectroscopic data

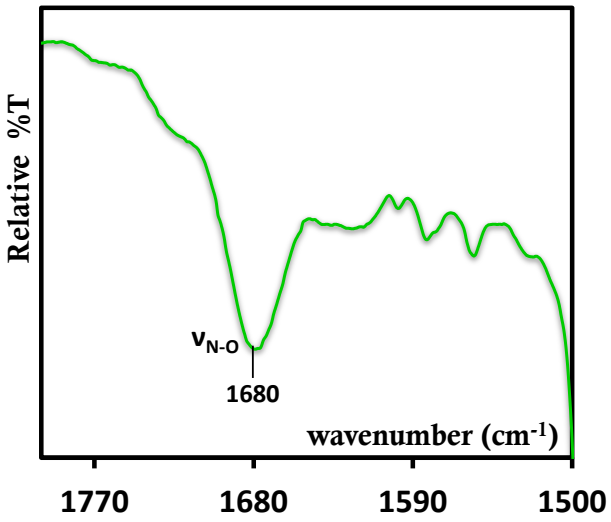

Figure S1. FTIR spectra of $\{FeNO\}^7$ complex generated in the reaction of $[Fe^{II}MARG\mathbf{H}]\mathbf{Cl}$ with $[NBu_4]NO_2$.

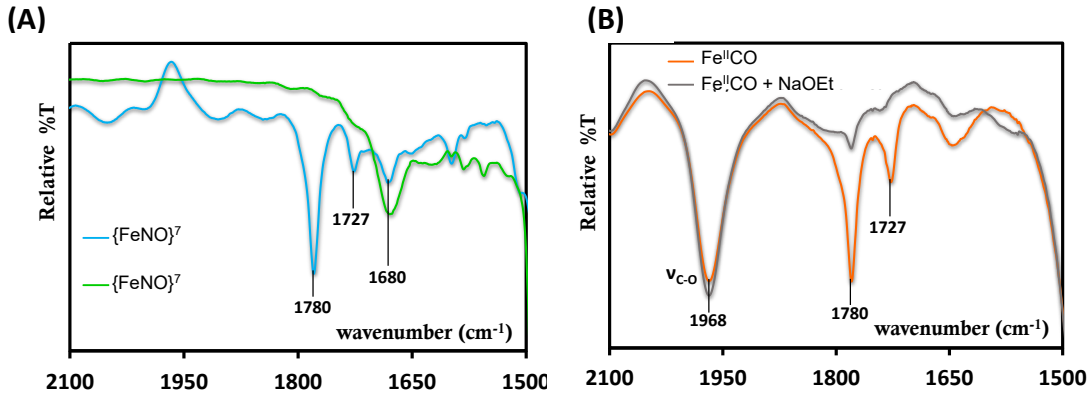

Figure S2. (A) FTIR spectra of pure $\{FeNO\}^7$ complex generated with the addition of Ph_3CSNO to the $[Fe^{III}MARG\mathbf{H}]\mathbf{Cl}_2$ solution (cyan) and the $\{FeNO\}^7$ complex generated with addition of $[NBu_4]NO_2$ to $[Fe^{II}MARG\mathbf{H}]\mathbf{Cl}$ (green). **(B)** FTIR spectra of pure $Fe^{II}CO$ complex of $[MARG\mathbf{H}]\mathbf{Cl}$ (orange) and the product generated after incubation of the complex with NaOEt for an hour (grey).

The FTIR spectrum of the pure $\{FeNO\}^7$ species generated from the reaction of $[Fe^{III}MARG\mathbf{H}]\mathbf{Cl}_2$ and Ph_3CSNO shows ν_{N-O} at 1680 cm^{-1} and characteristic vibrations of the protonated guanidinium arm at

1727 cm^{-1} and 1780 cm^{-1} (Figure S2A, cyan). However, the FTIR spectra of the $\{FeNO\}^7$ species generated in the reaction of the reduced porphyrin, [Fe^{II}MARG**H**]**Cl** with [NBu_4]NO_2 clearly indicates that the protons of the pendant guanidinium arm of the complex are consumed during the reaction as no corresponding vibrations are observed (Figure S2A, green). [Fe^{III}MARG**H**]$\mathbf{Cl_2}$ is reduced to the ferrous porphyrin and dry CO gas is bubbled into the aprotic solution of the reduced iron-porphyrin. The $\nu_{C\text{-}O}$ of this CO bound complex of the ferrous porphyrin is 1968 cm^{-1} whereas FTIR vibrations at 1727 cm^{-1} and 1780 cm^{-1} indicate that the guanidinium arm of the complex is protonated even after the reduction of ferric to ferrous porphyrin (Figure S2B, orange). When the CO bound complex of the ferrous porphyrin is incubated with dry NaOEt solution for at least 1 hour the characteristic vibrations of the protonated guanidinium arm are found to be diminished keeping the $\nu_{C\text{-}O}$ almost unperturbed (Figure S2B, grey). It indicates that NaOEt results in the deprotonation of the pendant guanidinium group of the complex. These results suggest that the reduction of [Fe^{III}MARG**H**]$\mathbf{Cl_2}$ results into [Fe^{II}MARG**H**]**Cl** where the pendant guanidine is protonated as the ferric porphyrin.

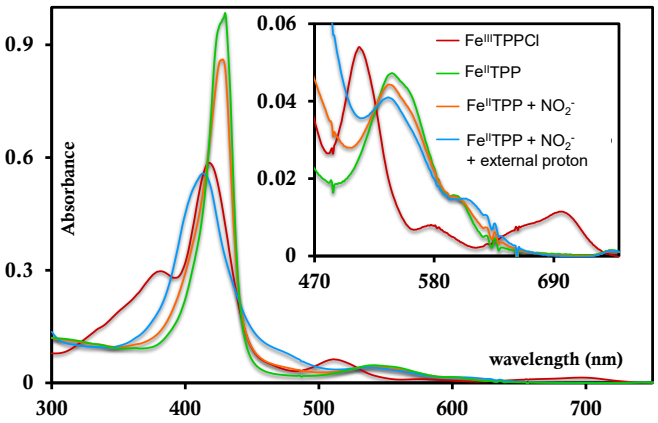

Figure S3. Absorption spectra of Fe^{III}TPPCl (dark red), Fe^{II}TPP (green) and the spectra of Fe^{II}TPP upon addition of [NBu_4]NO_2 (orange) followed by the addition of 2,6-xylidinium chloride as external proton source (sky blue).

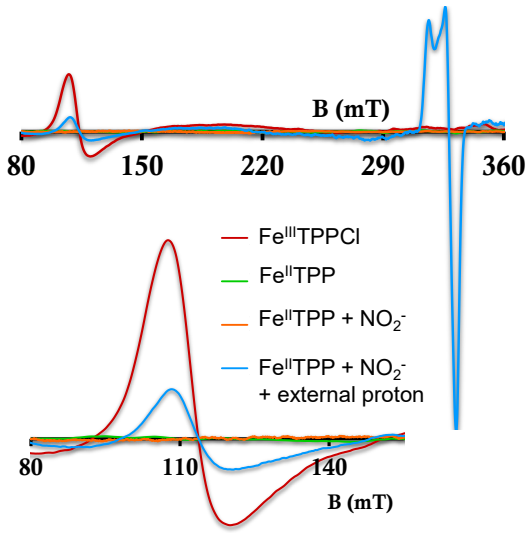

Figure S4. X-band EPR spectra of Fe^{III}TPPCl (dark red), Fe^{II}TPP (green) and the spectra of Fe^{II}TPP upon addition of [NBu_4]NO_2 (orange) followed by the addition of 2,6-xylidinium chloride as external proton source (sky blue).

Figure S3 and S4 suggest that the Fe^{II}TPPCl complex produces $\{FeNO\}^7$ species with $[NBu_4]NO_2$ only in presence of 2,6-xylididinium chloride (external source of protons) which produces the required protons in the solution to cleave the N-O bond of the NO_2^- bound to the ferrous centre.

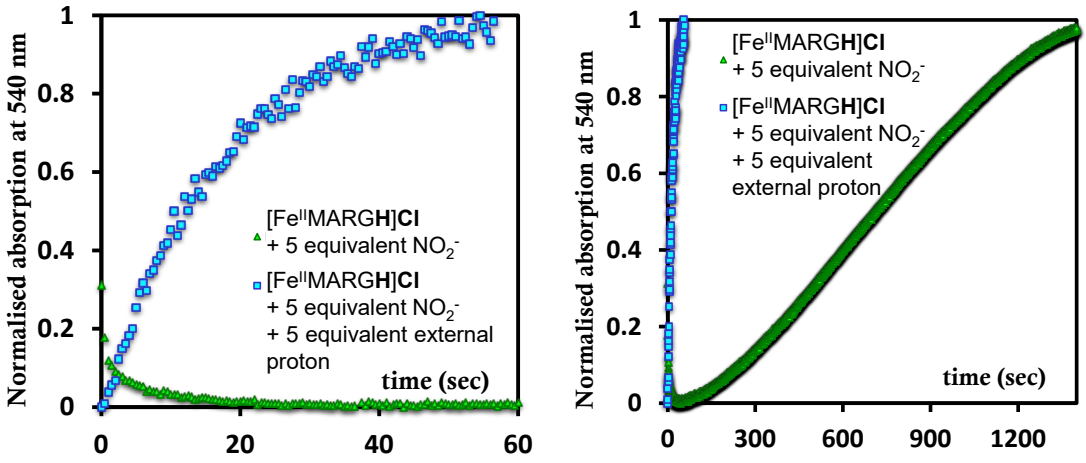

Figure S5. The corresponding kinetic trace followed at 540 nm regarding the formation of $\{FeNO\}^7$ complex upon addition of 5 equivalent $[NBu_4]NO_2$ to [Fe^{II}MARG**H**]Cl (green) and also the formation of the same complex upon simultaneous addition of 5 equivalent $[NBu_4]NO_2$ and 5 equivalent 2,6-xylidinium chloride (source of external proton) to [Fe^{II}MARG**H**]Cl (blue).

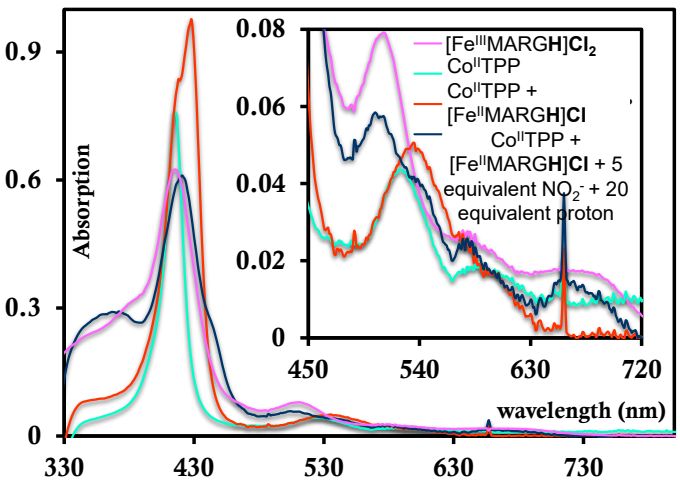

Figure S6. Absorption spectra of Co(II)TPP (sky blue), mixture of Co(II)TPP and [Fe^{II}MARG**H**]**Cl** (red) and that of the reaction of [Fe^{II}MARG**H**]**Cl** upon addition of 20 equivalent 2,6-xylidinium chloride (source of external protons) simultaneously with 5 equivalent $[NBu_4]NO_2$ and incubated with Co(II)TPP (dark Blue).

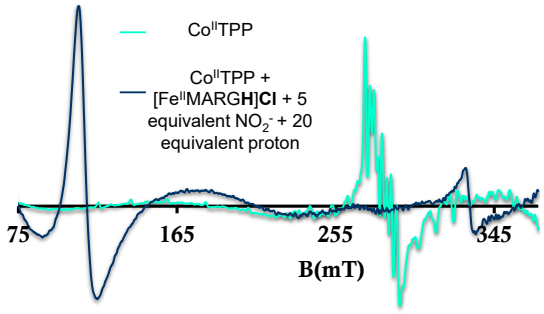

Figure S7. X-band EPR spectra of Co^{II}TPP (sky blue) and that of the reaction of [Fe^{II}MARG**H**]**Cl** upon addition of 20 equivalent 2,6-xylidinium chloride (source of external protons) simultaneously with 5 equivalent $[NBu_4]NO_2$ and incubated with Co^{II}TPP (dark Blue).

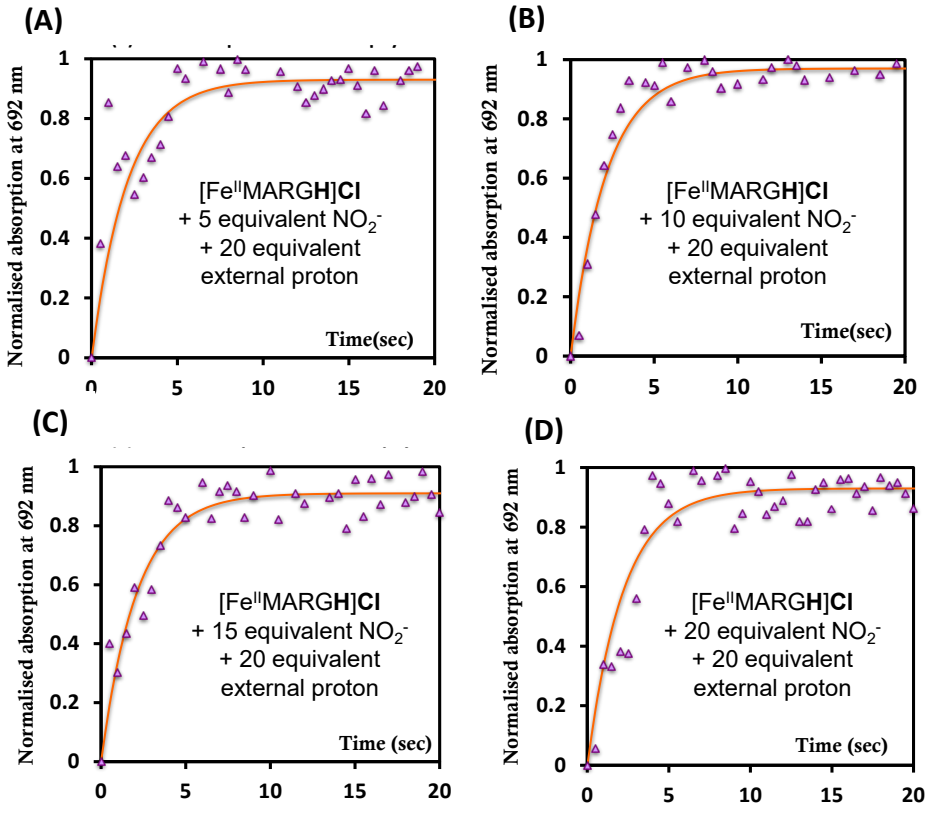

Figure S8. Kinetic trace followed at 692 nm regarding the formation of Fe^{III}-Cl species upon simultaneous addition of 5, 10, 15 and 20 equivalents $[NBu_4]NO_2$ and 20 equivalent 2,6-xylidinium chloride to the [Fe^{II}MARG**H**]**Cl**, (A), (B), (C), (D), respectively.

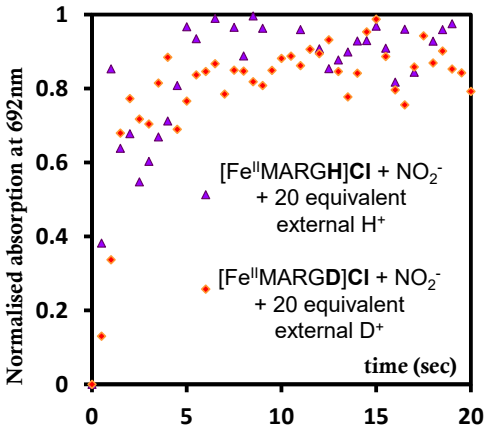

Figure S9. Kinetic trace followed at 692 nm regarding the formation of Fe^{III}-Cl species upon simultaneous addition of 20 equivalents $[NBu_4]NO_2$ and 20 equivalent 2,6-XylidiniumH chloride (as the external H^+ source) to [Fe^{II}MARG**H**]**Cl** complex (violet) and 20 equivalents $[NBu_4]NO_2$ and 20 equivalent 2,6-XylidiniumD chloride (as the external D^+ source) to [Fe^{II}MARG**D**]**Cl** complex (red).

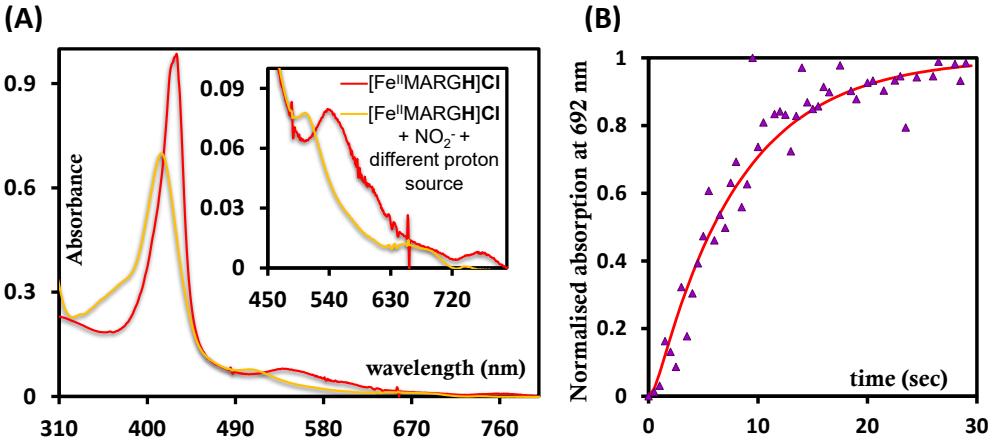

Figure S10. (A) The absorption spectrum of [Fe^{II}MARG**H**]**Cl** upon addition of 2,6-xylidinium *p*-toluene sulfonate simultaneously with nitrite (yellow) and **(B)** the corresponding kinetic trace followed at 692 nm regarding the formation of resultant ferric porphyrin species. The pseudo 1st order rate obtained from the data is 0.27 s^{-1}.

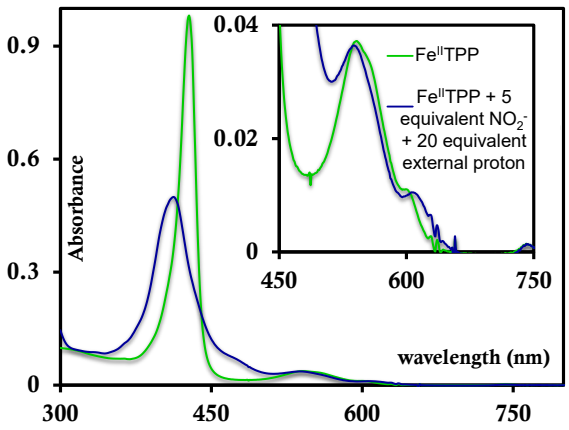

Figure S11. Absorption spectra of $Fe^{II}TPP$ (green), the product upon simultaneous addition of 5 equivalents $[NBu_4]NO_2$ and 20 equivalent 2,6-xylidinium chloride to $Fe^{II}TPP$ (blue).

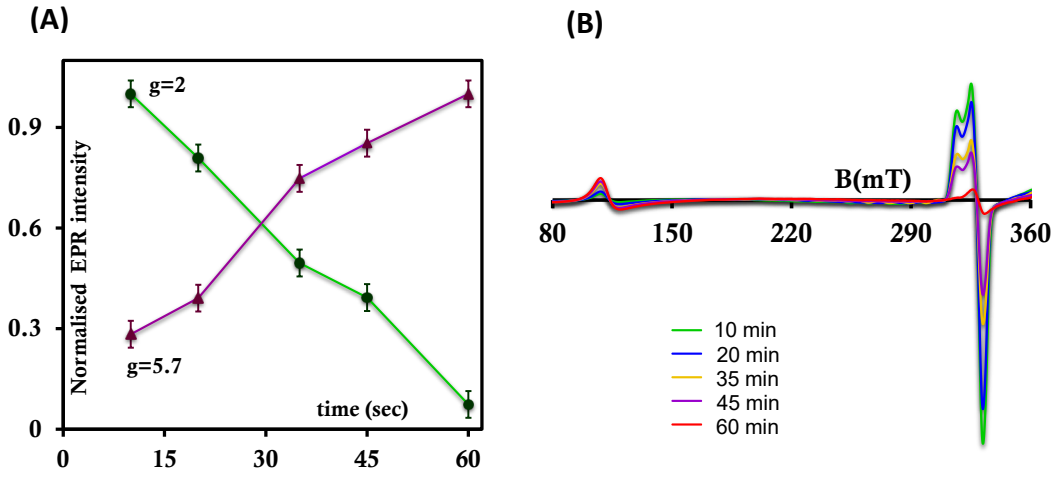

Figure S12. (A) Plot of normalized EPR intensities of the axial (violet) and rhombic (green) signals of $\{FeNO\}^7$ complex of [MARG**H**]**Cl** with time. **(B)** The corresponding X-band EPR data.

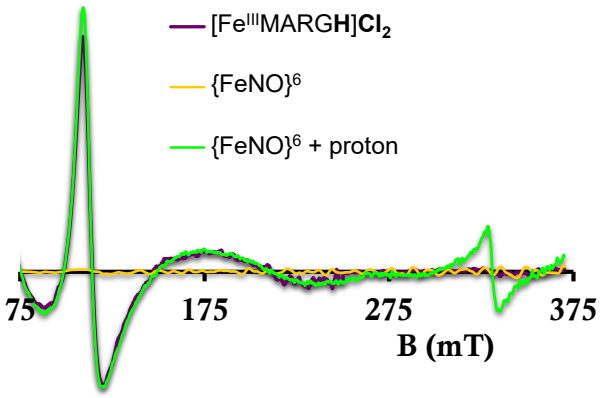

Figure S13. X-band EPR spectra of [Fe^{III}MARG**H**]**Cl$_2$** (violet), in-situ formed {FeNO}^{6} complex of it (yellow) and Fe^{III}-Cl species upon addition of 2,6-xylidinium chloride (as a source of external proton) to that {FeNO}^{6} complex of [MARG**H**]**Cl** (green).

11. Coordinates obtained from DFT optimizations

*11.1. {Fe(MARG**H**)NO}^{6} complex:*

Charge: +2, spin multiplicity: 1

Fe	3.58205200	8.83876900	6.52740400
N	5.33200300	9.37420800	5.78887700
N	2.79107100	9.08306600	4.71503300
N	1.76255800	9.09757500	7.28425300
N	4.33386700	9.15454600	8.34281300
C	6.75501800	9.05702700	7.81788300
C	4.80276400	9.63702000	3.36402100
C	3.47324600	9.19490500	3.50831400
C	1.49174500	8.69675800	4.34998700
C	7.03430200	10.14637200	4.38941700
C	7.59744400	9.90274000	5.61334900
C	6.55136300	9.40256200	6.46733300
C	5.65383200	9.74549700	4.47391300
C	1.40293400	8.49754900	2.92570600
C	2.62545700	8.82612600	2.40221200

C	2.26921400	9.38432500	9.71328400
C	3.64581200	9.15058900	9.55713800
C	1.39755100	9.36842600	8.60934800
C	0.40427700	8.68048700	5.23096000
C	4.53972200	8.86943500	10.65130100
C	5.66757700	8.92023000	8.69656100
C	5.78728600	8.69150500	10.11369600
C	-0.55668100	9.27009600	7.47509000
C	-0.02690500	9.53643400	8.71421000
C	0.55039400	8.98605900	6.59787700
H	7.50617300	10.56074100	3.50042500
H	8.62197100	10.08466500	5.93342000
H	0.51175700	8.17606100	2.38870400
H	2.93804300	8.81993300	1.35915900
H	4.23787500	8.79644500	11.69496500
H	6.71400700	8.44600300	10.62950300
H	-1.59803300	9.35727300	7.16200700
H	-0.54988200	9.84167700	9.61900900
C	8.14997200	8.91510700	8.31508600
C	8.63236300	9.70831700	9.38463100
C	9.02483400	7.98646900	7.70005600
C	9.95499400	9.57026100	9.82734100
H	7.97906600	10.46111600	9.83871300
C	10.33994800	7.83891100	8.16130000
H	8.65859800	7.36150500	6.87820100
C	10.80863700	8.63116000	9.22328900
H	10.32269000	10.20385600	10.64106700
H	11.00041000	7.10313400	7.69092700
H	11.83920000	8.52098000	9.57612300
C	-0.97511300	8.46932100	4.68323800
C	-1.50676000	9.38563400	3.74718400
C	-1.80883700	7.39292300	5.08789300

C	-2.79601700	9.23109500	3.21757000
H	-0.89128900	10.23896700	3.44553600
C	-3.11278300	7.24531800	4.57633800
C	-3.60051100	8.15659100	3.62887600
H	-3.17797100	9.96051600	2.49661500
H	-3.75248100	6.43523900	4.94264400
H	-4.61596300	8.04037400	3.23785600
C	1.73263200	9.60815600	11.08532200
C	0.74418900	8.76142400	11.64065500
C	2.22580000	10.68493500	11.86115100
C	0.26175500	8.98720700	12.93742100
H	0.38059100	7.90445200	11.06264700
C	1.72674100	10.91724100	13.15041400
H	2.98114200	11.35458500	11.43604900
C	0.74685800	10.06861000	13.69254800
H	-0.48931700	8.31375000	13.36346300
H	2.10311600	11.76490200	13.73223800
H	0.36436800	10.24717700	14.70270500
C	5.31657600	9.93914200	1.99922400
C	6.43616300	9.25221100	1.47124300
C	4.67714400	10.92260600	1.20610500
C	6.90215700	9.54382900	0.18169100
H	6.91982600	8.46849400	2.06435900
C	5.16003900	11.22302100	-0.07509100
H	3.82253700	11.47380700	1.61361500
C	6.27022700	10.53292600	-0.59122400
H	7.75895500	8.99452200	-0.22209200
H	4.67172900	12.00200500	-0.66974900
H	6.64204000	10.76509100	-1.59450700
N	-1.33418300	6.46066800	6.08001900
H	-0.86964800	6.87049100	6.89879100
C	-1.33123100	5.11544800	5.96281900

N	-1.07047600	4.36008700	7.05215400
N	-1.54369000	4.52374900	4.77316200
H	-0.89222400	3.36016700	6.97188900
H	-1.81627300	3.54416200	4.70749900
H	-1.65247500	5.10057800	3.93848400
H	-1.17966400	4.73918500	7.99103700
N	3.69780500	7.23468600	6.50889900
O	3.77950600	6.06444100	6.49277400

11.2. {Fe(TPP)NO}^{6} complex:

Charge: +1, spin multiplicity: 1

Fe	4.05411800	12.93826700	3.29770800
N	3.49363700	14.83103800	3.40162500
N	2.44698900	12.56478800	2.21100500
N	4.18684100	10.98505500	3.63050700
N	5.15491800	13.25468300	4.91536100
N	5.17191000	13.06953600	2.14961600
C	1.38348400	14.81493800	2.08146400
C	2.88243400	10.16494200	1.68454500
C	5.64519000	10.92299400	5.64933000
C	5.38012700	15.72894800	4.74794100
C	4.29974600	15.87648200	3.86599800
C	2.43421500	15.46302700	2.75256900
C	1.42630800	13.43820300	1.81536900
C	2.16179700	11.36669700	1.55422800
C	3.83392500	9.99718100	2.70173000
C	4.99476500	10.32661200	4.55519400
C	5.73536800	12.31694400	5.77789900
C	5.69965300	14.48052600	5.30864400
C	3.74624900	17.15161000	3.48804600
H	4.18168700	18.11599400	3.74450100
C	2.57897800	16.89565600	2.81938800

H	1.87164200	17.60725800	2.39657600
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H	0.47381500	10.65927400	0.25507300
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H	4.37675900	7.83106100	2.44430600
C	5.14935600	8.93863300	4.20014000
H	5.73910800	8.21894400	4.76561300
C	6.55658200	12.97793000	6.76008900
H	7.06953700	12.47577700	7.57821600
C	6.58244700	14.30701400	6.43246500
H	7.12399300	15.11244200	6.92551900
C	0.24195800	15.63535200	1.57691500
C	-0.02127100	15.75176900	0.19279000
H	0.63156800	15.24442800	-0.52594000
C	-1.09176300	16.53595500	-0.26176900
H	-1.27715000	16.62831000	-1.33722400
C	-1.91758800	17.20512500	0.65682400
H	-2.75565300	17.81293400	0.29982700
C	-1.66345700	17.09569700	2.03411200
H	-2.30632600	17.61158700	2.75521800
C	-0.58650400	16.32332600	2.49322200
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C	2.54428600	9.03185300	0.77410700
C	2.71956100	9.17902100	-0.62147300
H	3.12101800	10.11807400	-1.01805500
C	2.40734800	8.12457700	-1.49171500
H	2.56271300	8.24674300	-2.56891200
C	1.89901000	6.91739400	-0.98406300
H	1.65018000	6.09684300	-1.66523300
C	1.70486900	6.76745600	0.39928100

H	1.29322500	5.83464800	0.79912100
C	2.02860900	7.81402700	1.27506000
H	1.85515200	7.70258500	2.35090500
C	6.32829000	10.03573600	6.63861200
C	7.73279200	10.05642800	6.79826600
H	8.33793100	10.72537700	6.17656200
C	8.35348300	9.20440300	7.72372500
H	9.44350400	9.22123400	7.82892900
C	7.58223800	8.32886500	8.50622100
H	8.06869300	7.66815300	9.23151900
C	6.18621000	8.29971400	8.35266700
H	5.57941300	7.62143400	8.96191100
C	5.56184300	9.14031300	7.41941800
H	4.47251200	9.12151900	7.30430900
C	6.13675900	16.95059200	5.16402000
C	6.95534000	17.61953000	4.22691500
H	7.04255400	17.22659700	3.20785300
C	7.66714500	18.76939000	4.60109300
H	8.30700900	19.27255500	3.86836200
C	7.56061900	19.27157800	5.90839300
H	8.11395300	20.17116600	6.19779300
C	6.73843900	18.61976800	6.84249100
H	6.64078200	19.01427800	7.85953100
C	6.03132800	17.46460600	6.47598200
H	5.37588600	16.96871000	7.20055400
O	5.97571500	13.18084400	1.30396300

11.3. [Fe^{III}MARG**H**] -NO_2^-***:***

Charge: +1, spin multiplicity: 6

Fe	3.35895700	8.96759300	6.68345900
N	5.20319700	9.23804900	5.83198800
N	2.54254600	9.20129500	4.81743200

N	1.52673300	9.39671200	7.49995900
N	4.19902300	9.35765400	8.50448900
C	6.58392100	8.95482200	7.89344800
C	4.58442000	9.52496600	3.42848200
C	3.19031700	9.38194300	3.59606800
C	1.19680700	9.03529700	4.51928100
C	6.94969500	9.38151000	4.31081000
C	7.50594900	9.15764300	5.54754600
C	6.41691600	9.07835900	6.49282500
C	5.51659500	9.42191100	4.49047800
C	0.99642100	9.08476300	3.09026900
C	2.22278800	9.34435600	2.52306300
C	2.15535900	9.81031400	9.87376600
C	3.54483400	9.58162100	9.71126500
C	1.21789600	9.69634000	8.82437100
C	0.15796400	8.95308700	5.47271500
C	4.47557500	9.44218000	10.80604400
C	5.53293500	9.11340300	8.82803300
C	5.69831400	9.12390700	10.26141600
C	-0.77838200	9.41461600	7.78149400
C	-0.21800300	9.75764800	8.98844000
C	0.31208300	9.21991900	6.85257200
H	7.46416900	9.49197200	3.35728500
H	8.56194100	9.07299700	5.79973300
H	0.03248800	9.00197300	2.58749200
H	2.45214500	9.49823000	1.46929100
H	4.21939600	9.53800400	11.86027300
H	6.62862100	8.91560900	10.78789700
H	-1.83764800	9.34141000	7.53573100
H	-0.73228100	10.01430300	9.91356400
C	7.96675600	8.70516900	8.40752500
C	8.63580200	9.66178900	9.20452400

C	8.63019000	7.49853000	8.08741700
C	9.93514700	9.41431800	9.67242600
H	8.13955800	10.61056400	9.43681200
C	9.92630900	7.25147900	8.56406500
H	8.11455600	6.74857800	7.47746200
C	10.58210900	8.20811100	9.35652600
H	10.44532400	10.16956800	10.28007200
H	10.42342800	6.30694700	8.31772600
H	11.59539200	8.01540600	9.72490300
C	-1.19463300	8.50783200	4.99822600
C	-2.22851100	9.40489800	4.67378800
C	-1.45709200	7.11189500	4.91185400
C	-3.49261200	8.94283700	4.27015700
H	-2.02786400	10.47964000	4.73755000
C	-2.73920200	6.64568500	4.55700300
C	-3.74732200	7.56464000	4.22230200
H	-4.27963700	9.65884500	4.01330800
H	-2.97093400	5.57633400	4.60363300
H	-4.74054800	7.19485100	3.94783500
C	1.65988200	10.11822400	11.25272000
C	0.80984900	9.22438200	11.94270300
C	2.05294600	11.31595700	11.89213700
C	0.36026300	9.52535600	13.23738700
H	0.52098200	8.28103600	11.46605900
C	1.59612300	11.61691600	13.18414400
H	2.70673300	12.01774800	11.36251800
C	0.74928600	10.72296800	13.85990700
H	-0.28990200	8.81796600	13.76363300
H	1.90097000	12.55417400	13.66217800
H	0.39605000	10.95733500	14.86979100
C	5.12014500	9.74436000	2.04682500
C	5.00655000	8.74748700	1.05207800

C	5.75882100	10.96217700	1.72123500
C	5.51599100	8.96554500	-0.23722700
H	4.53375700	7.79108800	1.30219600
C	6.26249400	11.17939600	0.42970300
H	5.84554800	11.74383200	2.48406700
C	6.14278200	10.18236000	-0.55237600
H	5.42960900	8.17931300	-0.99526400
H	6.74703900	12.13216300	0.19027200
H	6.53915700	10.35198700	-1.55918100
N	-0.39921700	6.22147700	5.27033600
H	0.31136700	6.59230900	5.92969300
C	-0.03267800	5.07225100	4.65396700
N	1.03816900	4.41299700	5.12559700
N	-0.75461600	4.57260700	3.61918800
H	1.38717100	3.58214400	4.65338000
H	-0.37023600	3.81116200	3.06357800
H	-1.42322500	5.18783500	3.15407300
H	1.63121400	4.88214100	5.85300900
N	3.14953800	6.84834300	6.63779000
O	4.10729900	6.13065200	6.34103700
O	1.98760400	6.32855300	6.80439700

11.4. $Fe^{III}TPP\text{-}NO_2^-$***:***

Charge: 0, spin multiplicity: 6

Fe	4.05012700	12.94144100	3.27015200
N	3.43342100	14.90390700	3.41018700
N	2.38466900	12.58251900	2.10302500
N	4.15813800	10.91318600	3.65341500
N	5.23829900	13.24560300	4.93401600
C	1.44361200	14.88177300	1.90861600
C	2.67561700	10.12052200	1.81311400
C	5.81548200	10.89414300	5.51968000

C	5.23637300	15.73768800	4.91818800
C	4.16344700	15.91806300	4.01688100
C	2.40740800	15.53009700	2.71451000
C	1.44701500	13.49439400	1.63536100
C	2.04320800	11.35747600	1.54681000
C	3.66104400	9.92803000	2.80806400
C	5.02758300	10.26997500	4.52454000
C	5.91052600	12.29404000	5.69032600
C	5.69112000	14.48150500	5.37770900
C	3.59470100	17.20437300	3.67959700
H	3.97433600	18.16583400	4.02325400
C	2.50476200	16.96449400	2.88016000
H	1.83317700	17.69382000	2.42896300
C	0.48373200	12.82003900	0.79272800
H	-0.37705300	13.29285400	0.32153700
C	0.86450100	11.50258000	0.72148500
H	0.37111800	10.69189100	0.18678600
C	4.25898200	8.65197600	3.13384200
H	4.07458800	7.71885500	2.60319200
C	5.08828200	8.85942600	4.20795700
H	5.71392000	8.12947100	4.72010600
C	6.78028800	12.94892000	6.64361300
H	7.40606200	12.43942600	7.37524200
C	6.67013800	14.30018100	6.42645800
H	7.19361200	15.10488600	6.94121800
C	0.37795400	15.72519200	1.27802500
C	0.30098900	15.86942500	-0.12572300
H	1.04156100	15.36411700	-0.75539000
C	-0.69763700	16.66363400	-0.71004500
H	-0.73704800	16.76983200	-1.80007800
C	-1.63676300	17.32619700	0.09747600
H	-2.41653500	17.94566900	-0.35955000

C	-1.56995300	17.19167200	1.49400700
H	-2.30133200	17.70126500	2.13155500
C	-0.57053400	16.39951900	2.07975400
H	-0.52418700	16.28761100	3.16873100
C	2.23412300	8.93526900	1.01101000
C	2.46125800	8.90248800	-0.38353200
H	2.97805500	9.74391000	-0.85775100
C	2.05119700	7.79975500	-1.14837100
H	2.24388100	7.78670400	-2.22709900
C	1.40313100	6.71512900	-0.53452500
H	1.08206800	5.85501600	-1.13274800
C	1.16770800	6.73886000	0.85009600
H	0.65521600	5.90050700	1.33555100
C	1.58029400	7.83919100	1.61738100
H	1.38458900	7.86315000	2.69519700
C	6.63808300	10.01148800	6.40850500
C	8.05023500	10.04169400	6.36276700
H	8.54715900	10.71550700	5.65615200
C	8.81113200	9.20691600	7.19572400
H	9.90520700	9.23870100	7.14110900
C	8.17480500	8.32843300	8.08817700
H	8.76980500	7.67742600	8.73843600
C	6.77184500	8.28697500	8.14050200
H	6.26690700	7.60687300	8.83591000
C	6.00974200	9.11959400	7.30652800
H	4.91534300	9.09249700	7.35266200
C	5.90891500	16.97025200	5.44698100
C	6.73697700	17.73765800	4.59835000
H	6.88687900	17.41047700	3.56362100
C	7.37113900	18.89466100	5.07739300
H	8.01541200	19.47605900	4.40815400
C	7.18609700	19.30276300	6.40870200

H	7.68139200	20.20633500	6.78156600
C	6.36244900	18.54774400	7.25983500
H	6.20789200	18.86291400	8.29809400
C	5.72766400	17.38989600	6.78291300
H	5.07648100	16.80653000	7.44363900
N	5.49950500	13.13027200	1.77255400
O	5.49282400	12.27677800	0.86303100
O	6.30306300	14.08099100	1.83449600

11.5. *NO:*

Charge: 0, spin multiplicity: 2

O	0.51046600	-2.22996500	0.00000000
N	-0.66197000	-2.22996500	0.00000000

11.6. NO_2^-**:**

Charge: -1, spin multiplicity: 1

N	0.49933400	-2.27034600	0.00000000
O	-0.10068500	-1.12863400	0.00000000
O	1.78809400	-2.21912100	0.00000000

11.7. [Fe^{III}MARG**H**]-Cl **:**

Fe	3.34057900	9.16893900	6.65837400
N	5.19062200	9.14354500	5.79836700
N	2.49069700	9.31674900	4.78402600
N	1.49410100	9.67687500	7.49165200
N	4.20887000	9.39334100	8.51044700
C	6.56299600	8.89902800	7.86419000
C	4.54879400	9.41901700	3.39994500
C	3.14535700	9.41831500	3.57029600
C	1.14389900	9.21853100	4.51366600
C	6.91137700	9.09708200	4.25813000

C	7.46685900	8.88867500	5.49564900
C	6.39106800	8.93510200	6.45958200
C	5.48714300	9.25630600	4.44729700
C	0.93360800	9.25523500	3.08300400
C	2.16795500	9.41966400	2.50200000
C	2.18807400	9.93153900	9.87458900
C	3.57552300	9.69905300	9.70517500
C	1.22431600	9.84853000	8.84064300
C	0.12127800	9.15799500	5.49017100
C	4.54370600	9.66827500	10.77954200
C	5.54146800	9.15882900	8.80857700
C	5.74671900	9.30041600	10.23245900
C	-0.77818000	9.44032700	7.85279900
C	-0.20176500	9.73956100	9.06131300
C	0.28492800	9.41156900	6.87180700
H	7.42448800	9.12971800	3.29913500
H	8.51740200	8.73675300	5.73473700
H	-0.03540300	9.22862900	2.58573100
H	2.39455100	9.53030300	1.44327800
H	4.33193500	9.88943300	11.82345200
H	6.69183100	9.15102300	10.75022200
H	-1.83319700	9.25990300	7.65267800
H	-0.69547800	9.83245800	10.02640100
C	7.94553100	8.63437400	8.37679300
C	8.70364200	9.65417300	8.98557500
C	8.51163500	7.35078800	8.24524000
C	9.99760500	9.39476700	9.45394400
H	8.27965600	10.65902000	9.07760800
C	9.80291200	7.09220100	8.72159000
H	7.92626200	6.55108700	7.78140100
C	10.54897400	8.11284000	9.32582300
H	10.57794800	10.19839700	9.91700300

H	10.22589000	6.08807700	8.62238500
H	11.55871400	7.91033100	9.69457200
C	-1.21592300	8.64951000	5.04514700
C	-2.32719300	9.47409000	4.81045900
C	-1.37878400	7.24787200	4.90655800
C	-3.56557100	8.93157100	4.43852400
H	-2.20937200	10.55632500	4.91569400
C	-2.63087700	6.69699100	4.58700900
C	-3.71892600	7.54452000	4.33550300
H	-4.41529300	9.59313800	4.24978300
H	-2.77452500	5.61207900	4.60146800
H	-4.69218300	7.11309800	4.08665700
C	1.67920900	10.18710400	11.25895800
C	1.76002700	9.19407000	12.25660500
C	1.08845700	11.42574300	11.58056200
C	1.26534900	9.43746600	13.54356400
H	2.19410600	8.22012000	12.01102700
C	0.60299100	11.67021600	12.87111700
H	1.02467400	12.20609300	10.81567500
C	0.68921000	10.67658600	13.85532000
H	1.32595100	8.65345400	14.30426800
H	0.15818300	12.64122300	13.10841100
H	0.30677800	10.86654000	14.86240300
C	5.08692200	9.54477500	2.00692800
C	4.93870300	8.50119500	1.07237300
C	5.76155000	10.71738200	1.61325300
C	5.45275100	8.62741500	-0.22436400
H	4.43316200	7.57872400	1.37484300
C	6.26906000	10.84474200	0.31418700
H	5.87577400	11.53684800	2.32938200
C	6.11699700	9.80027400	-0.60733500
H	5.33961100	7.80417800	-0.93633300

H	6.78359100	11.76471600	0.02120600
H	6.51705100	9.89908400	-1.62060900
N	-0.24778900	6.40729000	5.17568900
H	0.38880600	6.71949100	5.92308400
C	0.27471400	5.47892000	4.34472200
N	1.47981800	4.96893100	4.62734800
N	-0.41728500	5.04064600	3.26794900
H	1.84642000	4.16779000	4.12461000
H	0.07892300	4.56315000	2.52196900
H	-1.26891200	5.53140500	3.00276600
H	2.07349500	5.41505500	5.35007700
O	3.44884900	11.46500700	6.49060700
H	2.57444800	11.73559300	6.82781000
C	4.47341000	12.31514500	7.04570400
H	4.32101800	13.35618900	6.71757200
H	4.49495500	12.26456900	8.14659100
H	5.42636800	11.94832200	6.64682500
Cl	2.83371700	6.81624500	6.83175600

11.8. *Fe^{III}TPP-Cl :*

Fe	4.03865500	12.93780000	3.29728400
N	3.43938900	14.93523000	3.41960800
N	2.33659200	12.56874800	2.12345800
N	4.18382500	10.88834100	3.60880400
N	5.26385500	13.25641500	4.93466800
C	1.55490200	14.91114300	1.79129200
C	2.54514800	10.09441300	1.91452300
C	5.95531200	10.90119100	5.35658800
C	5.14954000	15.74023600	5.04142900
C	4.10023800	15.93253700	4.11410200
C	2.45891100	15.55510300	2.66535800
C	1.50627400	13.52014600	1.55083800
C	1.96496000	11.34291500	1.59491200
C	3.57535000	9.89865700	2.86125900
C	5.10060200	10.26267800	4.43202500
C	6.02409900	12.29463900	5.57603300
C	5.67206400	14.48445300	5.42415900
C	3.51722500	17.21708100	3.78633700

H	3.83478500	18.17373700	4.19638800
C	2.50880800	16.98486800	2.88887100
H	1.85707000	17.71718800	2.41639900
C	0.57014300	12.86855800	0.66108900
H	-0.21200600	13.37184000	0.09594700
C	0.85502000	11.52794300	0.68548200
H	0.34675000	10.73077700	0.14654200
C	4.14920200	8.61255800	3.20342500
H	3.87759600	7.66233400	2.74800700
C	5.08487200	8.83653500	4.17739200
H	5.72255900	8.10439200	4.66891700
C	6.92848900	12.93761200	6.50571900
H	7.63728900	12.42172600	7.15055700
C	6.72332100	14.28809100	6.40026800
H	7.24093300	15.08260700	6.93410800
C	0.58137600	15.77372900	1.04234900
C	0.76093100	16.02143300	-0.33259400
H	1.62369000	15.58471100	-0.84474100
C	-0.14357700	16.82704400	-1.03620000
H	0.01409700	17.01429200	-2.10303200
C	-1.24232500	17.39527700	-0.37756300
H	-1.94903200	18.02380100	-0.92822400
C	-1.43063900	17.15541000	0.99007300
H	-2.28768200	17.59286900	1.51188800
C	-0.52446600	16.35202400	1.69471100
H	-0.67535500	16.16205500	2.76208700
C	2.01796400	8.88682200	1.19911800
C	2.28465600	8.69704700	-0.17128400
H	2.89127800	9.43590000	-0.70364900
C	1.79637900	7.56929700	-0.84343700
H	2.01961700	7.43359600	-1.90636000
C	1.03121100	6.61596000	-0.15820600
H	0.64933400	5.73560500	-0.68440300
C	0.75851800	6.79545700	1.20457200
H	0.15823100	6.05781400	1.74654800
C	1.24931900	7.92120400	1.87840900
H	1.03000900	8.06409700	2.94110600
C	6.87949100	10.03064400	6.15714900
C	8.25344100	9.97357100	5.85326800
H	8.64026000	10.56541400	5.01812900
C	9.11542400	9.16092500	6.60107400
H	10.17975200	9.12330600	6.34837300
C	8.61758900	8.39617100	7.66468800
H	9.29173400	7.76248000	8.24930000
C	7.25190600	8.44542200	7.97468600
H	6.85543200	7.85277100	8.80524800
C	6.38860100	9.25515300	7.22509300
H	5.32269400	9.29747400	7.46988300
C	5.74876800	16.96370500	5.66813700
C	6.54060000	17.84072500	4.90078200

H	6.72215400	17.61045400	3.84664100
C	7.10312800	18.98560800	5.47948100
H	7.72137200	19.65236600	4.87020400
C	6.88108000	19.27367700	6.83283500
H	7.32034400	20.16866500	7.28426800
C	6.09366000	18.40942500	7.60517800
H	5.91088400	18.62943200	8.66179400
C	5.53281000	17.26302400	7.02758300
H	4.91091000	16.59356300	7.62997200
O	2.26847800	12.65557900	4.97390200
H	1.52326600	12.62253900	4.34523200
C	1.96262300	13.57490800	6.03246300
H	1.08814800	13.23129800	6.61359500
H	2.84092100	13.59026900	6.69004800
H	1.78088100	14.59663000	5.65599300
Cl	5.56241900	13.15149500	1.64199700

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