Supplementary Information for "Using Porphyrin – Amino Acid Pairs to Model the Electrochemistry of Heme Proteins: Experimental and Theoretical Investigations"

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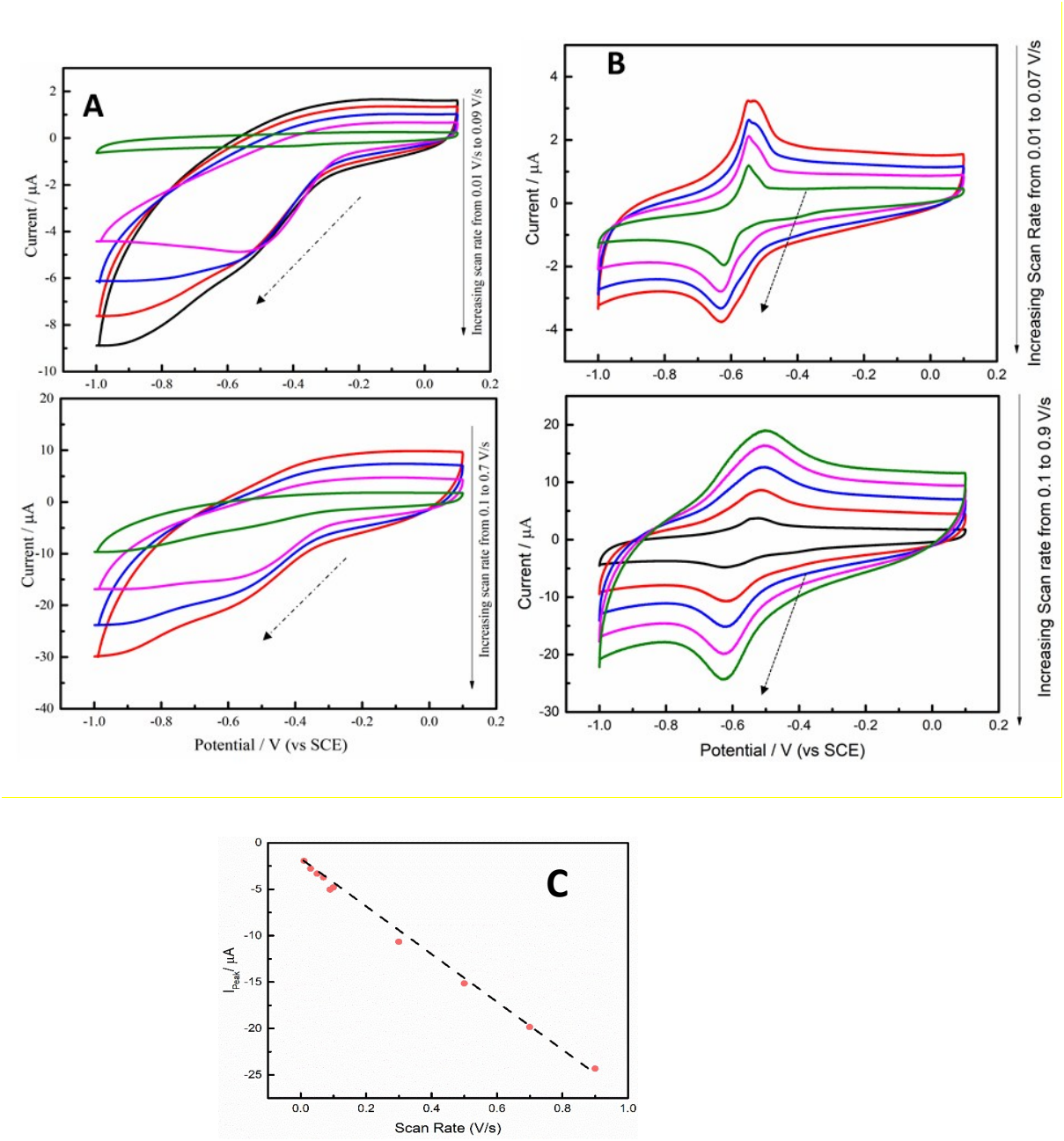

Figure S1: (A) Cyclic voltammograms of hemoglobin over a shorter potential window shown in the iron (III) – (II) reduction process. Voltammograms of different scan rates are superimposed on each other showing the shift in the reduction peak as scan rates are changed (marked by the dashed arrows in black) : 0.01 to 0.09 V/s (top) and 0.1 to 0.7 V/s (bottom). (B) Cyclic voltammograms of hemin showing the shifting of oxidation and reduction peaks as scan rate is changed (shift shown by the dotted arrow) – 0.01 – 0.09 V/s (top) and 0.1 to 0.9

V/s (bottom). (C) Linear current – scan rate response for hemin confirming a surface controlled process.

Concentration dependent UV-Vis spectra of Hemin:

A Lambert – Beer analysis of absorbance versus concentration is used to compute the molar extinction coefficient of the Soret band to 3.454 X 10^4 $M^{-1}cm^{-1}$ (λ_{max} = 387 nm).

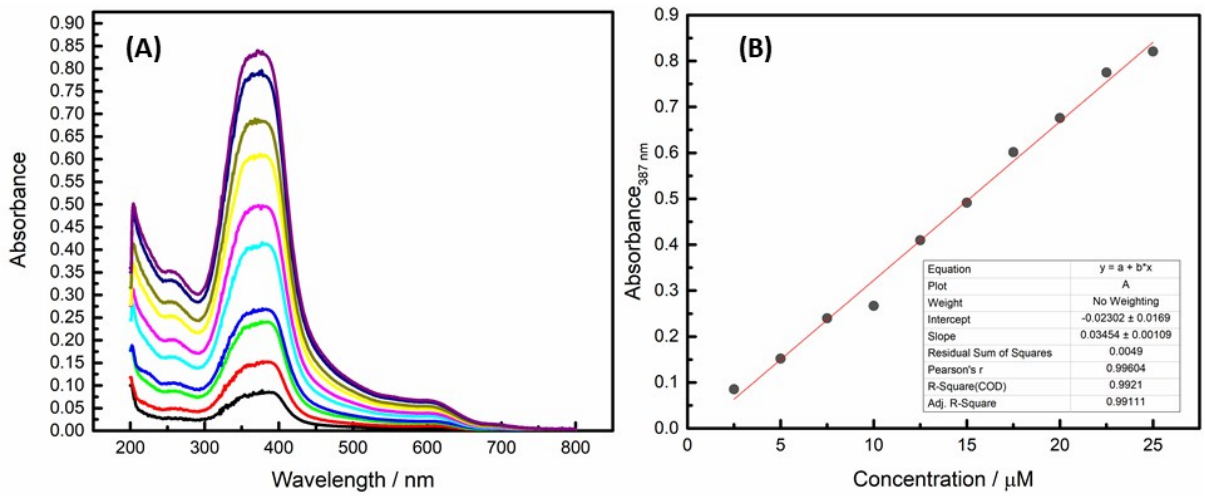

Figure S2: **(A)** Absorption spectra of hemin at different concentrations – 2.5 µM (black trace) to 25 µM (purple trace) showing the broad Soret band in the range 300 – 400 nm. **(B)** Absorbance versus concentration profile for λ_{max} = 387 nm (the fitting parameters are shown in the inset).

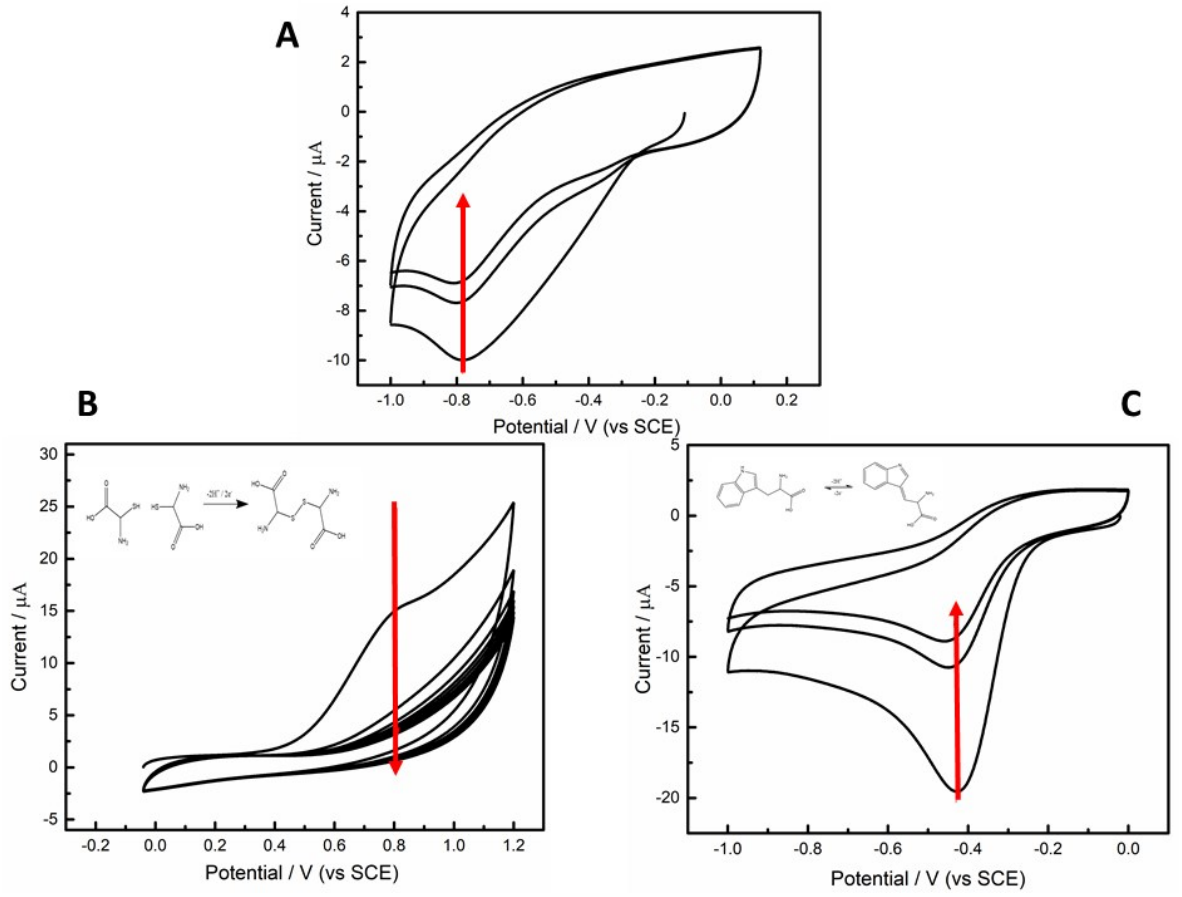

Figure S3: Electrochemical behavior of the three amino acids used in this study. Anticlockwise from top (A) histidine showing a reduction peak around ~ - 0.8V (B) cysteine showing oxidation around ~ 0.8V (C) tryptophan showing a prominent reduction around ~ -0.4V and a weak oxidation around ~ -0.2V. The redox peaks currents for all three systems decrease as electrochemical cycling is continued (denoted by red arrow) – indicating irreversible redox processes occurring at electroactive layers absorbed on electrode surface.

Representative concentration dependent UV-visible absorption spectra of hemin – amino acid systems:

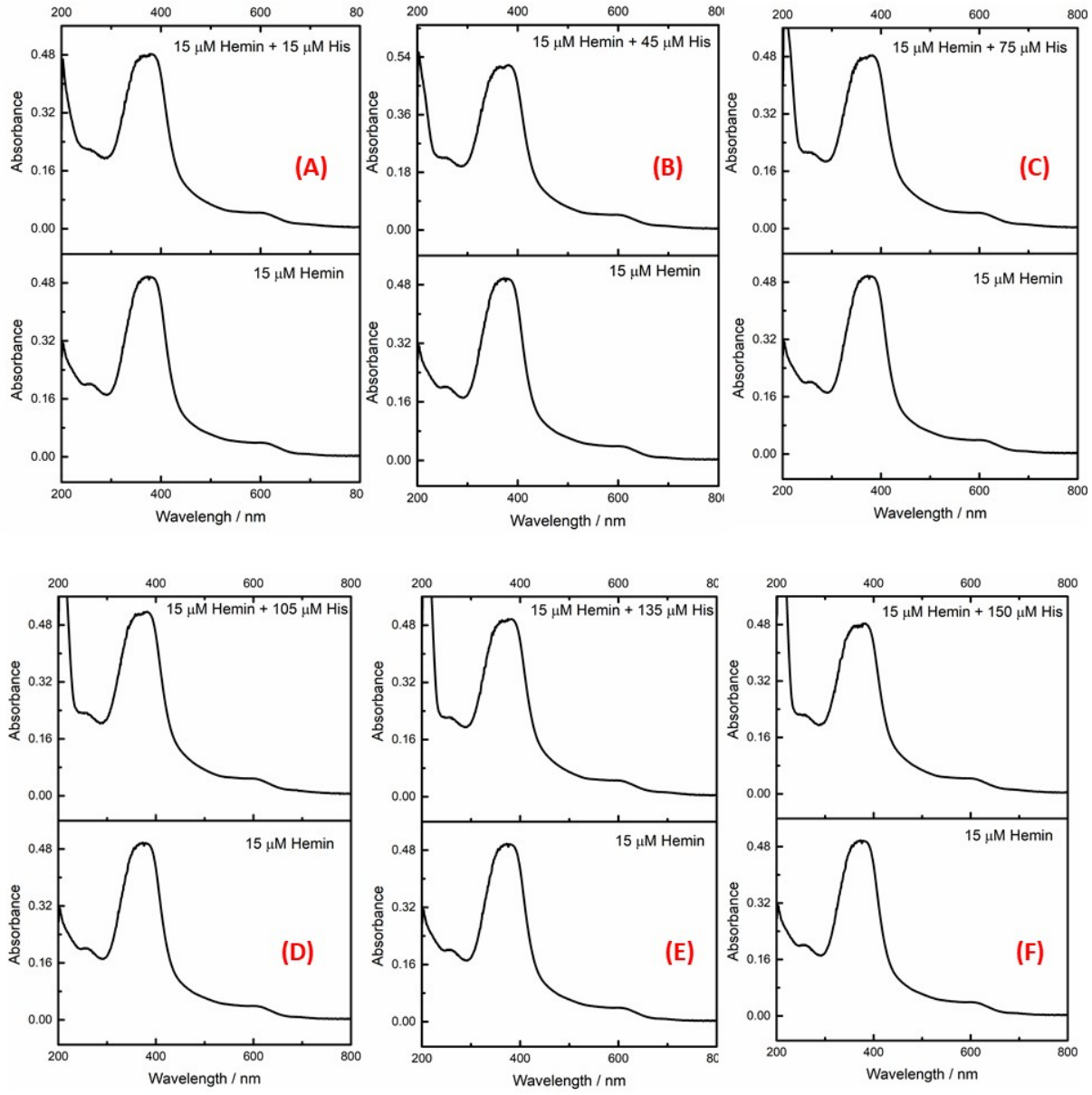

Figure S4: The absorption spectra of hemin alone (bottom) and hemin – histidine system (top) under different stoichiometric ratios – (A) 1:1; (B) 1:3; (C) 1:5; (D) 1:7; (E) 1:9; (F) 1:10. There is no change in the absorption pattern of hemin in the presence of histidine within the variation of stoichiometric rations shown.

We show here the concentration dependent uv-vis absorption spectra for a representative hemin – amino acid system (hemin – histidine). The absorption spectrum of hemin is dominated by the Soret band, which does not show any changes upon addition of histidine. There is no

change in the Soret band even when the stoichiometry of hemin – histidine is varied (1:1 – hemin : amino acid to 1: 10 – hemin : amino acid) (**Figure S4).** Aging the samples over one week does not result in any changes in the absorption spectra. (**Figure S5**)

This suggests that the interaction between hemin and histidine in solution is not strong enough to induce any observable changes in the electronic absorption spectrum. However, the DFT data strongly suggests that when hemin is placed in a solvent medium, among the three amino acids – tryptophan, cysteine, and histidine, histidine is the one which interacts most prominently with the iron centre of hemin. We observe this phenomenon electrochemically as well, where the electrochemical response of the hemin – histidine solution is characteristically very different from those of the other two amino acids. Additionally, there is a shift in the reduction peak potential of hemin in the presence of histidine.

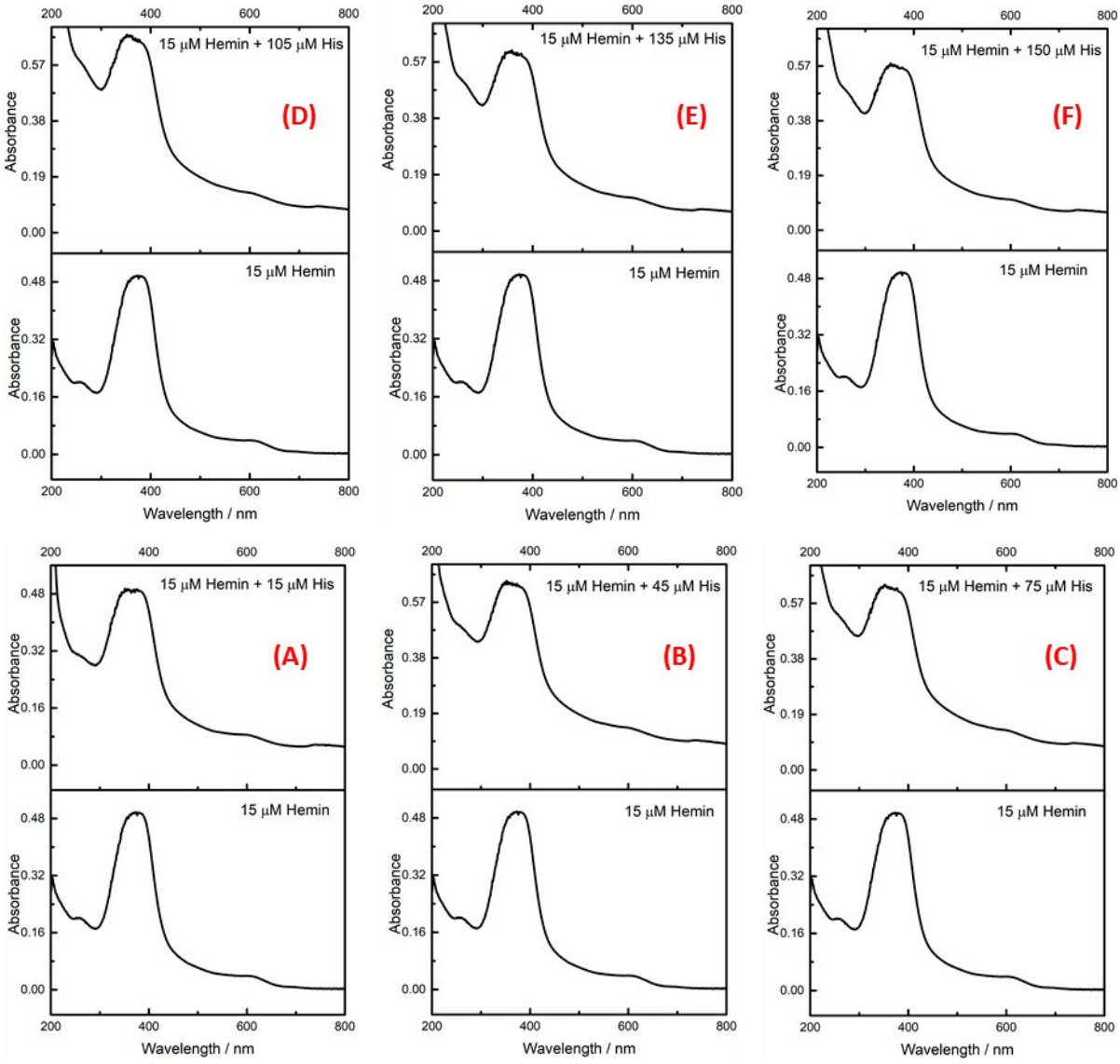

Figure S5: Electronic absorption spectrum of aged samples (after one week of preparation) of hemin (bottom) and hemin : histidine (top) in different stoichiometric ratios : (A) 1:1; (B) 1:3; (C) 1:5; (D) 1:7; (E) 1:9; (F) 1:10. No distinguishable changes in the Soret band are seen. There is an increase in baseline absorbance near the end absorption tail below 300 nm for all samples after aging.

Analysis of fluorescence spectra of hemin – tryptophan system:

There is no change in the electronic absorption signatures of hemin or the amino acids when they are mixed in solution (in different stoichiometries), even after aging the samples for a sufficiently long period of time. This shows that the interaction is not strong enough to allow changes in the Soret absorption bands. Electronic absorption spectra are not susceptible to changes in the presence of weak electronic interactions. However, electronic emission spectra are susceptible to even weak electronic interactions and we were able to show changes in the emission spectra of tryptophan in the presence of hemin (**Figure 6**).

In addition, we also looked at the absorption spectrum of the excited state of the tryptophan – hemin system. We see that the absorption fluorescence spectra show a gradual decrease and red shift of the tryptophan absorption band at 280 nm with increasing concentration of hemin indicating the interaction occurring at the excited state.

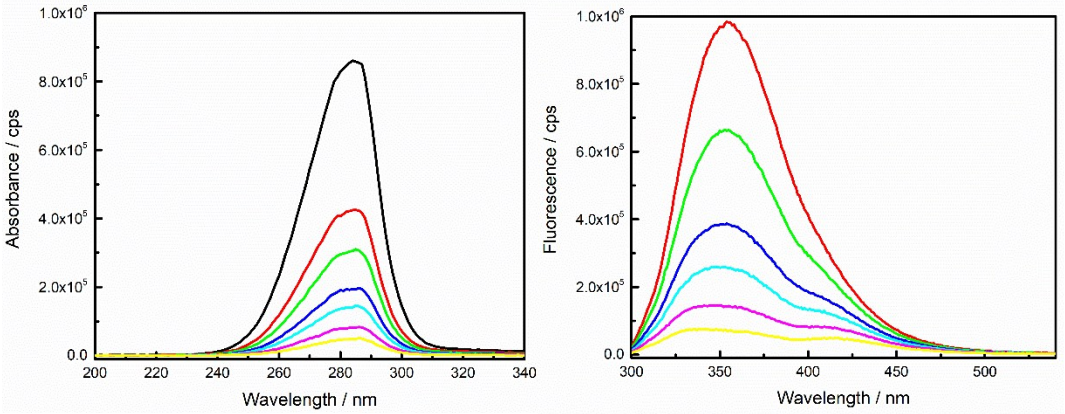

Figure S6: (Left) fluorescence spectra of hemin – tryptophan in the absorbance mode (λ_{em}=350 nm): showing the shift and gradual decay of the tryptophan absorption band at 280 nm (black trace: 5 µM pure tryptophan in solution) in the presence of hemin (red trace: 5µM to yellow trace: 30 µM in steps of 5 µM each). (Right) The corresponding emission spectra (λ_{ex}=280 nm) in the presence of hemin (red trace: 5µM to yellow trace: 30 µM in steps of 5 µM each).

Correction of absorption effects in fluorescence spectra:

Since the tryptophan – hemin emission spectra does not involve self absorption by the emitter, a direct correction methodology for the emission is not available in the literature. To analyse the effect of energy transfer from tryptophan to porphyrin, we superimpose the emission and absorption spectra of tryptophan and hemin respectively (**Figure S7**)

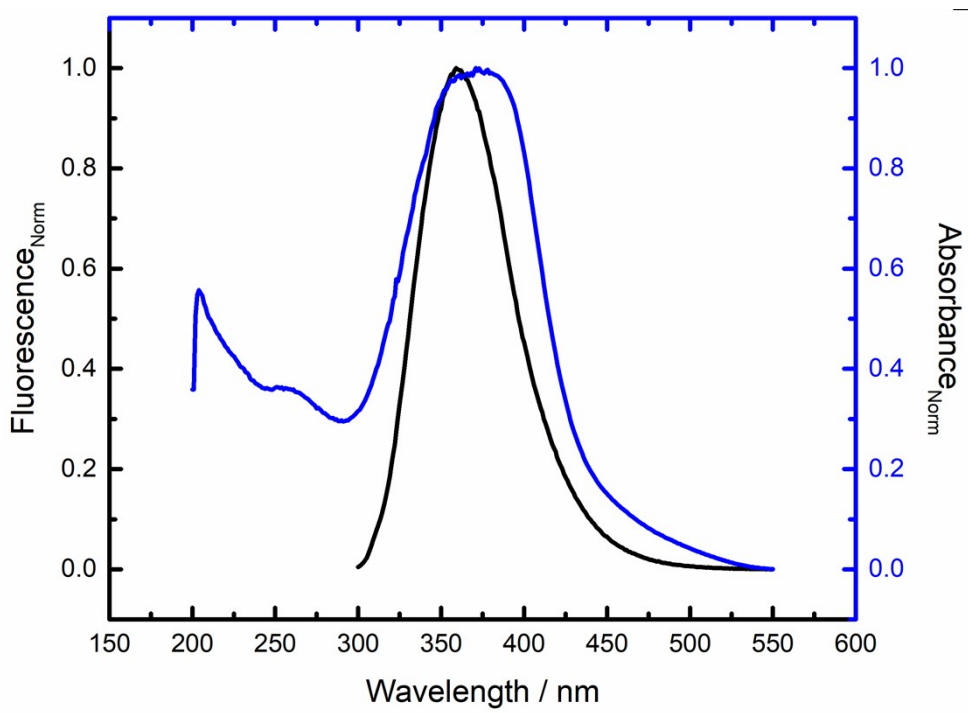

Figure S7: Emission spectrum of tryptophan (black trace; λ_{ex} = 280nm) and absorption spectrum of hemin in solution. The normalized overlap integral between the Soret absorption and tryptophan emission bands is nearly 0.992.

This overlap suggests possibility of an excitation energy transfer phenomenon occurring between tryptophan and hemin. The following characteristics are seen in the system:

- Fluorescence spectrum is modified in the region of spectral overlap.
- Steady state fluorescence intensity is decreased in the region of spectral overlap.
- The fluorescence decay of the donor is not shortened.

Literature shows that these may correspond to a radiative type of energy transfer. The appropriate correction factor is

$$a = \frac{1}{\emptyset_D^0} \int_0^\infty I_D(\lambda)\left[1 - 10^{-\varepsilon_A(\lambda) C_A l}\right] d\lambda$$

- C_A = molar concentration of the acceptor (i.e. Hemin)
- $\emptyset_D^0$ = fluorescence quantum yield of tryptophan in the absence of hemin
- l = thickness of sample
- $I_D(\lambda)$ and ε_A (λ) are the donor fluorescence intensity and the molar absorption coefficient of the acceptor respectively, with normalization condition $\int_0^\infty I_D(\lambda) d\lambda = 1$

Table S1: Coordinates of the complexes studied through Density Functional Theory.

[Fe^{II}(Por)]

Fe	0.00000000	0.32395000	0.00000000
N	-0.92589000	2.08831300	0.00000000
C	-0.35946700	3.33991500	0.00000000
C	-1.36779900	4.36971400	0.00000000
C	-2.57872400	3.73738700	0.00000000
C	-2.31024300	2.32062800	0.00000000
C	-3.27708200	1.34724300	0.00000000
C	-3.00949800	-0.03403200	0.00000000
N	-1.75520900	-0.60301900	0.00000000
C	-1.99137900	-1.98417000	0.00000000
C	-3.42431600	-2.26127600	0.00000000
C	-4.03723400	-1.03131000	0.00000000
H	-5.10352100	-0.81776900	-0.01033000
C	-1.01974200	-2.94913700	0.00000000
C	0.36216500	-2.68324000	0.00000000
N	0.93215200	-1.42867900	0.00000000
C	2.31297300	-1.66418100	0.00000000
C	2.58911000	-3.09663500	0.00000000
C	1.35835700	-3.71007600	0.00000000
H	1.14543100	-4.77648700	0.00000000

C	3.27919000	-0.69256600	0.00000000
C	3.01353100	0.68787600	0.00000000
N	1.76183800	1.25521200	0.00000000
C	1.99357300	2.63921100	0.00000000
C	3.40987100	2.90674100	0.00000000
C	4.04256500	1.69502300	0.00000000
H	5.10934600	1.48658900	0.01057000
H	3.84790800	3.90157200	0.00000000
C	1.02023600	3.60733600	0.00000000
H	1.33280000	4.65161200	0.00000000
H	4.32481800	-1.00041100	0.00000000
H	-1.32637600	-3.99507400	0.00000000
H	-4.32166400	1.65859800	0.00000000
H	-3.57376900	4.17484100	0.00000000
H	-1.15893800	5.43642100	0.00000000
C	3.93659300	-3.72691700	0.00000000
H	4.51905000	-3.42535000	-0.87734600
H	4.51706600	-3.42240200	0.89362300
H	3.85163000	-4.82034000	0.00000000
C	-4.05334200	-3.60939000	0.00000000
H	-3.74720600	-4.19114600	-0.89202300
H	-3.75260800	-4.18980700	0.87910000
H	-5.14681500	-3.52520800	-0.01119500

[Fe^{III}(Por)]

Fe	0.00000000	0.32361100	0.00000000
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C	2.58395700	3.73734200	0.01197900
C	2.29852700	2.32006600	0.01209900
C	3.27999200	1.33381400	0.02031300
C	3.02171200	-0.03645900	0.02036700
N	1.75517400	-0.61165100	0.01272300
C	1.98954700	-1.96873700	0.01598200
C	3.42942100	-2.26351800	0.02574300
C	4.04818000	-1.03724300	0.02843400
H	5.11476900	-0.82701700	0.03524200
C	1.00548500	-2.95142400	0.01120000
C	-0.36386200	-2.69742600	0.00000000
N	-0.94138000	-1.42907300	0.00000000
C	-2.29661500	-1.66352400	-0.01188400
C	-2.59077700	-3.10283700	-0.01101600
C	-1.36412300	-3.72250900	0.00000000
H	-1.15495400	-4.78931300	0.00000000
C	-3.27986100	-0.67692700	-0.02039300
C	-3.02005200	0.68970100	-0.02153700

N	-1.76125900	1.26171800	-0.01399500
C	-1.99396000	2.62646900	-0.01847200
C	-3.41078300	2.91135300	-0.02892300
C	-4.05057200	1.70621600	-0.03082700
H	-5.11806200	1.50234500	-0.03780000
H	-3.83996500	3.90958500	-0.03397300
C	-1.00540700	3.60866000	-0.01331800
H	-1.32353900	4.65134400	-0.01740400
H	-4.32323400	-0.99260400	-0.02663000
H	1.32249300	-3.99441900	0.01479700
H	4.32227600	1.65322600	0.02705800
H	3.58228300	4.16622600	0.01838500
H	1.17488800	5.44392300	0.00000000
C	-3.94121900	-3.71425000	-0.01848800
H	-4.52441700	-3.39793400	0.86187000
H	-4.51210700	-3.40307200	-0.90873700
H	-3.87002100	-4.80795800	-0.01488000
C	4.04078300	-3.61403500	0.03149400
H	3.72283500	-4.18918900	0.91654000
H	3.73189900	-4.19286500	-0.85431100
H	5.13446100	-3.54241800	0.03701500

[Fe^{II}(Por)---His]

Fe	1.38642900	0.16794300	0.29449400
N	1.44094300	1.36336400	1.88529200
C	1.73473700	2.72366800	1.93357700
C	1.49111900	3.25308200	3.24537600
C	1.01675400	2.22097000	4.01018200
C	0.99536200	1.05850400	3.17223300
C	0.65403500	-0.21082600	3.61192300
C	0.75978300	-1.35676000	2.84054600
N	1.16910800	-1.38777300	1.50545500
C	1.17926100	-2.74201100	1.18050200
C	0.80422000	-3.56040900	2.31576500
C	0.53091600	-2.67815300	3.33430300
H	0.20980000	-2.90798400	4.34787200
C	1.46220700	-3.24633400	-0.07683700
C	1.71820200	-2.46625200	-1.19518700
N	1.78839100	-1.07393600	-1.19863000
C	2.00055100	-0.74248100	-2.53700700
C	2.06982100	-1.92549100	-3.36730400
C	1.90504300	-2.98980000	-2.51141300
H	1.90092200	-4.04938000	-2.75713800
C	2.19396100	0.54465900	-3.00496400
C	2.25487400	1.67030600	-2.19656800
N	2.07497600	1.66989000	-0.81565400

C	2.29421400	2.99469900	-0.43622600
C	2.62976600	3.80175100	-1.57183700
C	2.59168500	2.98089300	-2.66843700
H	2.78286400	3.22965300	-3.70931000
H	2.85516800	4.86422100	-1.52605300
C	2.16040700	3.48267600	0.85471600
H	2.36533500	4.54039000	1.02348700
H	2.35354900	0.68496900	-4.07449100
H	1.44378800	-4.32800500	-0.21335000
H	0.32180100	-0.32058200	4.64468700
H	0.71631500	2.23164800	5.05482700
H	1.65585600	4.28931600	3.52991800
C	2.28905500	-1.94924700	-4.84313800
H	1.51186400	-1.37814600	-5.37472800
H	3.26048900	-1.50389200	-5.11067700
H	2.27259900	-2.98071700	-5.21674000
C	0.72596700	-5.05006700	2.33234300
H	-0.02803200	-5.41977800	1.61910100
H	1.68864600	-5.50625600	2.05343900
H	0.45260400	-5.40884100	3.33253200
O	-7.06690700	0.90070100	-1.08604100
C	-5.94110300	0.89729400	-0.62894100
C	-5.17057500	-0.35534000	-0.17078600
O	-5.21007300	2.04400500	-0.46840900
N	-6.00882400	-1.54787800	-0.10436600

H	-4.79166200	-0.14965700	0.84324400
C	-3.94908300	-0.62573100	-1.11220500
H	-5.74718000	2.79891800	-0.79535700
H	-6.47519900	-1.69709300	-1.00509100
H	-6.75813800	-1.40574600	0.57854200
H	-3.80926500	-1.71507500	-1.12108400
H	-4.19306500	-0.32910200	-2.14629400
C	-2.65154600	-0.01295700	-0.69612200
N	-2.45452100	1.34868700	-0.49655200
C	-1.42742500	-0.59508600	-0.45969900
H	-3.20489800	2.04562200	-0.54731700
C	-1.17685600	1.57335300	-0.14991600
N	-0.52087600	0.40093500	-0.12457400
H	-1.14827800	-1.64099400	-0.51132800
H	-0.76368500	2.54989600	0.07399400

[Fe^{II}(Por)---Cys]

C	1.90197500	2.67096500	3.22151500
C	2.17749200	1.74471600	2.16302100
C	0.79173200	2.20711500	3.87897300
H	2.48482100	3.56648700	3.42223200
C	3.19505800	1.90257600	1.23261300
N	1.26412500	0.69275600	2.17579900
C	0.40661900	0.98746600	3.23357300
H	0.27729800	2.64129300	4.73265800
C	3.40920800	1.05965600	0.15537200
H	3.84833000	2.76823300	1.34589400
C	-0.64379400	0.18095000	3.65027200
N	2.65108100	-0.07765200	-0.12724400
C	4.43010800	1.27171000	-0.84683300
C	-0.93357600	-1.06618600	3.11093700
H	-1.24306400	0.52214700	4.49497500
C	3.19200100	-0.56787300	-1.31611200
C	4.27190700	0.25413500	-1.76069900
C	5.42675400	2.38237100	-0.86142300
N	-0.27762700	-1.63397700	2.02484000
C	-1.92003100	-1.96307200	3.63992400
C	2.78064700	-1.72751400	-1.95996600
H	4.85214800	0.07344500	-2.66285300
H	4.93095300	3.36492100	-0.90745000

H	6.05018100	2.37494700	0.04636100
H	6.08863700	2.29386200	-1.73203200
C	-0.87486400	-2.88764900	1.87059200
C	-1.87193000	-3.10166100	2.87787300
H	-2.55926100	-1.74344900	4.49147500
C	1.81163300	-2.58844300	-1.47692400
H	3.28738700	-1.99166900	-2.88855500
C	-0.58958900	-3.78271300	0.85327800
H	-2.46615400	-4.00689200	2.97316300
N	1.09094600	-2.38970400	-0.29935600
C	1.47356900	-3.85445700	-2.09366400
C	0.30884300	-3.53588100	-0.17499100
H	-1.12881700	-4.73039900	0.84143000
C	0.54539400	-4.43506500	-1.26190400
C	2.04459600	-4.39325600	-3.36300800
H	0.05534700	-5.39921600	-1.37869400
H	1.85518100	-3.71429600	-4.20917900
H	3.13577600	-4.52438300	-3.28888900
H	1.59949200	-5.36783200	-3.59952800
Fe	1.06959700	-0.76811700	0.84979000
H	0.89751000	1.31653700	-1.95482900
C	0.16318200	1.80216400	-1.29755000
C	-0.77171900	2.67934000	-2.15165200
H	0.67481100	2.39022600	-0.52383900
S	-0.68374800	0.35378200	-0.51574100

N	0.01138600	3.23161300	-3.25903100
H	-1.58316800	2.07544500	-2.58179600
C	-1.38299800	3.81170700	-1.30546900
S	-2.11444200	1.27752700	0.70677100
H	0.64602600	3.97263100	-2.95070500
H	-0.59387100	3.60530500	-3.99242600
O	-0.82639400	4.35001300	-0.36192400
O	-2.57563700	4.20739800	-1.80668500
C	-3.57157700	0.15007900	0.52529900
H	-2.87609300	4.98938500	-1.29328000
C	-4.40860700	0.30203100	-0.77415000
H	-4.18203200	0.45702400	1.38838800
H	-3.26032300	-0.89258800	0.67706800
N	-5.73724500	-0.28590100	-0.63380800
H	-4.51769800	1.36458900	-1.02607900
C	-3.73850600	-0.43489400	-1.94159600
H	-6.31010000	0.23454500	0.03344100
H	-5.68942700	-1.26521500	-0.34047000
O	-3.49960100	-1.62958400	-1.93264300
O	-3.47237300	0.38313700	-2.98571100
H	-3.08013100	-0.16254000	-3.70400600

[Fe^{II}(Por)---Trp]

C	4.04339300	2.28451400	-2.37662400
C	3.51517200	1.21549400	-1.57832500
C	3.41857900	3.43315100	-1.96661900
H	4.80758000	2.16402500	-3.14048100
C	3.97561000	-0.10207000	-1.63881100
N	2.55673000	1.68087200	-0.69501600
C	2.50859800	3.06242500	-0.92131300
H	3.56195300	4.44917000	-2.32581900
C	3.51512200	-1.12329300	-0.83892300
H	4.76496600	-0.32448300	-2.35715900
C	1.74587800	3.95843300	-0.19920400
N	2.47975400	-1.00257500	0.09839100
C	4.01701800	-2.48335000	-0.88378600
C	0.88633500	3.60025000	0.83950900
H	1.82206600	5.01590900	-0.45385000
C	2.31937000	-2.27974600	0.60382100
C	3.25924700	-3.18825800	0.02135000
C	5.12176600	-2.98148700	-1.75378100
N	0.64445600	2.30340000	1.26061300
C	0.09069000	4.53912900	1.58015800
C	1.34660600	-2.66416200	1.53350100
H	3.32788300	-4.24504300	0.26943500
H	4.88779200	-2.83830700	-2.82060500

H	6.06237800	-2.44506600	-1.55279300
H	5.29345000	-4.05153300	-1.58264300
C	-0.34059200	2.42958500	2.24260200
C	-0.67414300	3.81053600	2.45176000
H	0.11386300	5.61615500	1.43425500
C	0.43756500	-1.80497500	2.10917500
H	1.31873900	-3.71546700	1.82098600
C	-0.96253500	1.37439400	2.88157800
H	-1.41066700	4.16463200	3.16856100
N	0.38441000	-0.42740300	1.87063600
C	-0.56679800	-2.20317300	3.07740700
C	-0.62462700	0.03108500	2.69899300
H	-1.75270000	1.60452300	3.59690200
C	-1.22322900	-1.04604200	3.42703000
C	-0.80249200	-3.58901500	3.57647200
H	-2.03716400	-0.93070600	4.13930700
H	-1.06990900	-4.27118500	2.75437600
H	0.09892800	-3.99926200	4.05863200
H	-1.61813500	-3.60001100	4.31023300
Fe	1.41073600	0.61173100	0.53318800
H	-3.75464600	-2.37604800	-0.12115100
C	-2.73341900	-2.34348100	-0.50392200
C	-2.06383200	-1.11733000	-0.66610300
C	-2.07306300	-3.52112200	-0.87549900
C	-2.47169500	0.26070700	-0.47808300

C	-0.73636900	-1.11045300	-1.16117700
C	-0.77738600	-3.48228200	-1.41026400
H	-2.57869700	-4.48114500	-0.76253500
C	-3.81655400	0.75972400	-0.05329700
C	-1.39402100	1.04603600	-0.84146000
N	-0.28654000	0.25028200	-1.16997100
C	-0.08136100	-2.26451500	-1.56155700
H	-0.29107900	-4.40891100	-1.71821800
C	-4.77113700	1.14557000	-1.22915200
H	-3.70767500	1.66939200	0.55336700
H	-4.32437000	0.00000000	0.56551100
H	-1.31301500	2.12827100	-0.88442700
H	0.32468000	0.56556700	-1.92948700
H	0.92302700	-2.24567500	-1.98480000
N	-5.99556000	1.71364000	-0.67264500
H	-4.27887400	1.90895100	-1.84776600
C	-5.03625200	-0.08948900	-2.10371400
H	-6.56520400	0.97393300	-0.24947800
H	-6.55832500	2.14088400	-1.41265500
O	-5.79367600	-0.99728100	-1.79955000
O	-4.32976800	-0.06028400	-3.26140300
H	-4.52984100	-0.88518900	-3.75746400

[Fe^{III}(Por)---His]

Fe	1.37896200	0.16962800	0.28728100
N	1.48421600	1.49730600	1.76246100
C	1.79990300	2.84636300	1.68510500
C	1.60773400	3.50042800	2.95720500
C	1.14313100	2.55447700	3.82145700
C	1.07046000	1.31689300	3.08523600
C	0.68822200	0.11246700	3.64074400
C	0.71751600	-1.09989500	2.96022000
N	1.09929600	-1.25970700	1.62835100
C	1.03128200	-2.63260600	1.41702900
C	0.61918100	-3.33706400	2.63044600
C	0.41879000	-2.36005400	3.57098400
H	0.10224000	-2.48207900	4.60397300
C	1.30630100	-3.26384000	0.22107000
C	1.63426400	-2.59787500	-0.95537300
N	1.76144800	-1.21366400	-1.08030700
C	2.04024900	-1.01738600	-2.42814900
C	2.10424800	-2.28733700	-3.14690600
C	1.85517900	-3.25509900	-2.20680300
H	1.81675700	-4.33231400	-2.34964600
C	2.27306400	0.20936100	-3.01694400
C	2.31587500	1.40988700	-2.31859600
N	2.10031500	1.54570900	-0.95478200

C	2.32201200	2.90123900	-0.70410100
C	2.68204900	3.59614500	-1.91516700
C	2.66930200	2.67268500	-2.91831900
H	2.88619700	2.81184000	-3.97413700
H	2.91092300	4.65732500	-1.96898100
C	2.20790800	3.50808800	0.53263600
H	2.42421000	4.57399500	0.60465900
H	2.47601500	0.23992600	-4.08731900
H	1.23793100	-4.35096700	0.18158200
H	0.37812400	0.10441200	4.68571700
H	0.87526400	2.66138300	4.86933500
H	1.80012000	4.55457800	3.13931800
C	2.38901600	-2.45005700	-4.59663400
H	1.65213100	-1.90806100	-5.21093100
H	3.38145600	-2.04529000	-4.85342700
H	2.36383900	-3.50944600	-4.87849400
C	0.46033600	-4.80863000	2.76696400
H	-0.29695800	-5.19342000	2.06490500
H	1.40308000	-5.33348100	2.54283600
H	0.15143900	-5.07008900	3.78610100
O	-7.06816200	0.90296400	-1.15058400
C	-5.94462800	0.92477100	-0.69800900
C	-5.14948000	-0.31813700	-0.22198800
O	-5.20610700	2.06073400	-0.56010300
N	-5.97466000	-1.48584000	-0.13610100

H	-4.75848700	-0.09774800	0.78182900
C	-3.93124500	-0.57283300	-1.20181200
H	-5.73533300	2.81767200	-0.89636800
H	-6.55421900	-1.68376100	-0.95261900
H	-6.47671400	-1.61464900	0.74076400
H	-3.79371500	-1.66008600	-1.25139100
H	-4.18987500	-0.23424800	-2.21778700
C	-2.64210900	0.02846000	-0.76370300
N	-2.42328500	1.39157600	-0.60131300
C	-1.43244300	-0.57104200	-0.47932100
H	-3.15477500	2.10386700	-0.68941900
C	-1.15164900	1.60272600	-0.23641300
N	-0.51584500	0.41658300	-0.16253800
H	-1.17891700	-1.62444400	-0.49661700
H	-0.72681800	2.57865100	-0.03321900

[Fe^{III}(Por)---Cys]

C	-1.45685500	-2.25242100	3.73266900
C	-1.86185600	-1.60485400	2.50935400
C	-0.49846000	-1.46326300	4.29811700
H	-1.86697100	-3.19089500	4.09634800
C	-2.83394100	-2.12105800	1.64368100
N	-1.17730600	-0.42371700	2.31771700
C	-0.32834100	-0.32483900	3.42689700
H	0.04804000	-1.61298400	5.22558400
C	-3.20666300	-1.52627300	0.46325200
H	-3.31558200	-3.05606400	1.92937800
C	0.49707400	0.74214600	3.70049100
N	-2.66784000	-0.33999700	-0.04632400
C	-4.21933700	-2.06928600	-0.44000100
C	0.58841100	1.88772000	2.89878100
H	1.09189000	0.71067600	4.61327300
C	-3.32408800	-0.15568800	-1.25212600
C	-4.27099100	-1.19889400	-1.50052000
C	-5.00377800	-3.31287200	-0.22130000
N	-0.05990600	2.06544700	1.69653300
C	1.38798500	3.03936400	3.24046800
C	-3.11254800	0.91642600	-2.13091200
H	-4.90318800	-1.25786200	-2.38303400
H	-4.34305300	-4.19324200	-0.16463800

H	-5.56464200	-3.26978400	0.72589400
H	-5.71602200	-3.46932900	-1.04027600
C	0.35141300	3.33518200	1.25987900
C	1.23747400	3.93862600	2.22575800
H	1.98398100	3.12762200	4.14508500
C	-2.25483500	1.95722700	-1.88053200
H	-3.68333100	0.92186700	-3.05939000
C	-0.01132900	3.92023400	0.07173000
H	1.68280900	4.92427900	2.11814400
N	-1.48486600	2.09937700	-0.72054400
C	-2.08010100	3.10650200	-2.76766600
C	-0.86315800	3.32544600	-0.87088700
H	0.38826700	4.90771800	-0.15914700
C	-1.21639900	3.94710900	-2.11196100
C	-2.72382600	3.28903400	-4.09529400
H	-0.84706700	4.91518100	-2.44167300
H	-2.42634300	2.48880800	-4.79233600
H	-3.82211000	3.25459900	-4.01645400
H	-2.43765400	4.25286600	-4.53292100
Fe	-1.23319500	0.77772300	0.73885900
H	-0.56873000	-1.41210100	-2.00075900
C	0.15866900	-1.81586400	-1.28320800
C	1.24216900	-2.61055100	-2.04942700
H	-0.34561400	-2.45325500	-0.54476100
S	0.80441200	-0.28944000	-0.46894100

N	0.63348000	-3.21824700	-3.21005100
H	2.04829200	-1.94889000	-2.39555300
C	1.85558400	-3.70037600	-1.12837700
S	2.17197100	-1.06103900	0.91425300
H	0.00000000	-3.99047100	-3.01838900
H	1.28000600	-3.43596200	-3.96699000
O	1.25069400	-4.25625000	-0.22904900
O	3.10715700	-4.01069600	-1.52045700
C	3.61377900	0.07743600	0.77867700
H	3.42444400	-4.76392400	-0.97437000
C	4.55396500	-0.14881900	-0.45445100
H	4.16231300	-0.16701900	1.70090900
H	3.29148600	1.12584100	0.82755200
N	5.86614100	0.40009300	-0.21218300
H	4.64842800	-1.22119800	-0.66381200
C	3.98910800	0.58153000	-1.68775900
H	6.45563000	-0.15642400	0.40639400
H	5.88068300	1.39265600	0.02822000
O	3.77232200	1.77844200	-1.71194400
O	3.79549100	-0.25484000	-2.73017100
H	3.47262800	0.27667600	-3.49265700

[Fe^{III}(Por)---Trp]

H	-5.00054500	-2.70106600	-0.14514900
C	-4.00691100	-2.55583800	-0.57210600
C	-3.35764000	-1.30837100	-0.49091800
C	-3.35125900	-3.61293300	-1.21898300
C	-3.70976000	-0.04150900	0.09288600
C	-2.05995400	-1.16699600	-1.05876700
C	-2.07374500	-3.44148700	-1.77040100
H	-3.84198400	-4.58414000	-1.29290400
C	-4.95165300	0.34733400	0.77556600
C	-2.60656500	0.82652800	-0.16125800
N	-1.65209800	0.15837300	-0.82721300
C	-1.39777300	-2.20379700	-1.69589300
H	-1.58400400	-4.28019500	-2.26719600
C	-6.05550600	1.05055100	-0.20411100
H	-4.75911100	1.10296200	1.54864300
H	-5.45383000	-0.51722200	1.22968200
H	-2.48228400	1.87055500	0.11304500
H	-0.75357000	0.55323200	-1.10568500
H	-0.40099500	-2.07973900	-2.11990200
N	-7.25010700	1.40641100	0.48649600
H	-5.58740400	1.94610200	-0.63005800
C	-6.39807600	0.05127500	-1.30912200
H	-7.79943800	0.61497200	0.82648100

H	-7.14529100	2.13696100	1.18951400
O	-7.17920800	-0.87255000	-1.16598700
O	-5.70450600	0.30132600	-2.43970500
H	-5.92334200	-0.39914600	-3.09410700
H	1.97175700	5.43207100	-1.79474200
C	2.16472500	4.36281800	-1.76549400
C	1.93080200	3.52198600	-0.62359900
C	2.64078100	3.55430500	-2.76411100
N	2.28104800	2.21766800	-0.89240000
C	1.33438200	3.96647900	0.56769600
C	2.73731300	2.22777700	-2.21612300
H	2.92111500	3.82433100	-3.77904900
Fe	2.18374600	0.65942000	0.33048300
C	0.94351600	3.13239200	1.59046300
H	1.10408700	5.02874500	0.65367100
C	3.30270200	1.15105400	-2.86175600
N	1.15388000	1.74622000	1.62246800
N	2.06709400	-0.88729800	1.54080100
N	3.23384900	-0.41025300	-0.94753900
C	0.15990900	3.53902400	2.72555800
C	3.57465600	-0.08020500	-2.24410200
H	3.63097900	1.28250000	-3.89305700
C	0.49195300	1.30891500	2.74644000
C	2.75749000	-2.07818100	1.44891000
C	1.27692200	-1.01560400	2.69277600

C	3.79925900	-1.67494200	-0.73691900
C	-0.14234000	2.40219100	3.42896500
H	-0.12974600	4.56474200	2.93945700
C	4.34076400	-1.12117000	-2.85565700
C	0.51402100	-0.01016900	3.23236600
C	3.61047000	-2.43577400	0.39050800
C	2.41807900	-2.95522600	2.52515300
C	1.47148100	-2.32202300	3.30064700
C	4.51920300	-2.11682300	-1.92071200
H	-0.72762000	2.30544200	4.33981500
H	4.72009600	-1.08966500	-3.87444000
H	-0.05425200	-0.21847300	4.13901900
H	4.09112900	-3.41254500	0.44460300
H	2.83554100	-3.94958800	2.66577400
C	0.78870700	-2.82936200	4.52273000
C	5.26841400	-3.39537300	-2.06480100
H	1.07499900	-2.24013600	5.40916700
H	-0.30608800	-2.76082300	4.42920100
H	1.05750000	-3.87640900	4.70859000
H	6.04123900	-3.49632000	-1.28684000
H	4.59605300	-4.26304000	-1.96770100
H	5.75546500	-3.44817900	-3.04614300

[Fe^{II}(Por)---His---Trp]

Fe	-1.44041000	-0.93834400	0.12031200
N	0.04573300	0.36838400	0.43897000
C	0.98193000	0.83889700	-0.47368700
C	1.78651300	1.87582600	0.11278800
C	1.32995400	2.05471100	1.39801200
C	0.26209500	1.11363500	1.59379700
C	-0.41756900	0.94631700	2.79224900
C	-1.37163400	-0.03378500	3.02378500
N	-1.83102600	-0.94566900	2.07971900
C	-2.73364700	-1.74870100	2.76821700
C	-2.83415900	-1.34990900	4.16000500
C	-1.98721100	-0.27030900	4.29772000
H	-1.78643500	0.31340700	5.19685500
C	-3.47104800	-2.77575200	2.20170000
C	-3.43130600	-3.12824300	0.85875500
N	-2.63430200	-2.52354800	-0.10520000
C	-2.95701300	-3.17074800	-1.29454800
C	-3.96946900	-4.18629400	-1.07856700
C	-4.24503300	-4.15358700	0.27301100
H	-4.95136200	-4.77232600	0.82772600
C	-2.36073100	-2.91880200	-2.51889800
C	-1.31305800	-2.02919000	-2.71861600
N	-0.74907100	-1.22109000	-1.73779800

C	0.28587700	-0.54801600	-2.37719200
C	0.37229700	-0.94220900	-3.75632100
C	-0.63126000	-1.85827500	-3.97150100
H	-0.88897900	-2.38434400	-4.89059800
H	1.10661800	-0.55627900	-4.46319200
C	1.10790100	0.40268800	-1.78586700
H	1.88328900	0.85912900	-2.40178700
H	-2.70253600	-3.49080200	-3.38269100
H	-4.14728500	-3.33776400	2.84726400
H	-0.14862200	1.59993600	3.62345100
H	1.68523300	2.75090500	2.15757100
H	2.59258500	2.39676100	-0.40352200
C	-4.55777000	-5.07869700	-2.12864700
H	-5.01899000	-4.49490600	-2.94424700
H	-3.78745800	-5.72453600	-2.58611500
H	-5.33144400	-5.72869200	-1.69362700
C	-3.69715700	-1.99878400	5.19886900
H	-4.76605200	-1.94869300	4.92585900
H	-3.44370100	-3.06608700	5.32432100
H	-3.57111200	-1.50142900	6.17207800
O	-7.52485000	5.10566600	-1.44697800
C	-6.53370800	4.49489400	-1.07766800
C	-6.49714600	3.49357700	0.09373800
O	-5.31432400	4.63645500	-1.68833800
N	-7.71850000	3.53126800	0.89992100

H	-5.64524200	3.77015400	0.74089600
C	-6.26716000	2.03407600	-0.43320100
H	-5.43237900	5.25953100	-2.44039500
H	-8.52423200	3.45255700	0.26512600
H	-7.80779500	4.46795700	1.31196400
H	-6.77958300	1.36997400	0.28080500
H	-6.77197300	1.90155100	-1.40855000
C	-4.84257700	1.58457800	-0.52057100
N	-3.85151200	2.25704500	-1.22239500
C	-4.21752300	0.47393800	0.00000000
H	-3.99869200	3.15651400	-1.68788100
C	-2.69020700	1.57815100	-1.11005600
N	-2.88267200	0.48023600	-0.37161000
H	-4.64020000	-0.31739000	0.61340500
H	-1.75437400	1.89658200	-1.55647800
H	6.30395600	-0.14534200	3.15292300
C	6.05222300	-0.17983400	2.09382900
C	6.52702600	0.63446800	1.03650300
N	5.16377300	-1.08800700	1.61296400
C	7.52898500	1.73491500	1.17491300
C	5.86873400	0.16282800	-0.15308600
C	5.01294600	-0.91852300	0.23212400
H	4.67943700	-1.78510000	2.17776300
C	9.02381600	1.28442100	1.00118900
H	7.46581100	2.18612800	2.17820700

H	7.33407100	2.52956600	0.43315400
C	5.91127900	0.55263400	-1.51443200
C	4.21547000	-1.61163700	-0.67768100
N	9.89501300	2.41115200	1.32404900
H	9.23512400	0.45593100	1.69623300
C	9.23068500	0.79161600	-0.44123500
C	5.11651500	-0.14053700	-2.44098800
H	6.56613600	1.36661500	-1.83861100
H	3.57153600	-2.43945800	-0.36829500
C	4.28310700	-1.20310200	-2.03183500
H	9.88441000	3.07976300	0.54388900
H	10.86335700	2.09066600	1.42955300
O	9.22349500	1.53149700	-1.42147900
O	9.43020100	-0.54632200	-0.50822700
H	5.14636700	0.14311100	-3.49670100
H	3.68200800	-1.73543100	-2.77438700
H	9.54513000	-0.77138900	-1.46000600