

# Spectroscopic Studies on Tetra (sulphonaphthyl) Porphine Iron (II) Solutions with Pyridine Substituents as a Ligands

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## ABSTRACT

Electronic absorption spectra at 15 °C, Stability constants and  $\Delta H$ ,  $\Delta G$ ,  $\Delta S$  of tetra (sulphonaphthyl) porphine iron (II) solutions with pyridine substituents as a ligands are reported and discussed. Evidence for only one iron (II) electronic environments , a low spin is found, and two as axial ligands can bind to four coordinate iron (II) porphine in one step from spectrophotometric titrations of Fe (II)TNPS with amines was observed. The presence of the naphthyl substituents on the methane carbons stabilizes the low spin iron (II) TNPS (L)<sub>2</sub> species, the pyridine substituents also are shown to play an important role and lowering the values of  $k_{eq}$  and ( $\Delta S$ ) as increasing the order of  $\delta$ - donor , addition to that, the  $\pi$ - electron acceptor (low  $pK_a$ ) are shown to have larger values for their  $k_{eq}$  and ( $\Delta H$ ) . Steric effects are also found lowering the values of  $k_{eq}$  for such ligand as 2- methyl pyridine.

## Introduction

The studying of the chemistry of iron (II) porphyrins in aqueous solution is of interest to chemists and biochemists for many reasons, three of which are:

1. Iron porphyrins, in particular protoporphyrin IX iron is the prosthetic group of a large number of metalloproteins [1], hence water soluble haems are useful in modeling its chemistry.
2. Because many natural products (e.g. chlorophylls, cytochromes and vitamin B12) contain these molecules [2].
3. Iron porphyrins because of their role as nature's catalysis [1] may well have industrial applications. Many workers [2-4] have studied the binding of axial ligands to four coordinate haem centers, they found no evidence for step –wise addition of the ligand and the formation of an octahedral complex was observed. They [5,6] found that the log  $B_2$  increased (its binding constant) with increasing basicity of the pyridine ligand , where,  
 $K_2 \gg K_1$ ,  $B_2 = K_2 \cdot K_1$



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A condition where  $\delta$ -effects predominate this for diacetyl deuterio porphyrin. Brault et al [7] have found slightly higher affinities of Fe (II) TPP for imidazole when compared with that pyridine, they found the binding for both ligands occurs in two steps (eq.2)



Other workers [8] have studied the binding of nitrogen ligands to the Fe(II)PP IX in aqueous solvent at high PH , they found the stability constant for Fe(II)PP IX complexes in alkali media is less than that for Fe(II)TPP complexes (e.g. imidazole, pyridine ) in Organic solvents .

In this work was studying the stability constant of pyridine substituent ligands to water soluble haem TNPS Fe(II) and to compare them with others soluble haem such as PP1X Fe(II), TPPS Fe(II) [9].

## Experimental

Tetra (solphonaphthyl) porphine iron (II) was prepared by reducing  $\mu$ -oxo bis tetra (solphonaphthyl) porphine iron (III),  $O(TNPSFe(III))_2$  in solution with

sodium dithionite. O(TNPS Fe(III))<sub>2</sub> was prepared as previously described[10].

The electronic absorption spectra were recorded on solutions that had been freshly prepared in a three-necked flask. One neck allowed N<sub>2</sub> in and out, another the samples to be removed, the third was used for a pH electrode .50 ml of TNPS Fe(III), solutions of appropriate concentration were used .The concentration of TNPS Fe(II)solution was 5X10<sup>-5</sup> M prepared at PH 12.8 in buffer of KCl +NaOH 0.1 M and adjusted to give a PH around 12.8, 3ml quartz cells were used, The spectra were obtained using 1 cm path length cells containing 2.5 ml of solution . The quartz cells are sealed under an N<sub>2</sub> atmosphere, and measured using a lambda 5G spectrophotometer. Spectrophotometric titrations on the addition of the ligand to the Fe (II)TNPS solutions were carried out ,( using an air protected syringe ) , in a covette closed by a Teflon cap , a minimum of 2 minutes of vigorous shaking was necessary to ensure establishment of the equilibrium before the spectrum was taken .

Every titration was repeated three times to get the average of the stability constant, and studied at different wave lengths and temperatures.

## Materials

All the nitrogenous ligands were purchased from Aldrich. These used were 4-methyl pyridine (4-mpy), 3,4-di methyl pyridine(3,4-dimpy),3- amino methyl pyridine (3-ampy),2-methyl pyridine (2-mpy).

## Results and Discussion

### 1- Visible spectra

On addition of excess of the nitrogen ligands to the solutions of TNPSFe (II), a dramatic change in the spectra results due to formation of complexes at high PHS' and gives three bands in their spectra, they are summarized in Table -1.The spectra of Fe (II) TNPS solutions with these strong ligands that are characterized by a set of three bands, α, β and γ bands and appear respectively from the longer to shorter wavelength. The visible absorption spectrum of these complexes are sharp and its assigned of low spin complexes ,this sharpening results from the change of the polymer to monomer breakdown of O-(Fe(II)TNPS)<sub>2</sub> or from high

spin to low spin iron(II)complexes.[13-15]. In this work it was observed that the soret band and other visible bands of iron (II) sulphonated and non –sulphonated porphyrins were shifted from the longer to the shorter wavelength upon addition of the ligands. It has been reported that the shift of the soret band of Fe(II)PP1X- amines to the longer wave length as a result of the π-electron density of the metal t<sub>2g</sub> orbitals moving to wards the periphery of the planar porphyrin nucleus but with unsaturated ligands such those in this work, the metal t<sub>2g</sub> orbitals (dxz,dyz) are involved in π-bonding with these ligands and this causes a decrease in the overlapping of metal t<sub>2g</sub> orbital with π-orbitals of the porphyrin ring via the nitrogen atoms, this causes a shift of the soret band to shorter wave length[11,16].

**Table-1** .Electronic absorption of Fe (II) TNPS with nitrogen ligands at 15 °C in aqueous solutions (PH=12.8)

| No. | Compounds               | γ(nm) | β(nm) | α(nm) |
|-----|-------------------------|-------|-------|-------|
| 1   | Fe (II) TNPS            | 444   | 569   | 608   |
| 2   | Fe (II) TNPS +py[11]    | 426   | 532   | 562   |
| 3   | Fe (II) TPPS +py[11]    | 424   | 529   | 562   |
| 4   | Fe (II) TNPS +3-ampy    | 426   | 531   | 563   |
| 5   | Fe (II) TNPS +4-mpy     | 427   | 530   | 561   |
| 6   | Fe (II) TNPS +3,4-dimpy | 427   | 531   | 562   |
| 7   | Fe (II) TNPS +2-mpy     | 425   | 530   | 560   |
| 8   | Fe (II) TPPS [12]       | 439   | 568   | 608   |

### 2- Spectrophotometric titrations

The reaction of nitrogenous ligands with Fe(II) TNPS solutions at high PH in aqueous solvent makes spectral changes .Well defined isosbestic points are observed, typical spectrophotometric titration are presented in figures 1,2.These reactions are rapid and quickly reach a point at which no further change in absorbance occurs, suggesting strong binding constants. These changes were similar for all these nitrogen ligands with different iron (II) porphyrin complexes [14] see table 2.

**Table -2:** Shows the spectrophotometric titration analysis of figures 1,2.

| No. | Compounds              | Log keqM <sup>-2</sup><br>± 0.05 | Slope<br>n±0.1 | T °C |
|-----|------------------------|----------------------------------|----------------|------|
| 1   | Fe (II) TPPS +py[9]    | 6.39                             | 1.91           | 15   |
|     |                        | 6.6                              | 1.82           | 30   |
| 2   | Fe (II) TNPS +py[9]    | 6.5                              | 1.66           | 15   |
|     |                        | 6.16                             | 1.80           | 15   |
| 3   | Fe (II) TNPS +4-mpy    | 6.0                              | 1.83           | 30   |
|     |                        | 5.9                              | 1.91           | 15   |
| 4   | Fe (II) TNPS +3,4dimpy | 5.5                              | 1.79           | 30   |
|     |                        | 5.8                              | 1.97           | 15   |
| 5   | Fe (II) TNPS +3-       | 5.8                              | 1.97           | 15   |

|   |                     |      |      |    |
|---|---------------------|------|------|----|
|   | ampy                | 5.6  | 1.92 | 30 |
| 6 | Fe (II) TNPS +2-mpy | 4.0  | 1.85 | 15 |
|   |                     | 3.85 | 1.79 | 30 |

Hill plots [22] were constructed to analysis these data, to measure the  $K_{eq}$  at different wave length and temperature ranges (15-30) °C see figure 3 and (eq. 3).

$$\text{Log} = A - A_0/A_\infty - A = \log K + n \log (L) \dots(\text{eq.3})$$

$\Delta H, \Delta G$  and  $\Delta S$  were calculated for these reactions from (eq.4- eq.7) and are presented in table-3. The Fe (II) TNPS bind two ligand molecules from slope ( $n > 1.5$ ) and the resulting complexes are low spin. Stability constants of Fe (II) TNPS with these pyridine substituents at similar temperature slightly higher values than for the Fe (II) TPPS and Fe (II) PP1X with the same ligands [8]. When plots of  $\log (A - A_0) / (A_\infty - A)$  vs.  $\log (L)$  [21] is the absorbance at the wave length of study of mixed species.  $A_0$  is the absorbance of Fe (II) TNPS in the absence of L and  $A_\infty$  is the absorbance in the presence of a large excess of L, were constructed, straight lines were obtained, see figure 3.

$$\Delta H = 19.14 T_1 T_2 (\log K_2 - \log K_1) / (T_2 - T_1) \dots(\text{eq.4})$$

**Or Table -3.** Thermodynamic parameters for amines binding in aqueous solutions of Fe (II) TNPS complexes.

| No. | Ligands  | $\Delta H(\text{Kcal/mol})$ | $\Delta G(\text{Kcal/mol})$<br>(288 k) | $\Delta S(\text{cal/mol})$<br>(288 k) |
|-----|----------|-----------------------------|--|---------------------------------------|
| 1   | Py       | -11.4±2.8*                  | -8.5±0.3                               | -10±5                                 |
| 2   | 4-mpy    | -9.7±2.9*                   | -8.2±0.3                               | -5.4±3                                |
|     |          | -7.98±2.0                   | -8.3±0.3                               | 1.38±0.06                             |
| 3   | 3-ampy   | -20.8±2.0*                  | -8.2±0.3                               | -44±8                                 |
|     |          | -10.64±1.8                  | -7.77±0.3                              | -9.94±0.47                            |
| 4   | 3,4dimpy | -10.5±2.4*                  | -8.7±0.3                               | -6.3±4                                |
|     |          | -5.32±1.2                   | -7.64±0.2                              | 8.05±0.5                              |
| 5   | 2-mpy    | -0.77±0.15*                 | -2.1±0.1                               | 5±1.0                                 |
|     |          | -3.99±0.16                  | -5.27±0.1                              | 4.44±0.6                              |

\* Fe (II)TPPS[9].

$$\Delta H = 4.576 T_1 T_2 (\log K_2 - \log K_1) / (T_2 - T_1) \dots(\text{eq.5})$$

$$\Delta G = 4.576 T \log K_{eq} \dots(\text{eq.6})$$

$$\Delta S = \Delta H - \Delta G/T \dots(\text{eq.7})$$

$\text{Log } B_2 (\log k_{eq})$  is estimated from the intercept of the portion of the graph, which as slope of 2(or more/less). The value of (n) is the slope which is known as the Hill constant [22], this value if less or more than two results from water solvent effect[17-20] (polar solvent)

it did not greatly affect the  $\log K_{eq}$  values. The structure of each ligand in this work and their pka are listed in table 4. As the value of pka only measures the  $\delta$ -donor ability of base ligand.

The variation in  $\Delta H$  from -3.99 to -10.64 kcal/mole reflects an increase in the Fe(II)-nitrogen ligand bond energy with increase  $\pi$ -accepting ability of the ligand, and 3-amino methyl pyridine which although  $\pi$ -accepting would be weaker than pyridine ( $\Delta H = -11.4$ ). The low value of  $\Delta H$  for 2-methyl pyridine (-3.99 kcal/mol) is reflects the weaker ligand bond to the iron, but lower value was found with Fe(II) TPPS  $\Delta H(-0.77$  kcal/mol)[9], that may be due to solvent interaction[12] as OH<sup>-</sup>, H<sub>2</sub>O act as axial ligands at these pHs .

It is clear from table 4 that the order found for increasing stability constant of the pyridine is directly related to the pka and when the order of  $\pi$ -accepter increase the stability constants also increases , the poor  $\delta$ -donor it might be expected to be a good  $\pi$ - accepter and will approach the haem closely.

### Conclusion

In this work the stability characteristics of numbers of pyridine substituents axial ligands were studied with Fe(II) TNPS in aqueous solutions . All found form low spin octahedral complexes.

The visible spectra of these complexes have been charaelerised in general by a set three bands which shift to shorter wave length compared to the unligated parent complexes. Stability constants for these complexes with these amines have been calculated at two temperatures for Fe(II) TNPS, from Hill plots.  $\Delta H, \Delta G$  and  $\Delta S$  have been calculated by using (eq.4). Hill plots [22] have been used to obtain the  $K_{eq}$  and Hill constants (n). The low values of the slopes and the  $K_{eq}$  for these ligands in this study in aqueous media have been explained as follows.

- The polar solvent might make solute. Solvent interactions and lower the both values [23].
- The polymerization and aggregation of this type of porpyrins (Fe(II) TNPS) complexes in aqueous solution will lower the values of  $K_{eq}$ [24].
- The aromatic amines (good  $\pi$ -electron acceptor) ligands have larger value  $K_{eq}$  than non-aromatic.
- The substituent position on pyridine play an important role, lowering the  $K_{eq}$  values for such ligands as 2-methyl pyridine due to the steric effects and have positive  $\Delta S(+4.44, +8.05)$  cal/mol for 2-

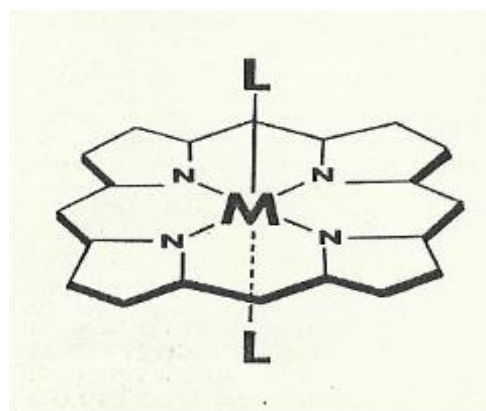
methyl pyridine and 3,4-dimethyl pyridine respectively.

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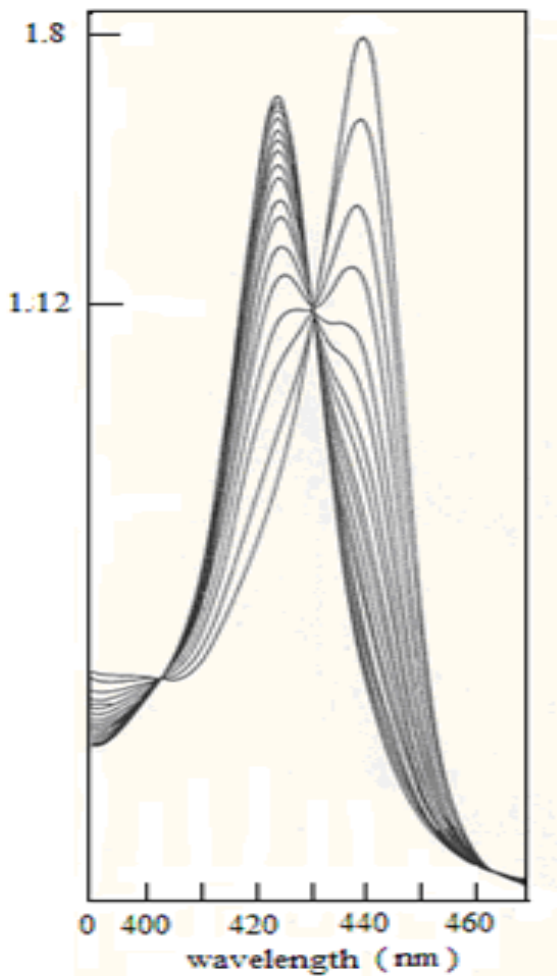
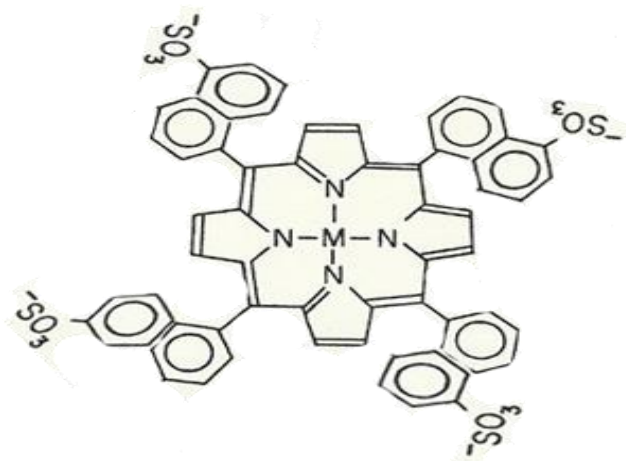


Figure -1. The soret band region of the titration Fe (II) TNPS with 4-methyl pyridine at 15 °C.

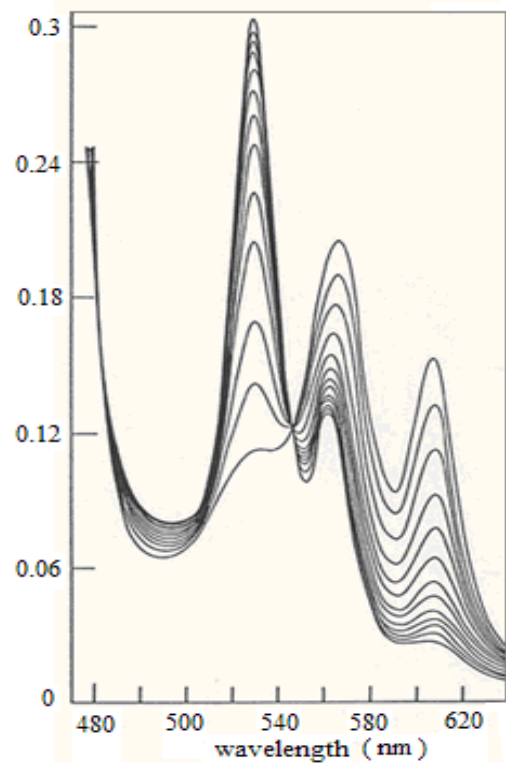


Figure-2. The visible region of the titration Fe (II)TNPS with 4-methyl pyridine at 15 °C.

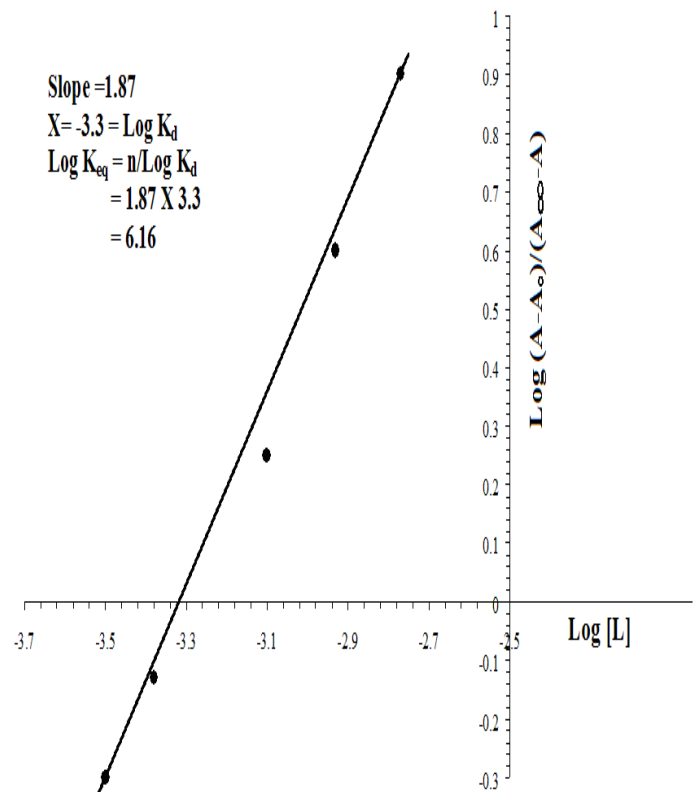


Figure -3. Hill plot for Fe (II) TNPS (4-mpy)<sub>2</sub> at 15 °C.

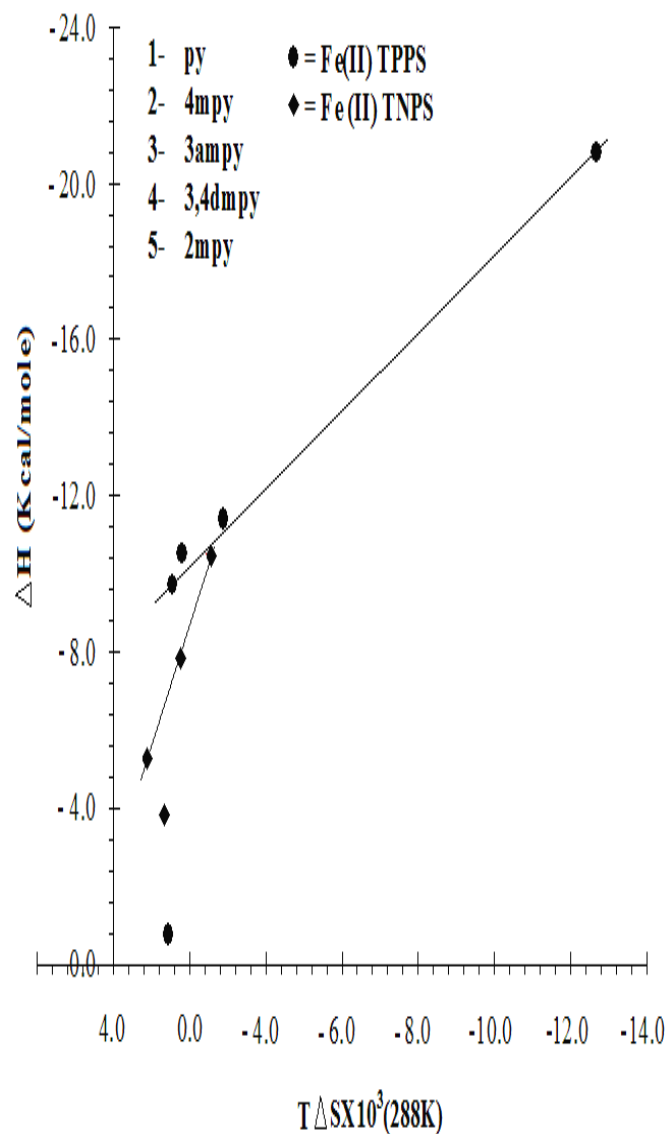


Figure -4. Show the relationship between  $\Delta H$  and  $T\Delta S$  for Fe (II) TNPS with amines.

Table -4. Order of PKa ( $\delta$ -base strengths) for substituted pyridine and their stability constants used in this work.

| No. | Pyridine and its substituents | PKa  | Ligands structure | Order of $\delta$ -donor | Order of $\pi$ donor |     |
|-----|-------------------------------|------|-------------------|--------------------------|----------------------|-----|
|     |                               |      |                   |                          | *                    | **  |
| 1   | 4-chloropyridine              | 3.83 |                   | Increases                | -                    | -   |
| 2   | Pyridine                      | 5.25 |                   |                          | 6.39                 | 6.5 |
| 3   | 4-methyl pyridine             | 5.98 |                   |                          | -                    | 6.3 |
| 4   | 3,4-dimethyl pyridine         | 6.46 |                   |                          | 6.58                 | 5.9 |
| 5   | 3-amino methyl pyridine       | 8.40 |                   |                          | 6.2                  | 5.8 |
| 6   | 2-methyl pyridine             | -    |                   |                          | -                    | -   |

\* Fe (II) TPPS [9] \*\* Fe (II) TNPS this work.

## دراسات طيفية لمحاليل رباعي سلفونفثايل بورفين حديد ثنائي مع مشتقات البريديين كليكاند

جهاد عبد طعيس

### الخلاصة

تم تسجيل ومناقشة طيف الامتصاص الالكتروني في درجة حرارة 15 م°، ثوابت الاستقرار ودوال الترمودانميكية ( $\Delta S$ ,  $\Delta G$ ,  $\Delta H$ ) لمحاليل رباعي سلفونفثايل بورفين حديد ثنائي مع مشتقات البريديين كليكاند. دليل على وجود مكون واحد فقط واطئ البرم الالكتروني لحديد ثنائي وكذلك اثنان من الليكاند يرتبط مع ذرة الحديد البروفينية المرتبطة بذرات النتروجين الاربعة وفي خطوة واحدة وتبينت مع خلال التسحيح الطيفي لمعقد Fe(II)TNPS مع الامينات المستخدمة. مجاميع النفثايل المعوضة في مجموعة ذرات الكربون تزيد من أستقرار معقد Fe(II)TNPSL2 واطئ البرم. مشتقات البريديين أظهرت بأن لها دور مهم في أنخفاض قيم ثوابت الاستقرار والطاقات الحرة، كلما ازدادت رتبة المانح الالكتروني نوع سكما، بينما مستقبلات الالكترونية نوع باي (واطئة ثوابت التآين) قد أظهرت أكبر قيم ثوابت الاستقرار والمحتوى الحراري ( $\Delta H$ ). الاعاقه الفراغية وجدت تخفض قيم ثوابت الاستقرار لبعض الليكاندات مثل 2-ميثايل بريدين.