

Synthesis And Spectral Characterization Of Substituted Tetraphenylporphyrin Iron Chloride Complexes - Greener Approach

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Abstract: A some new substituted tetraphenylporphyrin iron chloride complexes [RTPPFe(III)Cl] were synthesized by grind and stirring method and the spectral properties of free base porphyrins and iron porphyrin compounds. The experimental results showed that the one-pot method was superior method in the yields, reaction time and workup of reaction mixtures for the synthesis of iron porphyrin compounds. The highest yields (28.7%-43.4%) of RTPPFe(III)Cl were obtained in the SSA. A detailed analysis of ultraviolet-visible (UV-vis), infrared (IR) and far-infrared (FIR) spectra suggested the transformation from free base porphyrins to iron porphyrins. The red shift of the Soret band in ultraviolet-visible spectra due to the presence of *p*-nitrophenyl substituent's and the blue shift of Fe-Cl bond of TPPFeCl in far-infrared spectra were further explained by the electron transfer and molecular planarity in the porphyrin ring.

Keywords: SSA; Aldehyde; Porphyrin; Iron porphyrin; Spectral data.

INTRODUCTION:

In recent years substituted porphyrin-like complexes with conjugated macrocycles have been essential to the study of biomimetic chemistry^{1,2}, iatrolgy³, analytical chemistry⁴ and molecular electronic devices⁵. One of the most important applications of the porphyrin-like complexes is as a model for the natural enzyme peroxidase, in which the dioxygen has been activated by metalloporphyrins under mild conditions⁶. Especially, the iron porphyrin complexes are widely used as model compounds to simulate the catalytic behavior of cytochrome P450 enzymes in life processes⁷. They can be used as biomimetic catalysts to catalyze the selective oxidation of saturated hydrocarbons, aromatic hydrocarbons and their side chains with dioxygen⁸⁻¹⁰. The importance of iron porphyrin complexes in biological systems and biomimetic catalytic reactions have prompted

extensive studies on the synthesis of iron porphyrin compounds¹¹. Many new synthetic methods of metalloporphyrins have been developed, including the tetramerization of pyrrole¹²⁻¹⁶ and the self-condensation of dipyrromethene¹⁷⁻¹⁸. There into, the synthesis of substituted tetraphenylporphyrin compounds via the tetramerization of substituted benzaldehyde and pyrrole has also been improved by using different organic oxidants^{19,20}, carboxylic acids²¹ and solvents²². The tetraarylporphyrins were obtained for the first time by Rothmund²³⁻²⁴. Up to now, there exist two simple and practical methods of synthesizing porphyrin compounds. Adler and Longo firstly converted aromatic aldehyde and pyrrole to corresponding porphyrin complexes in a single refluxing carboxylic acid with air oxidation²⁵. The separation of products was relatively simple using the Adler-Longo method¹³, but the yields of porphyrins rarely exceeded 20%. Lindsey's group subsequently developed another synthetic strategy to

form substituted tetraphenylporphyrin compounds in CH_2Cl_2 solvent with BF_3 etherate as catalyst and *p*-chloranil as oxidant¹⁴. The Lindsey synthetic approach was more feasible for the larger scale synthesis²⁶ and obtained much higher yields of substituted tetraphenylporphyrins with the addition of salts²⁷. However, large diluent agents and expensive quinones were involved in the Lindsey method, which brought about the high cost of porphyrin synthesis and restricted their applications at present. Therefore, the Adler method are of the advantages of simple manipulation and ease of workup with low yields, while the Lindsey method can obviously improve the yields of porphyrins with costly and environmental impacts. Meanwhile, the synthetic methods are different for the metalloporphyrins with various structures in the porphyrin rings, which lead to the universal synthetic method impossible to be used in the porphyrin complexes with various substituent's. Therefore, the study on synthetic methods for conveniently improving the yields of metalloporphyrin complexes is of great significance. In this present research work, a series of substituted tetraphenylporphyrin iron chloride complexes were synthesized with green method using silica sulfuric acid. Simultaneously, the structures of above porphyrin-like complexes were characterized by UV, IR, FIR and elemental analysis.

MATERIALS AND METHODS:

All chemicals were obtained commercially and used as received unless otherwise noted. Before

use Pyrrole was redistilled. CH_2Cl_2 was dehydrated. Neutral Al_2O_3 was baked at 100 °C for 5 h. Chromatography was performed on neutral Al_2O_3 . UV-Vis spectra were recorded in CH_2Cl_2 with a HITACHI U-3010 spectrophotometer. IR spectra were recorded as KBr pellets via a perkin-Elmer spectrophotometer. FIR spectra were recorded on a Bruker FT-IR VERTEX 70 spectrometer. The data of elemental analysis were obtained with an elemental analyzer.

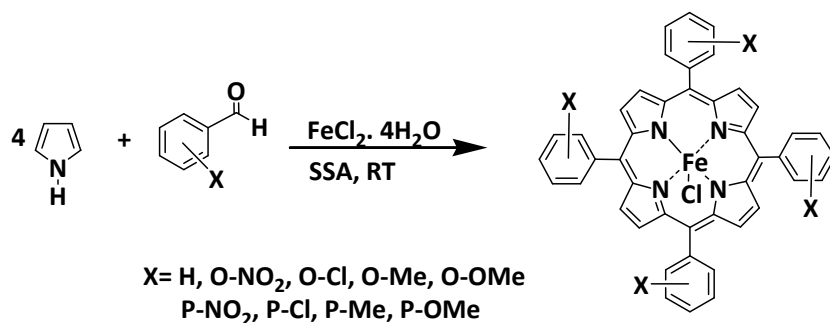
SYNTHESIS-ONE-POT METHOD:

RTPPFeCl I: The mixture of Substituted benzaldehyde (1 mmol), silic-sulfuric acid (20 mg), freshly distilled pyrrole (1.2 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2 g, 10 mmol) was added into the reaction pot and grind it. The mixture was stirred for about 50 min. When the thin-layer chromatography (alumina) indicated no free base porphyrins at this point, the reaction was stopped. The crude mixture was filtered and washed with methanol three times. The further purification by column chromatography on alumina using 100% CH_2Cl_2 removed the porphyrin isomers and use of acetone/ethyl acetate (1:1) as eluent gave the final products. The iron porphyrin was eluted as the second band, leading to the pure compound obtained after solvent elimination (yield up to 28.9%). Other iron porphyrin complexes (RTPPFeCl) were prepared with the same procedure. The ratios of mixed solvents and the yields of porphyrins were listed in Table-1.

TABLE 1:

Sr no.	Compounds	Molecular Formula	Calcd % (found)	Total Yields
1	<i>o</i> - $\text{NO}_2\text{TPPFeCl}$	$\text{C}_{44}\text{H}_{24}\text{N}_8\text{O}_8\text{ClFe}$	C 59.35, H 2.64, N 12.52	28.9
2	<i>o</i> - ClTPPFeCl	$\text{C}_{44}\text{H}_{24}\text{N}_4\text{Cl}_5\text{Fe}$	C 62.44, H 3.16, N 7.01	32.7
3	<i>o</i> - $\text{CH}_3\text{TPPFeCl}$	$\text{C}_{48}\text{H}_{36}\text{N}_4\text{ClFe}$	C 59.35, H 2.74, N 12.68	35.3
4	<i>o</i> - $\text{OCH}_3\text{TPPFeCl}$	$\text{C}_{48}\text{H}_{36}\text{N}_4\text{ClFeO}_4$	C 69.36, H 4.73, N 6.78	33.6
5	TPPFeCl	$\text{C}_{44}\text{H}_{28}\text{N}_4\text{ClFe}$	C 74.29, H 4.07, N 7.92	41.8
6	<i>p</i> - $\text{NO}_2\text{TPPFeCl}$	$\text{C}_{44}\text{H}_{24}\text{N}_8\text{O}_8\text{ClFe}$	C 59.35, H 2.74, N 12.68	32.9
7	<i>p</i> - ClTPPFeCl	$\text{C}_{44}\text{H}_{24}\text{N}_4\text{Cl}_5\text{Fe}$	C 62.32, H 3.31, N 6.66	42.3
8	<i>p</i> - $\text{CH}_3\text{TPPFeCl}$	$\text{C}_{48}\text{H}_{36}\text{N}_4\text{ClFe}$	C 59.43, H 2.89, N 12.96	43.4
9	<i>p</i> - $\text{OCH}_3\text{TPPFeCl}$	$\text{C}_{48}\text{H}_{36}\text{N}_4\text{ClFeO}_4$	C 69.30, H 4.68, N 6.86	38.9

The synthetic reactions are shown in Scheme 1.



Scheme 1. Synthesis of iron porphyrin complexes by the one-pot method.

SPECTRAL ANALYSIS OF RTPPFE(III)Cl:

The structures of all free base porphyrins and substituted tetraphenylporphyrin iron(III) chlorides were characterized through UV-vis and the spectral data are listed in Table -2.

By comparing the UV-vis data in Table 1, it was noticed that four absorption bands presented at the Q band and the maximum wavelength absorption (λ_{max}) presented at the Soret band along with the formation of free base porphyrins. When the metal ion was inserted into the porphyrin ring and then coordinated with four N atoms, the iron ion located in the center of the porphyrin ring to form the iron porphyrin compounds. Then the number and intensity of the Q bands decreased and the Soret band occurred slightly red shift (e.g. *o*-CITPP to *o*-CITPPFeCl, from 412 nm red shift to 418 nm), which was the characteristics of iron porphyrin compounds formed. The reason might be that the structure symmetry of iron porphyrin compounds with C_{4v} point groups was improved and the energy gap decreased comparing with free base porphyrins with D_{2h} point groups. Therefore, the UV-vis spectra of iron porphyrin compounds were obviously different from those of free base porphyrins. It also could be observed that the absorption band in the UV-vis region of iron porphyrin compounds with $-\text{NO}_2$ group located at ~ 422 nm, which revealed the red shift compared with other iron porphyrin compounds. The reason might be that the strong electron-withdrawing $-\text{NO}_2$ group decreased the electronic density of the porphyrin ring. Thus, the energy levels of π_1 and π_2 orbitals were increased and the energy gap between HOMO and LUMO of the porphyrin ring became smaller. The $\pi \rightarrow \pi^*$ electron excitation of the porphyrin ring required absorbing the light of smaller energy (longer wavelength), accordingly the absorption band (Soret band) occurred red shift and located in the long

wavelength region. Infrared and far-infrared spectra data of above porphyrin compounds were listed in Table 3.

As shown in Table 2, the IR absorption frequencies were different for free base porphyrins and iron complexes with different functional groups. It was found that the N-H bond stretching and bending frequencies of free base porphyrins located at $\sim 3,300$ cm^{-1} and ~ 960 cm^{-1} . When the iron ion was inserted into the porphyrin ring, the N-H bond vibration frequency of free base porphyrins disappeared and the characteristic functional groups of Fe-N bond formed at $\sim 1,000$ cm^{-1} , which indicated the formation of iron porphyrin compounds [30]. The bands at $2,923\sim 3,133$ cm^{-1} were assigned to the C-H bond of the benzene ring and pyrrole ring. The bands at $1,494\sim 1,682$ cm^{-1} and $1,334\sim 1,352$ cm^{-1} were assigned to the C=C stretching mode and the C=N stretching vibration respectively. The bands at ~ 800 cm^{-1} and ~ 750 cm^{-1} were respectively assigned to the C-H bond bending vibration of *para*-substituted and *ortho*-substituted phenyl ring. The FIR characterization of Fe-Cl bond vibration located at $359\sim 379$ cm^{-1} . The above results were in good agreement with the substituted tetraphenylporphyriniron chlorides as expected. Moreover, it could be well observed that the Fe-Cl bond vibration frequency (379 cm^{-1}) of TPPFeCl was obviously higher than that in other substituted tetraphenylporphyrin iron chlorides. Generally, the vibration frequency shifted to the higher frequency region (blue shift) as the bond energy increased. Owing to the fact TPPFeCl has a MOOP structure³⁰ it was roughly planar and this led to better resonance effects than RTPPFeCl with a ruffling structure. Accordingly, the bond energy of Fe-Cl bond in TPPFeCl increased and the vibrational frequency greatly shifted to the higher region.

TABLE- 2. UV-vis data of free base porphyrins and substituted tetraphenylporphyrin iron chlorides.

Sr.No.	Compounds	max (nm)	
		Soret bands	Q bands
1	<i>o</i> -NO ₂ TPP	421	516 ,551, 593, 650
2	<i>o</i> -ClTPP	412	511 ,542 ,587 ,642
3	<i>o</i> -CH ₃ TPP	416	512, 544, 589, 645
4	<i>o</i> -OCH ₃ TPP	417	512 ,545 ,589, 643
5	TPP	417	514, 538, 585, 620
6	<i>p</i> -NO ₂ TPP	424	516, 551 ,594 ,604
7	<i>p</i> -ClTPP	418	514, 549, 589, 645
8	<i>p</i> -CH ₃ TPP	419	516, 551,592, 647
9	<i>p</i> -OCH ₃ TPP	421	518, 555, 593, 650
10	<i>o</i> -NO ₂ TPPFeCl	422	510, 579
11	<i>o</i> -ClTPPFeCl	418	505, 576
12	<i>o</i> -CH ₃ TPPFeCl	416	511, 585
13	<i>o</i> -OCH ₃ TPPFeCl	418	513
14	TPPFeCl	418	507, 572
15	<i>p</i> -NO ₂ TPPFeCl	421	514, 584
16	<i>p</i> -ClTPPFeCl	417	509, 573
17	<i>p</i> -CH ₃ TPPFeCl	418	452, 511
18	<i>p</i> -OCH ₃ TPPFeCl	420	509, 572

TABLE - 3. IR / FIR data of free base porphyrins and iron porphyrin compounds.

Sr No.	Compound Name	IR Spectral Data
1	TPP	3309 (966), 3051, 1594, 1352, 732
2	<i>o</i> -ClTPP	3325 (967), 3056, 1626, 1346, 750
3	<i>o</i> -CH ₃ TPP	3315 (965), 3016, 1599, 1348, 739
4	<i>o</i> -OCH ₃ TPP	3322 (966), 3070, 1580, 1349, 753
5	<i>o</i> -NO ₂ TPP	3321 (968), 3060, 1606, 1349, 722
6	<i>p</i> -NO ₂ TPP	3323 (967), 3055, 1595, 1347, 800.
7	<i>p</i> -ClTPP	3315 (965), 3024, 1627, 1349, 796
8	<i>p</i> -CH ₃ TPP	3317 (967), 3024, 1561, 1349, 798
9	<i>p</i> -OCH ₃ TPP	3320 (967), 2925, 1596, 1346, 805
10	TPPFeCl	2923, 1597, 1340, 750, 991, 379
11	<i>o</i> -ClTPPFeCl	2923, 1673, 1334, 754, 999, 370
12	<i>o</i> -CH ₃ TPPFeCl	3014, 1598, 1332, 753, 998, 361
13	<i>o</i> -OCH ₃ TPPFeCl	2934, 1596, 1334, 756, 998, 360
14	<i>o</i> -NO ₂ TPPFeCl	2925, 1607, 1345, 740, 999, 367
15	<i>p</i> -NO ₂ TPPFeCl	2925, 1595, 1346, 802, 999, 368
16	<i>p</i> -ClTPPFeCl	3133, 1682, 1338, 805, 999, 359
17	<i>p</i> -CH ₃ TPPFeCl	3022, 1494, 1338, 799, 999, 360
18	<i>p</i> -OCH ₃ TPPFeCl	2923, 1605, 1334, 810, 998, 359

RESULTS AND DISCUSSION:

Nine substituted tetraphenylporphyrin iron chloride compounds were prepared using the one-pot mixed method. It was well known that the prominent advantages of synthesizing metalloporphyrins by using one-pot mixed method were that much higher yields of metalloporphyrin complexes

could be obtained after shorter reaction times with simple workup of the reaction mixtures. It could be found that the synthetic yields of porphyrins were improved by the one-pot method, and the yields of substituted tetraphenylporphyrin iron chlorides were much higher (from 28.9% to 43.4%). For the synthesis of porphyrins the polarity and acidity of

the reaction system may be conveniently improved, further promoting the deprotonation ability of $-H$ in pyrrole and the protonation strength of $C=O$ in the aromatic aldehyde. Simultaneously, the ratio of mixed method also had an important influence on the synthesis of substituted tetraphenylporphyrins. By changing the ratio of mixed method, the polarity of mixed method could be better adjusted to increase

the collision frequencies of reactant molecules and accelerate the formation of porphyrins in the one-pot mixed system. Moreover, the one-pot mixed method was valid for different substituted benzaldehydes and the reaction time was shorter than that in other method. Therefore, the one-pot mixed method was an efficient one to synthesize tetraphenylporphyrin iron compounds with different substituents.

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