

Research Article

Effects of Core and/or Peripheral Protonation of *meso*-Tetra(2-, 3-, and 4-pyridyl)Porphyrin and *meso*-Tetra(3-methylpyridyl)Porphyrin on Their UV-vis Spectra

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Received 11 June 2012; Revised 19 July 2012; Accepted 20 July 2012

Academic Editor: Christophe Dujardin

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Core and/or peripheral protonation of *meso*-tetra(pyridyl)porphyrins, H₂(py)P, with weak and strong acids have been studied by UV-vis spectroscopy. The results support the proposal that the position of the Soret as well as the Q(0,0) bands of the dications is influenced by π donation from the *meso* substituents to the porphyrin core. The red shift of the Q(0,0) band of H₂t(py)P dications with 2-, 3-, and 4-pyridyl substituents does not correlate with the order of π electron donor ability of the *meso* groups. The decreased electron donation from the central nitrogen atoms to the acids on going from 3-pyridyl group to 4- and 2-pyridyl ones has been used to explain this observation. In spite of the negative effect of N-methylation of pyridyl substituents on the basicity of the central nitrogen atoms of *meso*-tetra(3-methylpyridyl)porphyrin, H₂t(3-Mepy)P, protonation of H₂t(3-Mepy)P occurs with weak and strong acids. The blue shift of the Q(0,0) bands upon protonation of H₂t(3-Mepy)P with weak and strong acids clearly shows the importance of resonance interactions between the π -systems of porphyrin and the aryl substituents on the position of the band.

1. Introduction

Core protonation of porphyrins with weak and strong Lewis and protic acids has been the subject of many studies since the late 1970s [1–10]. X-ray crystallographic studies on many porphyrin dications have shown a distorted (mainly saddled) conformation of the aromatic macrocycle [1, 4–6]. In other words, protonation of central nitrogen atoms of porphyrin may be used to induce nonplanarity in porphyrins. Several properties of porphyrins and metalloporphyrins including their redox potentials, basicity, and axial ligand binding affinity which can influence the biological function of porphyrin cofactors in proteins are known to be modified by nonplanar distortions of the aromatic macrocycle. Host-guest interactions and the enantioselectivity of catalytic epoxidation can be also tuned by the out-of-plane deformations [11]. On the other hand, nonplanar porphyrins and the influence of the

out-of-plane deformations of the macrocycle on their UV-vis spectroscopy have been of great interest to both experimental and computational chemists [6–8, 11, 12]. Indeed, the spectral changes caused by the out-of-plane deformation of porphyrins might be used to probe the structures of hemes, chlorophylls, and related photosynthetic pigments, and other tetrapyrrole cofactors in proteins [11]. While in free base porphyrins, the *meso*-aryl groups are nearly perpendicular to the porphyrin mean plane [2, 13], the dihedral angles between the aryl substituents at *meso*-positions, and the porphyrin mean plane substantially decrease upon protonation of porphyrin core, leading to enhanced resonance interactions between the π -system of porphyrin and that of the aryl substituents [2, 6, 7] and consequently, the difference between the electron-withdrawing/donating ability of various *meso*-substituents is more pronounced compared to the case of the free base porphyrins. The dependence

of the position of the Q(0,0) bands of the dications of a series of *para*-substituted *meso*-tetraarylporphyrins on the electronic effects of *meso*-substituents has been studied in our previous work [8]. Also, the position of the Q(0,0) band of the dication of a series of *meso*- and/or β substituted porphyrins with CF₃COOH was found to correlate with the electron-withdrawing or electron-donating ability of the groups at the periphery of the porphyrin macrocycle [14].

X-ray crystallography confirmed the formation of a hexaprotonated salt upon protonation of *meso*-tetra(4-pyridyl)porphyrin with HCl in water [1]. In the present work, core and full protonation of *meso*-tetra(2-, 3-, and 4-pyridyl)porphyrins, H₂t(py)P, and diprotonation of *meso*-tetra(3-methylpyridyl)porphyrin, H₂t(3-Mepy)P (Figure 1) with different acids are reported. The influence of electronic effects of the *meso*-substituents on the amount and direction of the shifts of the Soret and the Q(0,0) bands has been studied and compared. The results clearly demonstrate the importance of protonation or N-methylation (in the case of H₂t(3-Mepy)P) of the pyridyl groups on the shifts of the Soret and Q(0,0) bands of the core protonated H₂t(py)P.

2. Experimental

2.1. Instrumental. ¹H NMR spectra were obtained on a Bruker Avance DPX-400 MHz spectrometer. The absorption spectra were recorded on a Pharmacia Biotech Ultraspec 4000 UV-Vis spectrophotometer.

2.2. Preparation of the Free Base Porphyrins. *meso*-tetra(pyridyl)porphyrins were synthesized and purified according to the literature methods [15–17] with some modifications, explained in our recent work [18]. H₂t(3-Mepy)P was prepared and purified using the procedure described by Paster-nack et al. [16, 19].

2.3. Full Protonation of the Porphyrins. A sample of H₂t(py)P was dissolved in 20 mL of dichloromethane and 5 mL of concentrated strong acid (aqueous solution of HNO₃, HCl, HClO₄, H₂SO₄ or HNO₃ with pH adjusted to zero) acid was added. The mixture was stirred until the disappearance of the Soret band due to the free base porphyrin in the UV-vis spectra of the organic phase. As we have shown previously, due to the high dielectric constant of water, there is no detectable difference between the UV-vis spectrum of the dications of a given H₂t(py)P with different acids in water [20]. The formation of hexaprotonated species under this pH condition was previously confirmed by X-ray crystallographic studies [1]. It is noteworthy that the hexaprotonated species H₂t(py)P is completely insoluble in dichloromethane and therefore it cannot be extracted with dichloromethane from the acidic (pH = 0) aqueous phase [18].

2.4. Preparation of the Diprotonated Species of H₂t(py)P and H₂t(3-Mepy)P. The pyridyl groups of H₂t(py)P are less basic than the pyrroline nitrogen atoms; it has been indicated

that upon protonation of pyrroline nitrogen atoms of *meso*-di(2-, 3-, or 4-pyridyl)porphyrins ($\approx 10^{-5}$ to 10^{-4} M) with H₂SO₄ in ethanol ($\approx 10^{-5}$ to 10^{-3} M), the pyridyl groups remain intact and only protonation of the porphyrin core occurs [21]. It should be noted that although Aronoff's spectrophotometric titration of H₂tpp with CF₃COOH in nitrobenzene has given an intermediate spectrum attributed to a monoprotonated moiety, [H₃TTP]⁺, there has been no evidence for a monoprotonated intermediate between the free base and the diprotonated porphyrin in chloroform and dichloromethane [14, 19, 20]. Accordingly, addition of 2:1 molar ratio of acid (including HNO₃, HCl, HClO₄, H₂SO₄, HNO₃, H₂C₂O₄, and CF₃COOH) to H₂t(py)P in dichloromethane gives the diprotonated porphyrins. Due to the presence of an equilibrium between the diprotonated species and the free base porphyrins (especially in the case of weak acid, i.e., CH₃COOH), under high dilution conditions which is usually used to prepare the UV-vis spectra, the Soret band of the free base porphyrin is also observed in addition to that of the diprotonated porphyrin. In this condition, an excess amount of acid should be used for completeness of the reaction [8, 20]. Figure 2 demonstrates the UV-vis spectrum of a solution of H₂t(3-py)P ($\sim 10^{-5}$ M) in dichloromethane after the addition of concentrated perchloric acid in 1:1 molar ratio. Here, the absorption bands due to the free base porphyrin ($\lambda_{\max} = 418$ nm) and the corresponding dication, [H₄t(3-py)P](ClO₄)₂ ($\lambda_{\max} = 453$ nm), are observed.

H₂t(3-Mepy)P is insoluble in dichloromethane and consequently the reactions with acids were performed in methanol. In the case of H₂t(3-Mepy)P, due to the decreased basicity of the pyrroline nitrogen atoms caused by the methylation of pyridyl groups, excess amounts of acid (beyond 2:1 molar ratio of acid to porphyrin) should be used to ensure the completion of the reaction (Figure 3). However, the employment of excess amounts of acid led to no detectable change in the position of the Soret and Q(0,0) bands.

3. Results and Discussion

3.1. Shift of the Soret and Q(0,0) Bands of H₂t(py)P in Reaction with Strong Acids. Hexaprotonation of H₂t(2-, 3-, or 4-py)P with HCl in water (pH = 0) leads to red shift of the Soret bands and the blue shift of the Q(0,0) bands (Table 1). Diprotonation of these porphyrins with HCl (Table 2), on the other hand, causes the shifts of the bands to longer wavelengths. Also, the shifts of the Soret bands are significantly larger than those observed in hexaprotonation of the porphyrins.

There are several factors which may influence the position of the absorption bands of porphyrin diacids including the out-of-plane deformation of porphyrin core, shift of electron density from the pyrroline nitrogens to the acids, and enhanced coplanarity of the *meso* aryl substituents and the porphyrin mean plane [2, 4, 8, 14, 20]. According to the four orbital model of porphyrin spectra, the electron densities of the a_{1u} orbitals are on the α and β carbon atoms and those of the a_{2u} orbitals are largest on the *meso* positions and central nitrogen atoms [22]. In other words, the *meso* carbon atoms

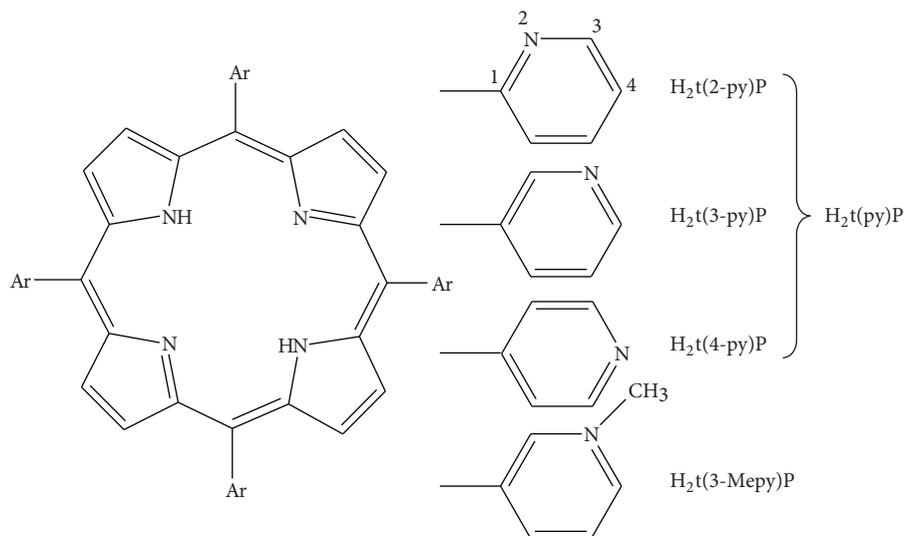
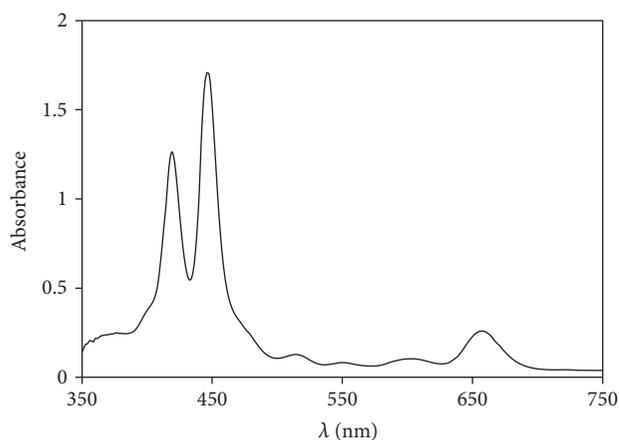
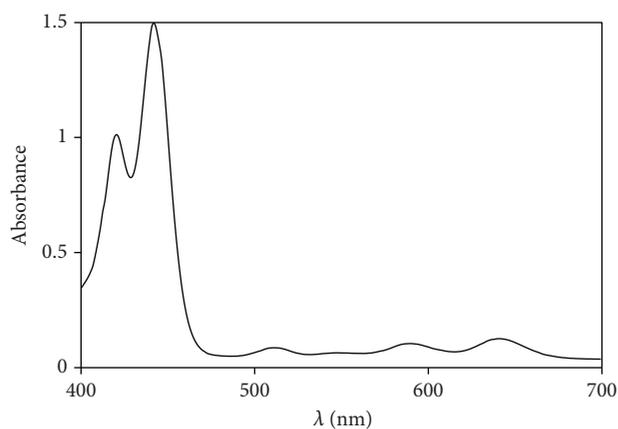


FIGURE 1: The porphyrins used in this study.

FIGURE 2: The free base $H_2t(3\text{-py})P$ ($\lambda_{\max} = 418$ nm) in equilibrium with $[H_4t(3\text{-py})P](ClO_4)_2$ ($\lambda_{\max} = 453$ nm) in dichloromethane (see the text).FIGURE 3: The free base $H_2t(3\text{-Mepy})P$ ($\lambda_{\max} = 419$ nm) in equilibrium with $[H_4t(3\text{-Mepy})P](Cl)_2$ ($\lambda_{\max} = 433$ nm), in methanol; 1 : 2 molar ratio of $H_2t(3\text{-Mepy})P$ to HCl was used.

lie on the nodal planes of the a_{1u} orbitals and therefore the a_{2u} to e_g transitions of the dications, that is, the Q bands are expected to be strongly influenced by the change of π -donor ability of the *meso* groups. The red shift of the Q(0,0) bands of diprotonated *meso*-tetra(pyridyl)porphyrins compared to the blue shifts of the corresponding bands of the hexaprotonated species may be attributed to the weaker π donor ability of the protonated pyridyl substituents with respect to the nonprotonated ones. The observed shift of the Soret band of porphyrins upon protonation with different acids is primarily due to the saddling of porphyrin core [8, 12, 14], but as we have previously suggested [8], a through space (i.e., without the necessity of the presence of a chemical bond) interaction between the HOMOs of *meso* aryl groups and the porphyrin π system (Figure 4) may be considered causing the red shift of the Soret band [8].

It is noteworthy that different bulk of the substituents at *meso* positions is an important factor influencing the extent of saddling of porphyrin core, the dihedral angle between the aryl groups and the porphyrin mean plane, and consequently the shift of the absorption bands [4]. However, in the absence of substitution of the *ortho* positions of *meso* aryl groups with bulky substituents such as $-CH_3$ and $-Cl$ [4], the aryl groups have approximately the same steric bulk.

The observed red shift of the long wavelength band of the dications of $H_2t(\text{py})P$ with HCl (Table 2) decreases in the order $[H_4t(2\text{-py})p](Cl)_2 > [H_4t(4\text{-py})p](Cl)_2 \gg [H_4t(3\text{-py})P](Cl)_2$. Meot-Ner et al. show that the basicity of the pyrroline nitrogens of porphyrin as well as the UV-vis spectral shifts upon the core protonation of a series of porphyrins with weak or strong electron-donating groups at the *meso* positions correlate to predominantly resonance type interactions between the aryl groups and

TABLE 1: UV-vis spectral data for hexaprotonation of $H_2t(py)p$ with HCl in water ($pH = 0$)^a.

Porphyrins and the dications	Soret band (λ/nm)	Q(0,0) band (λ/nm)
$H_2t(2-py)p$	417.0	642.0
$[H_6t(2-py)p](Cl)_6$	436.3	636.2
$\Delta\nu$ (cm^{-1}) ^b	-106.0	142.0
$H_2t(3-py)p$	418.0	646.4
$[H_6t(3-py)p](Cl)_6$	435.0	636.0
$\Delta\nu$ (cm^{-1})	-935.0	253.0
$H_2t(4-py)p$	416.0	643.0
$[H_6t(4-py)p](Cl)_6$	440.8	636.2
$\Delta\nu$ (cm^{-1})	-1352	166.0

^aSee Section 2.3 for details. The hexaprotonated species are completely insoluble in dichloromethane. ^b $\Delta\nu$ (cm^{-1}) = $10^7(1/\lambda_2 - 1/\lambda_1)$, relative to the corresponding free base porphyrin.

TABLE 2: UV-vis spectral data for the interaction of $H_2t(py)P$ with HCl in CH_2Cl_2 ^a.

Porphyrins and the dications	Soret band (λ/nm)	Q(0,0) band (λ/nm)
$H_2t(2-py)P$	417.0	642.0
$[H_4t(2-py)P](Cl)_2$	471.3	662.2
$\Delta\nu$ (cm^{-1})	-2762.9	-475.2
$H_2t(3-py)P$	418.0	646.4
$[H_4t(3-py)P](Cl)_2$	451.0	647.5
$\Delta\nu$ (cm^{-1})	-1750.9	-26.2
$H_2t(4-py)P$	416.0	643.0
$[H_4t(4-py)P](Cl)_2$	470.2	661.0
$\Delta\nu$ (cm^{-1})	-2770.9	-425.3

^aSee Section 2.3 for details.

porphyrin aromatic system [2]. In other words, raising of the electron density on the a_{2u} orbital by electron-donating substituents causes the observed red shift of the Q(0,0) band of strongly electron-donating porphyrins such as *meso*-tetra(4-hydroxyphenyl)porphyrin. The relative success of the electrophilic substitution reactions of pyridine correlates with the electron density distribution at the various positions of the pyridine ring; electrophilic attack at pyridine occurs at the *meta* positions relative to the heteroatom [23, 24]; according to the resonance forms of pyridine, a positive charge spreads on the aromatic ring which decreases as *meta* \leq *para* < *ortho* [23]. In the case of $[H_4t(2-py)P](Cl)_2$, $[H_4t(4-py)P](Cl)_2$, and $[H_4t(3-py)P](Cl)_2$, the *meso* position of the macrocycle is attached to the *ortho*, *para*, and *meta* positions of the pyridyl group, respectively (Figure 5).

Accordingly, the pyridyl groups of $[H_4t(3-py)P](Cl)_2$ are expected to be better electron-donating groups to the a_{2u} orbital in comparison with those of $[H_4t(4-py)P](Cl)_2$ and $[H_4t(2-py)P](Cl)_2$. On the basis of the above discussion, the observed red shift of the Q(0,0) bands of these porphyrins does not correlate with the order of electron donor ability of the pyridyl substituents. Also, the same trend was observed for the dications of $H_2t(py)P$ with oxalic, nitric, and sulfuric

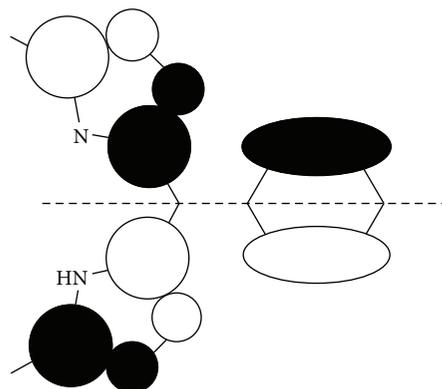


FIGURE 4: A possible through space interaction between the porphyrin a_{1u} orbital and one of the e_{1g} orbitals of the aryl group [8].

acid (see Tables S1–S3) (see supplementary materials available online at <http://dx.doi.org/10.1155/2013/713745>).

Indeed, the order is contrary to that one would predict from the electronic properties of the *meso* groups. In a previous work [8], we have shown that while the saddling of porphyrin core and the enhanced coplanarity of the *meso* aryls and porphyrin aromatic system lead to the red shift of the Q(0,0) band [1, 2, 12], the shift of electron density from the central nitrogen atoms (donors) to the acids (acceptors) causes the blue shift of the Q(0,0) band. The presence of strong electron-donating groups such as 4-methoxyphenyl at *meso* positions was shown to compensate the blue shift caused by the donor-acceptor interactions and result in the large red shift of the band upon protonation of *meso*-tetra(4-methoxyphenyl)porphyrin with CF_3COOH [8]. On the other hand, the large blue shift of the Q(0,0) band of *meso*-tetra(*n*-propyl)porphyrin dications is consistent with the lack of proper π electron-donating groups at the *meso* positions.

In comparison of the three porphyrins with pyridyl substituents, the larger blue shift of the band in the case of $[H_4t(3-py)P](Cl)_2$, caused by the better electron donation from the central nitrogen atoms to the acid molecule, seems to be responsible for the observed order of shift of the Q(0,0) bands.

According to data of Tables 1, 2, 3, and 4 and Table S1–S3, the larger shift of the Soret band for a given $H_2t(py)P$ occurs in the protonation with HCl. The size and hydrogen bond acceptor ability of the counteranion of porphyrin dications play an important role in the extent of saddling of porphyrin core and stability of the adduct [1, 6, 8, 9, 20]. It has been shown that in a series of diprotonated *meso*-tetra(phenyl)porphyrin, $[H_4TPP](X)_2$ ($X = F, Cl, Br, I$), the degree of saddling of porphyrin core increases with increasing size of the halide. It was suggested that the necessity to optimize the hydrogen bond interactions between the halides and the dication is an additional factor in determining the actual degree of saddling [6]. Accordingly, the larger size of Cl^- relative to the oxygen residues of ClO_4^- and CF_3COO^- as well as the stronger hydrogen bond of $Cl-H$ than that of $O-H$ may explain the increased red shift of the Soret band for the dications with HCl.

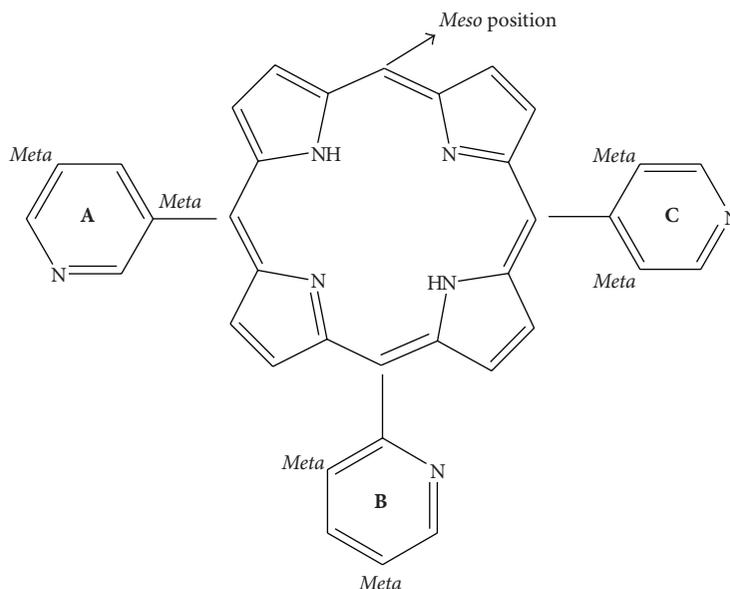


FIGURE 5: The *meta* positions of pyridyl substituents relative to the *meso* carbon atoms of H₂t(3-py)P (A), H₂t(2-py)P (B), and H₂t(4-py)P (C).

TABLE 3: UV-vis spectral data for the diprotonated H₂t(py)P with CF₃COOH in CH₂Cl₂^a.

Porphyrins and the dications	Soret band (λ/nm)	Q(0,0) band (λ/nm)
H ₂ t(2-py)P	417.0	642.0
[H ₄ t(2-py)P](CF ₃ COO) ₂	443.0	647.0
Δν (cm ⁻¹)	-1407.0	-121.0
H ₂ t(3-py)P	418.0	646.0
[H ₄ t(3-py)P](CF ₃ COO) ₂	442.0	645.0
Δν (cm ⁻¹)	-1299.0	33.0
H ₂ t(4-py)P	416.0	643.0
[H ₄ t(4-py)P](CF ₃ COO) ₂	442.0	638.0
Δν (cm ⁻¹)	-1409.0	112.0

^aSee the footnotes of Table 2.

TABLE 4: UV-vis spectral data for the dications of H₂t(py)P with HClO₄ in CH₂Cl₂^a.

Porphyrins and the dications	Soret band (λ/nm)	Q(0,0) band (λ/nm)
H ₂ t(2-py)P	417.0	642.0
[H ₄ t(2-py)P](ClO ₄) ₂	471.3	663.3
Δν (cm ⁻¹)	-2762.9	-500.2
H ₂ t(3-py)P	418.0	646.4
[H ₄ t(3-py)P](ClO ₄) ₂	458.9	653.1
Δν (cm ⁻¹)	-2132.2	-158.7
H ₂ t(4-py)P	416.0	643.0
[H ₄ t(4-py)P](ClO ₄) ₂	469.0	661.0
Δν (cm ⁻¹)	-2720	-425.3

^aSee the footnotes of Table 2.

3.2. *Interaction of H₂t(py)P with CH₃COOH as a Weak Acid.* We have reported the interaction of *meso*-tetra(aryl)- and *meso*-tetra(alkyl)porphyrins with weak carboxylic acids in 2007 [8]. In spite of the lower basicity of *meso*-tetra(pyridyl)porphyrins with respect to *meso*-tetra(phenyl) porphyrin [2, 21], interaction of the former with CH₃COOH is evident from the shift of the absorption bands in the UV-vis spectra (Table 5).

3.3. *Interaction of H₂t(3-Mepy)P with Weak and Strong Acids.* With regard to the significant influence of the *meso* substituents on the basicity of *meso*-tetra(aryl)porphyrins [2, 21], methylation of the pyridyl substituents of H₂t(3-py)P which creates a positive charge over the pyridyl moiety is expected to decrease the basicity of H₂t(3-Mepy)P compared to the nonmethylated porphyrin. As in the case of H₂t(3-py)P, upon the addition of weak and strong acids to the solution

of H₂t(3-Mepy)P in methanol, the color changed into green, indicating the interaction of H₂t(3-Mepy)P with the acids. The blue shift of the Q(0,0) band (Table 6) of H₂t(3-Mepy)P in reaction with all the acids is in line with the decreased electron donor ability of the *meso* substituents (vide supra).

4. Conclusion

In summary, the results of this study indicate the importance of resonance-type substituent effects on the shifts of the Soret as well as the Q(0,0) bands of H₂t(py)p dications with weak and strong acids. The lack of correlation between the red shift of the Q(0,0) band of H₂t(py)P dications with the order of π electron donor ability of the *meso* substituents seems to be due to the negative effect of the shift of electron density from the pyrrolenine nitrogen atoms to the acids on the red

TABLE 5: UV-vis spectral data for interaction of H₂t(py)P with CH₃COOH in CH₂Cl₂^{a,b}.

Porphyrins and the dications	Soret band (λ/nm)	Q(0,0) band (λ/nm)
H ₂ t(2-py)P	417.0	642.0
[H ₄ t(2-pyp)P](CH ₃ COO) ₂	440.8	654.3
Δν (cm ⁻¹)	-1294.0	-293.0
H ₂ t(3-py)P	418.0	646.4
[H ₄ t(3-py)P](CH ₃ COO) ₂	444.0	652.0
Δν (cm ⁻¹)	-1400.9	-132.8
H ₂ t(4-py)P	416.0	643.0
[H ₄ t(4-py)P](CH ₃ COO) ₂	428.9	639.6
Δν (cm ⁻¹)	-722.1	82.7

^aSee the footnotes of Table 2. ^bExcess amounts of acetic acid was used to complete the reaction (see Section 2.4 for details).

TABLE 6: UV-vis spectral data for protonation of H₂t(3-Mepy)P with different acids in methanol.

Porphyrins and the dications	Soret band (λ/nm)	Q(0,0) band (λ/nm)
H ₂ t(3-Mepy)P	419.3	639.7
[H ₄ t(3-Mepy)P](CH ₃ COO) ₂	437.4	632.8
Δν (cm ⁻¹) ^a	-987.0	168.0
[H ₄ t(3-Mepy)P](Cl) ₂	433.1	639.6
Δν (cm ⁻¹)	-1281.0	2.4
[H ₄ t(3-Mepy)P](HSO ₄) ₂	436.3	632.8
Δν (cm ⁻¹)	-929.0	168.0
[H ₄ t(3-Mepy)P](CF ₃ COO) ₂	433.5	631.5
Δν (cm ⁻¹)	-781.0	201.0

^aRelative to the bands of H₂t(3-Mepy)p.

shift of the band. Contrary to H₂t(py)P, protonation of H₂t(3-Mepy)P with different acids only causes the blue shifts of the Q(0,0) band, indicating the significance of the π electron-donating strength of the *meso* substituents on the energy of the a_{2u} to e_g transitions. In spite of the decreased basicity of the central nitrogen atoms of H₂t(3-Mepy)P compared to H₂t(py)P, caused by the methylation of the pyridyl groups, the former may be also protonated with CH₃COOH as well as the strong acids.

Acknowledgments

The Support of this work by the Institute for Advanced Studies in Basic Sciences (IASBS) and Damghan University Research Council is acknowledged.

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