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Synthesis and characterization of new molecular complexation between free base meso-tetraarylporphyrins and nitrosonium ion as π -acceptor

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1. Introduction

Porphyrins because of their important role in photosynthesis, oxygen transport and biological redox processes are one of the most interest class of compounds in biochemistry [1]. It is reported that porphyrins react with various acceptors for formation molecular complexes contain tilted porphyrin core. In these molecular complexes, pyrrolic nitrogen atoms act as electron donors to acceptor molecule and two pyrrolic protons remained in the porphyrin macrocycle [2–10]. Reactions with NO⁺, known as nitrosation reactions, are the most well-studied. Nitrosation reactions become biologically relevant through a process called transnitrosation. This process involves the transfer of the nitrosonium cation between a protein centers containing sulfur or nitrogen. Alterations in cellular function via transnitrosation occur when NO⁺ is transferred between nucleophilic centers of proteins [11]. This process will result in cellular damage when NO⁺ interacts with a critical center of a protein, resulting in modification and alteration of protein function. This phenomenon is exemplified with the transnitrosation of amines and sulfur to yield N-nitrosamines and S-nitrosothiols, respectively. N-nitrosamines have been found to be chemical modifiers of nucleic acids and therefore represent potent mutagens and carcinogens [12]. In this work we synthesized new molecular complexes from meso-tetraarylporphyrins (Fig. 1) and nitrosonium ion. Mole ratio for the porphyrins and

ABSTRACT

NOBF₄ reacts with para-substituted meso-tetraarylporphyrins, $H_2t(4-Xp)p$, at room temperature for formation of green molecular complexes, $[H_2t(4-Xp)p(NO)]BF_4$. Mole ratio for the porphyrins and nitrosonium ion in the molecular complexes was 1:1, $[H_2T(4-X)PP(NO)]BF_4$. FT-IR, UV–Vis, (¹H and ¹³C) NMR spectral data, elemental analysis and molar conductivity indicated that NO⁺ (as electron acceptor) is bound to the lone electron pairs of the two pyrrolenine nitrogens in a side of the porphyrin plane. In these molecular complexes, two pyrrolic nitrogen atoms of the porphyrin core coordinate to the acceptor and two protons of the pyrrolic nitrogen atoms have been remained on the porphyrin macrocycles. Molecular complexation of meso-tetraarylporphyrins with NO⁺ produces a large downfield shift for the NH signal. © 2011 Elsevier B.V. All rights reserved.

nitrosonium ion in the molecular complexes was 1:1, $[H_2t(4-Xp)p(NO)]BF_4$. In these complexes a nitrosonium ion accepts two lone electron pairs of pyrrolic nitrogens in one porphyrin molecule. It has been reported that meso-tetraarylporphyrins react with π -acceptors of DDQ (dichloro-dicyano-benzoquinione) and TCNE (tetracyanoethylene) for formation of 1:2 molecular complexes as sole product [7,8]. But in this work, nitrosonium ion (as π -acceptor) produced 1:1 molecular complexation with the meso-tetraarylporphyrins in contrast to known 1:2 (donor: π -acceptor) molecular complexation [7,8]. This article presents the first example of 1:1 molecular complexation between the meso-tetraarylporphyrins and π -acceptors.

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2. Experimental

2.1. Material and measurements

All chemicals used in this study were purchased from Merck. Pyrrole (Fluka) was distilled before use and was reacted with benzaldehyde and various *para*-substituted benzaldehydes (CH₃, OCH₃, Cl, CH(CH₃)₂) (Merck) in the presence of nitrobenzene as oxidant and propionic acid as solvent [13].

A Bruker 400 MHz spectrometer was used for ¹H NMR and ¹³C NMR spectra of porphyrins and those molecular complexes in CDCl₃ solvent. The residual CHCl₃ in the 99.8% atom CDCl₃ gave a signal at 7.27 ppm which was used as a reference. The electronic absorption spectra were recorded in chloroform solution on a GBC Cintra 6 UV–Vis spectrophotometer. To record FT-IR spectra,



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X=H, CH₃, CH(CH₃)₂, OCH₃, Cl

Fig. 1. Meso-tetraarylporphyrins, H₂t(Xp)p.

a Magna 550 Nicolet instrument was employed (using KBr pellets). The molar conductance of the molecular complex (in acetonitrile) and diprotonated species (in methanol) of the porphyrins was measured on a METROHM 644 conductometer.

2.2. General procedure

0.05 mmol NOBF₄ dissolved in 10 ml acetonitrile and added to 0.05 mmol of meso-tetraarylporphyrins in 15 ml chloroform and the mixture was stirred for 10 min. With slow evaporation of the solvent at room temperature, afford the green molecular complex, $[H_2t(P-Xp)p(NO)]BF_4$. The completion of the reaction was determined by the disappearance of the Soret band (~420 nm) of the porphyrins in those UV–Vis spectra. The results of elemental analyses for the molecular complexes which were dried under vacuum oven for 12 h at 60 °C were consistent with 1:1 mol ratio, $[H_2t(4-Xp)p(NO)]BF_4$. The synthesized molecular complexes are decomposed to the related porphyrins at 150 °C.

2.2.1. [H₂tpp(NO)]BF₄

Anal. Calc. for C₄₄H₃₀N₅OBF₄: C, 72.2; H, 4.4; N, 9.6. Found: C, 71.3; H, 4.0; N, 9.2%. UV–Vis (CHCl₃): 445.5, 661.5. ¹H NMR (CDCl₃): δ –2.80 (s, 2H, NH), δ 8.64–8.65 (d, 8H, o), δ 8.03–8.06 (t, 8H, m.p.), δ 8.79 (s, 8H, β). IR (KBr): ν_{NH} (~3320 cm⁻¹). Λ_{M} (in acetonitrile) = 134.3 Ω^{-1} cm² mol⁻¹.

2.2.2. [H₂t(4-CH₃p)p(NO)]BF₄

Anal. Calc. for C₄₈H₃₈N₅OBF₄: C, 73.2; H, 4.9; N, 8.9. Found: C, 72.1; H, 4.5; N, 8.6%. UV–Vis (CHCl₃): 448.3, 669.4. ¹H NMR (CDCl₃): δ –2.80 (s, 2H, NH), δ 2.79 (s, 12H, CH₃), δ 8.49–8.50 (d, 8H, o), δ 7.82–7.84 (d, 8H, m), δ 8.72 (s, 8H, β). IR (KBr): ν_{NH} (~3320 cm⁻¹). Λ_{M} (in acetonitrile) = 132.9 Ω^{-1} cm² mol⁻¹.

2.2.3. $[H_2t(4-CH(CH_3)_2p)p(NO)]BF_4$

Anal. Calc. for C₅₆H₅₄N₅OBF₄: C, 74.7; H, 6.1; N, 7.8. Found: C, 73.5; H, 5.8; N, 7.4%. UV–Vis (CHCl₃): 446.8, 661.9. ¹H NMR (CDCl₃): δ –2.90 (s, 2H, NH), δ 1.59–1.61 (s, 12H, CH₃), δ 3.34–3.38 (s, 4H, CH), δ 8.54–8.56 (d, 8H, o), δ 7.87–7.89 (d, 8H, m), δ 8.73 (s, 8H, β). IR (KBr): v_{NH} (~3320 cm⁻¹). Λ_{M} (in acetonitrile) = 158.0 Ω^{-1} cm² mol⁻¹.

2.2.4. [H₂t(4-OCH₃p)p(NO)]BF₄

Anal. Calc. for C₄₈H₃₈N₅O₅BF₄: C, 67.7; H, 4.5; N, 8.2. Found: C, 66.5; H, 4.2; N, 8.0%. UV–Vis (CHCl₃): 453.0, 686.8. ¹H NMR (CDCl₃): δ –2.76 (s, 2H, NH), δ 4.17 (s, 12H, OCH₃), δ 8.52–8.54 (d, 8H, o), δ 7.54–7.56 (d, 8H, m), δ 8.58 (s, 8H, β). IR (KBr): $\nu_{\rm NH}$ (~3320 cm⁻¹). $\Lambda_{\rm M}$ (in acetonitrile) = 149.7 Ω^{-1} cm² mol⁻¹.

2.2.5. [H₂t(4-Clp)p(NO)]BF₄

Anal. Calc. for C₄₄H₂₆N₅OBF₄: C, 60.8; H, 3.0; N, 8.1. Found: C, 59.7; H, 2.7; N, 7.8%. UV–Vis (CHCl₃): 448.8, 663.8. ¹H NMR (CDCl₃): δ –2.84 (s, 2H, NH), δ 8.53–8.55 (d, 8H, o), δ 8.04–8.06 (d, 8H, m), δ 8.78 (s, 8H, β). IR (KBr): $\nu_{\rm NH}$ (~3320 cm⁻¹). $\Lambda_{\rm M}$ (in acetonitrile) = 133.1 Ω^{-1} cm² mol⁻¹.

2.3. Diprotonation of the meso-tetraarylporphyrins

To H₂t4-(Xp)p solution (in chloroform) was added excess hydrochloric acid. Evaporation of the solvent produced diprotonated porphyrins as green solids that those molar conductivities in methanol solutions were: $[H_4t(4-OCH_3p)p]Cl_2$ ($\Lambda_M = 165 \ \Omega^{-1} \ cm^2 \ mol^{-1}$), $[H_4t(4-CH_3p)p]Cl_2$ ($\Lambda_M = 204 \ \Omega^{-1} \ cm^2 \ mol^{-1}$), $[H_4tp]Cl_2$ ($\Lambda_M = 213 \ \Omega^{-1} \ cm^2 \ mol^{-1}$), $[H_2t(4-Clp)p]Cl_2$ ($\Lambda_M = 179 \ \Omega^{-1} \ cm^2 \ mol^{-1}$), $[H_4t(4-CH(CH_3)_2p)p]Cl_2$ ($\Lambda_M = 179 \ \Omega^{-1} \ cm^2 \ mol^{-1}$).

3. Results and discussion

3.1. UV-Vis spectra

An evidence for formation of the molecular complexes of mesotetraarylporphrins and NOBF4 was UV-Vis spectral data. Porphyrins have an intense Soret band at 400-420 nm and there are 3-4 Q-bands at 500-650 nm because of electron transition within the porphyrin core. Upon the addition of NOBF₄ to free base [H₂t(4-Xp)p], the UV–Vis spectrum of the porphyrins is red shifted, Fig. 2. These red shifts provide evidence for the out of plane distortion of the porphyrins core, which causes a strong interaction to occur between the aryl rings and porphyrin π -system [2–10]. The UV-Vis spectra for the titration of the NOBF₄ into $[H_2t(4-CH_3p)p]$ (0.5:1, 0.75:1, 1:1, excess:1) showed a new absorption band at 448.3 nm, and shrinking of the 418.9 nm peak, which belong to the 1:1 molecular complex and $H_2t(4-CH_3p)p$, respectively. The spectrum of the 0.5:1 NOBF₄-H₂t(4-CH₃p)p reaction mixture clearly demonstrates the superimposition of the [H₂t(4-CH₃p)p] and $[H_2t(4-CH_3p)p(NO)]BF_4$ spectra. The employment of an excess of NOBF₄ beyond the 1:1 mole ratio led to no detectable changes in the spectrum of the [H₂t(4-CH₃p)p(NO)]BF₄ complex. Consequently, The UV-Vis titration results showed that mole ratio of porphyrin to nitrosonium ion was 1:1.

3.2. ¹H and ¹³C NMR spectra

The ¹H NMR spectra of H_2 tpp and its molecular complex with NOBF₄ are shown in Fig. 3. When the amount of NOBF₄ is less than H_2 tpp, the spectra of the porphyrin and the related molecular complex are superimposed. An excess amount of NOBF₄ caused no change in the spectum of the 1:1 molecular complex. As a result, the molecular complex between H_2 tpp and NOBF₄ had 1:1 ratio.



Fig. 2. UV–Vis spectra of (a) $H_2 tpp$ (b) $[H_2 tpp(NO)]BF_4$ molecular complex in chloroform solution.



Fig. 3. ¹H NMR spectra of (a) H₂tpp (b) [H₂tpp(NO)]BF₄ molecular complex in CDCl₃.

Upon formation of the molecular complex, β -protons shift to upfield and the aryl protons shift to downfield. With the molecular complexation of meso-tetraarylporphyrins and nitrosonium ion, the NH protons signal small shifted to upfield and are observed at -2.76 to -2.90 ppm. The shift to upfield is similar to the molecular complexation of meso-tetraarylporphyrins with electron acceptor of BF₃ [10]. Weak hydrogen bonding between the F atoms of BF₃ and the hydrogen atoms of NH is suggested as main factor in the upfield shifts of NH signals [10]. However, it may more reasonable that high electronegativity of F atoms causes an increase in the shielding of the NH protons and in result the upfield chemical shifts. ¹H NMR spectral shifts upon molecular complexation of different meso-tetraarylporphyrins with NOBF₄ indicate that π -resonance effect is predominantly transmitted from aryl substituents to the porphyrin core in the molecular complexes [2–10].

The ¹³C NMR spectrum of H₂t(4-CH₃p)p shows six signals in the aromatic region: one broad signal for β -carbons (131.4 ppm) and five sharp signals (C₁ = 139.7, C₂ = 134.9, C₃ = 127.8, C₄ = 137.7 and C_{meso} = 120.5) [7,8]. The α -carbons peak at about 145 ppm is weak to be seen. ¹³C NMR spectrum of the molecular complex, [H₂t(4-CH₃p)p(NO)]BF₄, had seven signals in the aromatic region: 124.2 (C_{meso}), 130.1 (C_{β}), 130.5 (C₃), 138.3 (C₁), 139.9 (C₂), 141.9(C₄), 147.3 (C_{α}). Molecular complexation of H₂t(4-CH₃p)p with NOBF₄ sharpens the α -carbon signal. Further, it causes an upfield shift in C_{β} and C₁ signals and a downfield shift in the lines of C_{meso}, C₂, C₃, C₄. Molecular complexation of H₂t(4-CH₃p)p with various acceptors causes the similar changes in the ¹³C NMR spectra [2,3,7,8].

3.3. Molar conductivity measurements

The UV–Vis, ¹H NMR (except for the N–H chemical shift) and ¹³C NMR spectra of the molecular complexes are similar to the correspondence spectra of the their diprotonated porphyrin species [14], but the molar conductivities of $[H_2t(4-Xp)p(NO)]BF_4$ complexes (in acetonitrile) and $[H_4t(4-Xp)p]Cl_2$ (in methanol) were completely different. The measurements of molar conductivity showed that the molecular complexes were 1:1 electrolytes whereas the diprotonated porphyrins were 1:2 electrolytes [15]. The remarkable spectral correspondence between the molecular complexes and their diprotonated species is related to analogous tilted porphyrin core structures in two species.

3.4. FT-IR spectra

Nitrosonium ion (NO⁺) shows a band around 2200 cm⁻¹ that is assigned to N \equiv O stretching vibration [16]. In the molecular complexes, [H₂t(4-CH₃p)p(NO)]BF₄, it has been seen that stretching vibration of the NO⁺ shifted to lower frequencies and were observed around 1285–1295 cm⁻¹. This band is related to stretching vibration of N–O single bond. Nitrosonium ion has an empty π^* orbital and is accepted two lone electron-pairs from two pyrrolic nitrogens of the meso-tetraarylporphyrins. On the other hand, meso-tetraarylporphyrins show NH stretching band around 3320 cm⁻¹ [17], that upon the molecular complexation with NOBF₄ is lost. This may be related to hydrogen bonding between hydrogen atoms of N–H and one F atom of BF₄⁻⁻ in the molecular complexes.

3.5. Proposition of the structure

The UV–Vis, ¹H NMR and ¹³C NMR correspondences between spectral data of the molecular complexes of meso-tetraarylporphyrins with σ - or π -acceptors or diprotonated species and [H₂t(4-CH₃p)p(NO)]BF₄ suggests a similar structure for the porphyrin core in all of those species, with non-coplanar pyrrole rings tilted alternatively up and down. This conformation causes the lone pairs of two pyrrolic nitrogens to act as the electron donors to one NO⁺ cation, which is located above or below the mean plane of the porphyrin, and so two hydrogen atoms of pyrroles (N–H) are located on the other side of the porphyrin plane (Fig. 4). In the proposed structure, the bond between oxygen and nitrogen atoms is single and a negative charge locates on the oxygen atom of nitrosonium ion.

Nitrosonium ion is a strong electrophile and can be add to aromatic rings, but some evidences showed that nitrosonium ion interacts to pyrrolic nitrogens and nitrosation of aryl rings was not done in our reaction system. Firstly, the molecular complexes decomposed to the related poprhyrins by adding water to solution of those in chloroform. Secondly, the ¹H NMR spectra of the molecular complexes were quite symmetry (a singlet for β -hydrogens, two doublets for ortho- and meta-hydrogens) whereas ¹H NMR spectra of porphyrins contain NO group on the aryl rings are unsymmetry. Consequently, in our reaction system is only occurred the molecular complexation with the pyrrolic nitrogens.

The presence of a singlet for β -protons in the ¹H NMR spectrum of [H₂tpp(NO)]BF₄ molecular complex is in contrast to unsymmetrical pyrrole rings in the proposed structure (Fig. 3b). Because the



Fig. 4. Only the tetrahedrally tilted pyrrolenine nitrogens of a porphyrin core are shown. Two pyrrolenine nitrogen atoms act as electron donors to a nitrogen atom of nitrosonium ion and BF_4^- is as counter ion.

ring inversion of the tilted core conformation of the porphyrin is fast on the NMR time scale [2,3,10].

4. Conclusion

The reaction of NOBF₄ with meso-tetraarylporphyrins (H₂t(p-Xp)p) produced green molecular complexes, [H₂t(4-Xp)p(NO)]BF₄. The results of UV–Vis, ¹H NMR (β - and aryl protons) and ¹³C NMR spectra showed tilted porphyrin core of the produced compounds was similar to porphyrin diacids [14] and the molecular complexes of meso-tetraarvlporphyrins with various acceptors [2-10]. Consequently, two nitrogen atoms of pyrrolic in porphyrin act as electron donors to a nitrosonium ion.

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