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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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ABSTRACT

$NOBF_4$ reacts with para-substituted meso-tetraarylporphyrins, $H_2t(4\text{-}Xp)p$, at room temperature for formation of green molecular complexes, $[H_2t(4\text{-}Xp)p(NO)]BF_4$. Mole ratio for the porphyrins and nitrosonium ion in the molecular complexes was 1:1, $[H_2T(4\text{-}X)PP(NO)]BF_4$. FT-IR, UV–Vis, ($^1H$ and ^{13}C) 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.

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 nitrosonium ion in the molecular complexes was 1:1, $[H_2t(4\text{-}Xp)p(NO)]BF_4$. 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.

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 (CH_3, OCH_3, Cl, $CH(CH_3)_2$) (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 ^{13}C NMR spectra of porphyrins and those molecular complexes in $CDCl_3$ solvent. The residual $CHCl_3$ in the 99.8% atom $CDCl_3$ 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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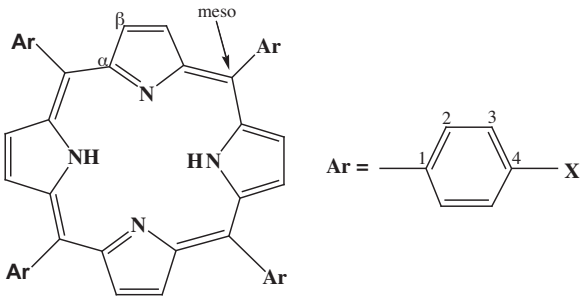

Fig. 1. Meso-tetraarylporphyrins, H_2t(Xp)p.

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 $NOBF_4$ 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. [H_2tpp(NO)]BF_4

Anal. Calc. for $C_{44}H_{30}N_5OBF_4$: C, 72.2; H, 4.4; N, 9.6. Found: C, 71.3; H, 4.0; N, 9.2%. UV–Vis ($CHCl_3$): 445.5, 661.5. ^{1}H NMR ($CDCl_3$): 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} cm^2 mol^{-1}.

2.2.2. [H_2t(4-CH_3p)p(NO)]BF_4

Anal. Calc. for $C_{48}H_{38}N_5OBF_4$: C, 73.2; H, 4.9; N, 8.9. Found: C, 72.1; H, 4.5; N, 8.6%. UV–Vis ($CHCl_3$): 448.3, 669.4. ^{1}H NMR ($CDCl_3$): δ −2.80 (s, 2H, NH), δ 2.79 (s, 12H, CH_3), 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} cm^2 mol^{-1}.

2.2.3. [H_2t(4-$CH(CH_3)_2$p)p(NO)]BF_4

Anal. Calc. for $C_{56}H_{54}N_5OBF_4$: C, 74.7; H, 6.1; N, 7.8. Found: C, 73.5; H, 5.8; N, 7.4%. UV–Vis ($CHCl_3$): 446.8, 661.9. ^{1}H NMR ($CDCl_3$): δ −2.90 (s, 2H, NH), δ 1.59–1.61 (s, 12H, CH_3), 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): ν_{NH} (~3320 cm^{-1}). Λ_M (in acetonitrile) = 158.0 Ω^{-1} cm^2 mol^{-1}.

2.2.4. [H_2t(4-OCH_3p)p(NO)]BF_4

Anal. Calc. for $C_{48}H_{38}N_5O_5BF_4$: C, 67.7; H, 4.5; N, 8.2. Found: C, 66.5; H, 4.2; N, 8.0%. UV–Vis ($CHCl_3$): 453.0, 686.8. ^{1}H NMR ($CDCl_3$): δ −2.76 (s, 2H, NH), δ 4.17 (s, 12H, OCH_3), δ 8.52–8.54 (d, 8H, o), δ 7.54–7.56 (d, 8H, m), δ 8.58 (s, 8H, β). IR (KBr): ν_{NH} (~3320 cm^{-1}). Λ_M (in acetonitrile) = 149.7 Ω^{-1} cm^2 mol^{-1}.

2.2.5. [H_2t(4-Clp)p(NO)]BF_4

Anal. Calc. for $C_{44}H_{26}N_5OBF_4$: C, 60.8; H, 3.0; N, 8.1. Found: C, 59.7; H, 2.7; N, 7.8%. UV–Vis ($CHCl_3$): 448.8, 663.8. ^{1}H NMR ($CDCl_3$): 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): ν_{NH} (~3320 cm^{-1}). Λ_M (in acetonitrile) = 133.1 Ω^{-1} cm^2 mol^{-1}.

2.3. Diprotonation of the meso-tetraarylporphyrins

To H_2t4-(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 (Λ_M = 165 Ω^{-1} cm^2 mol^{-1}), [H_4t(4-CH_3p)p]Cl_2 (Λ_M = 204 Ω^{-1} cm^2 mol^{-1}), [H_4tpp]Cl_2 (Λ_M = 213 Ω^{-1} cm^2 mol^{-1}), [H_2t(4-Clp)p]Cl_2 (Λ_M = 199 Ω^{-1} cm^2 mol^{-1}), [H_4t(4-$CH(CH_3)_2$p)p]Cl_2 (Λ_M = 179 Ω^{-1} cm^2 mol^{-1}).

3. Results and discussion

3.1. UV–Vis spectra

An evidence for formation of the molecular complexes of meso-tetraarylporphrins and $NOBF_4$ 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 $NOBF_4$ to free base [H_2t(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 $NOBF_4$ 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 $NOBF_4$-H_2t(4-CH_3p)p reaction mixture clearly demonstrates the superimposition of the [H_2t(4-CH_3p)p] and [H_2t(4-CH_3p)p(NO)]BF_4 spectra. The employment of an excess of $NOBF_4$ beyond the 1:1 mole ratio led to no detectable changes in the spectrum of the [H_2t(4-CH_3p)p(NO)]BF_4 complex. Consequently, The UV–Vis titration results showed that mole ratio of porphyrin to nitrosonium ion was 1:1.

3.2. ^{1}H and ^{13}C NMR spectra

The ^{1}H NMR spectra of H_2tpp and its molecular complex with $NOBF_4$ are shown in Fig. 3. When the amount of $NOBF_4$ is less than H_2tpp, the spectra of the porphyrin and the related molecular complex are superimposed. An excess amount of $NOBF_4$ caused no change in the spectum of the 1:1 molecular complex. As a result, the molecular complex between H_2tpp and $NOBF_4$ had 1:1 ratio.

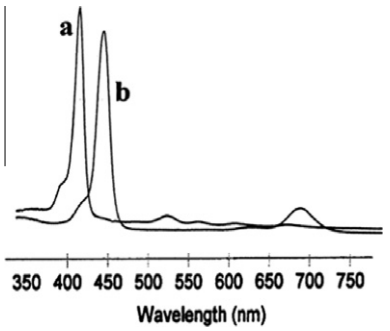

Fig. 2. UV–Vis spectra of (a) H_2tpp (b) [H_2tpp(NO)]BF_4 molecular complex in chloroform solution.