

Synthesis, spectral and electrochemical redox properties of *N*-methyl fused nickel(II) porphyrin

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ABSTRACT: *N*-methyl fused nickel(II) porphyrin was synthesized by a facile synthetic route in excellent yield. The effect of the electron-donating methyl group on spectral and electrochemical redox properties was analyzed by comparing the electrochemistry with that of its precursors. *N*-methylated fused nickel(II) porphyrin exhibited a red-shifted absorption spectrum ($\Delta\lambda_{max} = 6-13$ nm) and a 180 mV anodic shift in the first ring oxidation as well as a 210 mV shift in reduction with respect to its Ni(II)-fused porphyrin precursor (Ni^{II}-(NH)TPP). However, the absorption spectral features and redox potentials of *N*-methyl fused nickel(II) porphyrin are marginally shifted as compared to its immediate precursor, β -formyl Ni(II)-fused porphyrin. Notably, Ni(II)(N-CH₃)(CHO)TPP exhibited a third oxidation at 1.51 mV, corresponding to oxidation of Ni(II) to Ni(III) due to the presence of "push–pull" β substituents.

KEYWORDS: synthesis of fused porphyrins, *N*-methylation, spectral and electrochemical properties.

INTRODUCTION

Porphyrins are aromatic, highly conjugated molecules with high thermal and chemical stabilities [1-3]. They have many intriguing properties, and hence nature has chosen them for many important life processes and functions [4, 5]. Porphyrinoids play important roles in oxygen transport [6] and photosynthesis [7, 8] and also act as cofactors to many enzymes like cytochromes [9] and methyl coenzyme reductase [10]. They have also been exploited by scientists for use in different material and medicinal applications such as catalysis [11], artificial light harvesting [12], supramolecular assemblies [13], sensing [14], nonlinear optics [15] and drugs [16]. The properties of porphyrins can be tailored for specific functions by appending appropriate meso and/ or β substituents [17, 18]. The nature and number of the substituents affect the physicochemical and redox properties of the porphyrins [19]. Their properties can also be changed by extending the π -conjugation in various ways such as fusion, extension and dimerization [20].

 π -Extended porphyrins have useful applications in the fields of solar energy harvesting and photodynamic therapy (PDT). π -Extended porphyrins formed by dimerization using different linkers were known as early as 1970 [21]. Since then, such porphyrin dimers/polymers have been widely explored [22, 23]. Fused porphyrins with polycyclic aromatic hydrocarbons are one of the most promising candidates in the field of molecular electronics and molecular nanotechnology since they contain heteroatoms and can mimic doped graphene. To date, a number of systems have been prepared by fusion of benzene, naphthalene, pyrene, azulene, anthracene, corannulene and other aromatic moieties to the meso- and β -positions of the porphyrin macrocycle [24–26]. Fusion of aromatic moieties with porphyrin core leads to extensive π -delocalization, leading to enhanced absorption and efficient emission in the near IR region [27]. Different approaches have been used to synthesize fused porphyrins. For example, oxidative ring closure is particularly important for fusion of aromatic moieties [28]. Ziessel et al. reported the formation of triphenylene-fused porphyrins using the same protocol. Similarly, Osuka et al. have reported the formation of highly planar diarylaminefused porphyrins with highly stable radical cations [29]. Quinone-fused porphyrins have also been reported for clinical applications for photoacoustic imaging of tumors and cardiovascular tissues [30]. In our quest to develop novel porphyrins for PDT and DSSC applications, we

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Chart 1. Molecular structures of the synthesized porphyrins



Scheme 1. Synthesis of N-methylated porphyrin Ni(II)(N-CH₃)(CHO)TPP

hereby report the synthesis of an *N*-methylated fused Ni(II) porphyrin (Ni(II)(N-CH₃)(CHO)TPP) along with comparing its electrochemical properties with its parent porphyrin derivatives (Chart 1).

RESULTS AND DISCUSSION

N-methylated nickel(II) porphyrin, Ni(II)(N-CH₃) (CHO)TPP was synthesized in 94% yield using a modified literature method [31]. The final step involved *N*-methylation in DMF using CH₃I as the methylating agent and K_2CO_3 as base (Scheme 1). Ni(II)(N-CH₃) (CHO)TPP was characterized by UV-vis, NMR and

MALDI-TOF mass spectroscopic techniques (Fig. 1 and Figs S1–S3, SI).

Absorption and electrochemical properties

The UV-vis absorption spectra of Ni(II)(N-CH₃) (CHO)TPP and its precursors Ni(II)(NH)TPP and Ni(II) (NH)(CHO)TPP were measured in CHCl₃ at 298 K, and the corresponding spectral data is presented in Table 1. The Soret band was observed in the range of 420–455 nm and Q bands in the range of 550–635 nm. A marginal red shift ($\Delta\lambda_{max} = 6-13$ nm) was observed when the methyl group was introduced at the nitrogen of Ni(II)(NH) (CHO)TPP to obtain Ni(II)(N-CH₃)(CHO)TPP which



Fig. 1. ¹H NMR spectrum of Ni(II)(N-CH₃)(CHO)TPP in CDCl₃ at 298 K

Table 1. UV-vis absorption spectral data of fused porphyrins in CHCl₃ at 298 K

| Porphyrin | B and Q bands, λ_{max} , nm | | | | |
|------------------------------------|--|--|--|--|--|
| Ni(II)(NH)TPP | 421 (7.07 × 10 ⁴), 554 (6.02 × 10 ³), 588 (8.71 × 10 ³), 625 (1.51 × 10 ⁴) | | | | |
| Ni(II)(NH)(CHO)TPP | 448 (1.20×10^{5}), 561 (1.00×10^{4}), 627 (1.58×10^{4}) | | | | |
| Ni(II)(N-CH ₃)(CHO)TPP | 454 (1.14×10^{5}), 574 (7.41×10^{3}), 633 (1.38×10^{4}) | | | | |

Values in parentheses refer to ε in Lmol⁻¹ · cm⁻¹.

exhibited the electron releasing effect of methyl group as shown in Fig. S1, SI.

¹H NMR and ¹³C NMR of Ni(II)(N-CH₃)(CHO)TPP recorded in CDCl₃ are shown in Fig. 1 and Fig. S2, SI. The signals obtained match with the proposed structure. The peaks around 9.5 ppm and 4.6 ppm correspond to aldehyde and *N*-methyl functionalities. The MALDI mass spectrum of Ni(II)(N-CH₃)(CHO)TPP is shown in Fig. S3, SI. The obtained molecular ion peak matches with the proposed structure.

Electrochemical redox potentials of the porphyrins were recorded in CH_2Cl_2 containing 0.1M TBAPF₆ as the supporting electrolyte at 298 K. The comparative cyclic voltammograms are shown in Fig. 2 and the relevant data is given in Table 2. The first oxidation potential of the porphyrins varies in the range of 0.57 to 0.78 V, whereas the first reduction potential varied from -0.95 to -1.17 V. The first ring oxidation potential of CHO-appended *N*-fused porphyrin Ni(II)(NH)(CHO)TPP was 210 mV, anodically shifted as compared to the porphyrin devoid of the formyl group, Ni(II)(NH)TPP. This is attributed to the electron withdrawing effect of the formyl group. Similarly, Ni(II)(NH)(CHO)TPP was 220 mV harder to reduce compared to Ni(II)(NH)TPP. The difference between the first oxidation potentials of Ni(II)(NH) (CHO)TPP and Ni(II)(N-CH₃)(CHO)TPP was only 30 mV. Similarly the difference between their first reduction potentials was only 10 mV. Notably, Ni(II)(N-CH₃) (CHO)TPP exhibited a third oxidation potential at 1.51 V, corresponding to metal centered oxidation of Ni(II) to Ni(III) due to the presence of push–pull β substituents.

EXPERIMENTAL SECTION

Chemicals and instrumentation

Pyrrole, benzaldehyde, propionic acid, $Ni(OAc)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and CH_3I were purchased from HiMedia,



Fig. 2. Comparative cyclic voltammograms of fused porphyrins in CH_2Cl_2 at 298 K

Table 2. Electrochemical redox potentials (in V vs. Ag/AgCl) of fused porphyrins in CH_2Cl_2 at 298 K

| Porphyrin | Oxidation (V) | | | Reduction (V) | | ΔE |
|--|---------------|------|------|---------------|-------|------------|
| | Ι | II | III | Ι | II | (V) |
| Ni(II)(NH)TPP | 0.57 | 1.05 | _ | -0.95 | -1.21 | 1.52 |
| Ni(II)(NH)(CHO)TPP | 0.78 | 1.12 | _ | -1.17 | -1.48 | 1.95 |
| Ni(II)(N-CH ₃)(CHO) TPP | 0.75 | 1.07 | 1.51 | -1.16 | -1.51 | 1.91 |

Scan Rate = 0.1V/s. Pt working, Pt wire counter electrode and Ag/AgCl reference electrode were used.

India and used as received. DMF, NaHCO₃ and K_2CO_3 were purchased from Rankem, India and used as received. POCl₃, P(OEt)₃, Acetic Anhydride were received from Thomas Baker, India. Glacial Acetic acid was received from Merck, India. TBAPF₆ was recrystallized twice with ethanol and vacuum dried before use. Different solvents were dried over P₂O₅ prior to use.

Optical absorption spectra were recorded using an Agilent Cary 100 spectrophotometer using a pair of quartz cells of 3.5 mL volume and 10 mm path length. ¹H NMR spectra were recorded using a JEOL ECX 400 MHz spectrometer using CDCl₃ as solvent. Mass spectra were measured using a Bruker Ultraflextreme-TN MALDI-TOF-MS spectrometer using HABA, [2-(4'-hydroxy-benzeneazo)benzoic acid] as matrix. Electrochemical

measurements were carried out using a CH instrument (CH 620E). A three-electrode assembly consisting of a platinum working electrode, Ag/AgCl as a reference electrode and Pt-wire as a counter electrode was used. Concentration of all the porphyrins was maintained at 1 mM during the electrochemical studies. All measurements were performed in triple-distilled CH₂Cl₂ containing 0.1 M TBAPF₆ as the supporting electrolyte, which was degassed by argon gas purging.

Synthesis of Ni(II)(N-CH₃)(CHO)TPP. 50 mg (0.069 mmol) of Ni(II)(NH)(CHO)TPP was taken in a 250 mL round-bottomed flask containing 15 mL of DMF. K_2CO_3 (200 mg, 20 equiv.) and 25 µL of methyl iodide (20 equiv.) were added to the above solution. The resulting solution was stirred for 5 h. After completion of the reaction, 100 mL of distilled water was added. The precipitated porphyrin was filtered through a G4 crucible. Recrystallization was carried out using a CHCl₂/MeOH mixture (1:4, v/v). Yield of the porphyrin was found to be 94% (50 mg). UV-vis (CHCl₃): λ_{max} in nm (ϵ in Lmol⁻¹cm⁻¹): 454 (1.14 \times 10⁵), 574 (7.41 \times 10³), 633 (1.38×10^4) ; ¹H NMR: δ (ppm): 9.23, 8.76 (2d, 1 + 1H, J = 4Hz, pyrrole), 8.55 (AB, 2H, J = 4Hz, pyrrole), 8.50 (AB, 2H, J = 4Hz, pyrrole), 8.79 (dd, 1H, J = 8Hz, cyclized phenyl), 8.19 (dd, 1H, J = 8Hz, cyclized phenyl), 8.04– 7.92 (m, 6H, H_{ortho}), 7.77-7.64 (m, 11H, 9H_{meta+para} + 2H cyclized phenyl), 4.62 (s, 3H, CH₃), 9.58 (s, 1H, CHO); ¹³C NMR (100 MHz; CDCl₃): 186.00, 144.63, 143.80, 141.71, 140.40, 138.00, 133.46, 128.44, 127.13, 122.35, 116.80, 114.10, 113.03, 29.73 ppm; MALDI-TOF-MS (m/z): found 726.23 [M]⁺, calcd. 726.44: Anal. Calcd for C₄₆H₂₉N₅NiO · 0.5CHCl₃: C, 76.05; H, 4.02; N, 9.64. Found: C, 75.93; H, 3.86; N, 8.99.

CONCLUSIONS

N-methyl fused porphyrin, (Ni(II)(N-CH₃)(CHO)TPP), was synthesized in excellent yield and its spectral and electrochemical redox properties compared to known fused porphyrins, Ni(II)(NH)(CHO)TPP and Ni(II)(NH) TPP. Ni(II)(N-CH₃)(CHO)TPP exhibited considerable red shift ($\Delta\lambda_{max} = 12-33$ nm) in its absorption spectrum as compared to Ni(II)(NH)TPP, whereas a marginal red shift ($\Delta\lambda_{max} = 6 \text{ nm}$) was observed with respect to Ni(II) (NH)(CHO)TPP. Ni(II)(N-CH₃)(CHO)TPP exhibited a 180 mV anodic shift in the first oxidation as compared to Ni(II)(NH)TPP due to the presence of electron-withdrawing β -formyl functionality, but a 30 mV cathodic shift with respect to Ni(II)(NH)(CHO)TPP due to the electrondonating nature of N-methyl substituent. The redox tunability was achieved due to 'push-pull' β substituents at the porphyrin periphery. Notably, Ni(II)(N-CH₃)(CHO) TPP exhibited a third oxidation at 1.51 mV, corresponding to oxidation of Ni(II) to Ni(III) due to the presence of 'push-pull' β substituents. The utilization of Ni(II) (N-CH₃)(CHO)TPP in photodynamic therapy (PDT), nonlinear optics (NLO) and sensor applications is in progress.

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Supporting information

Figures S1–S3 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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