Research Article

Synthesis, Characterization, and Spectroscopic Studies of Bis-(*meso*-4-methoxyphenyl)-Benziporphyrin and Its Pd-Metal Complex

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Benziporphyrin systems are widely explored, yet alternative improved synthetic routes towards these systems are needed. Here, a fairly and efficient synthesis of the free base and its metal complex is well designed. Dimethoxybenzene dicarbinol intermediate was prepared in excellent yields by reacting 4-methoxyphenylmagnesium bromide with isophthalaldehyde in diethyl ether. Reaction with equivalent pyrrole and pentafluorobenzaldehyde in the presence of trifluoroacetic acid (TFA), followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), provided good yields of bis-(*meso*-4-methoxyphenyl)-benziporphyrin. Metalation of the free base was performed using palladium(II) acetate salt in acetonitrile. All intermediates and the final products are fully characterized using NMR, HMRS, and UV-Vis spectroscopies and briefly discussed.

1. Introduction

The porphyrins are a remarkably adaptable family of tetrapyrrolic macrocycles, and various metal-porphyrin complexes have shown interesting biological activities, including oxygen transportation (hemoglobin), redox processes (cytochromes), and photosynthesis (chlorophylls). [1, 2]. Researchers have made several modifications to the parent skeleton and explored various applications and investigated UV-Vis absorption spectra properties corresponding to their structure [3–9]. Benziporphyrin derivatives are described for the first time in the 1990s. Benziporphyrins are a class of porphyrins in which one of the pyrrole moieties is substituted by a benzene ring where the benzene ring is connected either at 1,3- or 1,4-positions through replacing pyrrole subunits [10–13]. Presently, benziporphyrin and its derivatives attracted substantial attention and become a theme of interest in supramolecular chemistry [14].

Nearly all metals form coordination complexes with the porphyrin and its derivative nucleus, and in some cases, these exhibit valuable organometallic catalytic properties. Organometallic derivatives of benziporphyrin such as Cd, Zn, Hg, and Ni have been investigated and explored well [15, 16]. The proton NMR spectrum of the free base benziporphyrin shown in Figure 1 has no indication of aromatic properties of the ring [17–19]. Electron donating substituents, such as *tert*butyl- or methoxy-, promotes a diatropic property which is meaningfully improved upon protonation [17–20]. Furthermore, the physical property of benziporphyrins influenced by the positions of the substituents [21–25].

Incorporation of methoxy groups on the benziporphyrin ring at carbon 2-position will assist for better charge delocalization where the ring becomes a fully conjugated system. In delocalization, the conjugative capacity of the 6π electrons of benzene would decrease. From the above point of view, substituents and their position on the benzene ring could

FIGURE 1: Chemical structure of methoxybenzporphyrin resonance.

regulate the spectroscopic properties of benziporphyrins (Figure 1) [26]. The free base form of the methoxybenzporphyrin can be protonated by acidic solution; as a result the protonated species will be stabilized through the resonance of lone pair electrons of oxygen atoms of the methoxy-at the C-2 and C-4 positions. Thus, the incorporation of atoms with possible sets of substituents having delocalized electrons will have a fundamental impact on absorption. In this context, the incorporation of substitutes onto appropriate positions of the ring will allow enhancing the physical and chemical properties of the synthesized benziporphyrin. In this work, an efficient synthesis protocol of intermediate dicarbinol **3** is reported in excellent yield. Also, the target compounds benziporphyrin **2** and its metal complex **1** were synthesized and their spectroscopic characteristics were recorded well and briefly discussed.

2. General and Synthesis

2.1. Materials and Methods. ^1H -NMR and ^{13}C -NMR spectra were recorded on Bruker Avance 300 MHz and 100 MHz Bruker instrument spectrometers using TMS as the internal standard and chloroform- d_3 , acetonitrile- d_3 , acetone- d_6 , and DMSO- d_6 as deuterated solvents. Data are reported as follows: chemical shift in ppm (δ), multiplicity (*s*: singlet, *d*: doublet, *t*: triplet, *q*: quartet, *dd*: doublet of doublets), coupling constant *J* (Hz), integration, and assignment. Mass spectra were recorded on Voyager DE-STR MALDI-TOF (for higher molecular weights) and JEOL JMS-700 GC mass spectrometers. UV-Vis spectral studies were performed using Varian Cary 100 Conc. Spectrophotometer and were recorded between 900 and 200 nm. The optical studies were carried out with a quartz cuvette of the path length of 1 cm. Pyrrole was used after distillation under reduced pressure. All other solvents and chemicals were purchased from commercial sources and were used as such unless otherwise mentioned. Column chromatography was performed on silica gel with pore size 60 Å, 230–400 mesh particle size. The starting materials for the syntheses were purchased from Sigma-Aldrich, TCI, or Alfa Aesar. All UV-Vis titrations were performed using HPLC grade acetonitrile purchased from Aldrich.

2.2. 1,3-Bis[(4-methoxyphenyl)hydroxymethyl]benzene (3). 1,3-Bis[(4-methoxyphenyl)hydroxyl]benzene **3** was synthesized in one-pot preparation protocol through the

addition of 4-methoxyphenylmagnesium bromide (20 mL, 1M solution) in diethyl ether to an ether solution (100 mL) contacting isophthalaldehyde (1 g, 7.45 mmol). The mixture was stirred for 30 min and quenched with 1% H_2SO_4 (20 mL) followed by solid Na_2CO_3 was added until the liberation of CO_2 ceased. The organic phase is separated from the crude through filtration. The organic phase extracted and dried with MgSO_4 further concentrated under reduced pressure to afford crude 1,3-bis[(4-methoxyphenyl)hydroxyl]benzene as pale yellow oil. The crude was further purified using column chromatography (hexane:ethyl acetate = 4:1) to obtain 960 mg, in 96% yield.

^1H NMR (300 MHz, CDCl_3): δ = 7.39 (*s*, 1H, Ar-H), 7.23 (*d*, *J* = 8.0 Hz, 4H, Ar-H), 7.10–7.20 (*m*, 3H, Ar-H), 6.80 (*d*, 4H, *J* = 8.0 Hz, Ar-H), 5.71 (*d*, *J* = 4.0 Hz, 2H, OH), 5.59 (*d*, *J* = 4.0 Hz, 2H, *meso*-H), 3.70 (*s*, 6H, CH_3); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 159.37, 146.97, 139.05, 128.60, 125.58, 125.07, 114.44, 74.71, 55.71. MS Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4$ 350.1518, Found 350.0513.

2.3. 11,16-Bis(pentafluorophenyl)-6,21-di(4-methoxyphenyl)-benzporphyrin (2). 1,3-Bis(4-methoxyphenylhydroxyl)benzene (**3**) (280 mg; 0.8 mmol) in 300 mL chloroform was stirred for 10 min, while slowly bubbling nitrogen and a round-bottom flask were covered with aluminum foil. Then, freshly distilled pyrrole (160 μL ; 2.4 mmol) and pentafluorobenzaldehyde (198 μL ; 1.6 mmol) were added *via* syringe, followed by 0.20 mL of trifluoroacetic acid. The resulting mixture was stirred for 3 h at room temperature. The initially colorless solution turned orange and then became a deep red color. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.40 g; 6.0 mmol) was added and the mixture was stirred for an additional 1 h. The crude solution was evaporated under reduced pressure and the residue was purified on a silica gel column. Tetraphenylporphyrin and other unidentified brown side products were eluted first, followed by a dark green band corresponding to compound **2**. Recrystallization from chloroform-methanol mixture gave pure product 210 mg, 15% yield as a green powder.

^1H NMR (300 MHz, CDCl_3): δ = 10.38 (*s*, 1H, NH), 7.36 (*s*, 1H, Ar-H), 7.34 (*d*, *J* = 2.0 Hz, 4H, Ar-H), 7.25 (*m*, 1H, Ar-H), 7.01 (*m*, 4H, Ar-H), 6.98 (*dd*, *J* = 2.0 Hz, 2H, Ar-H), 6.87 (*d*, *J* = 5.0 Hz, 2H, pyrrolic-H), 6.63 (*s*, 2H, pyrrolic-H), 6.49 (*d*, *J* = 5.0 Hz, 2H, pyrrolic-H), 3.89 (*s*, 6H, CH_3); MS Calcd for $\text{C}_{48}\text{H}_{25}\text{F}_{10}\text{N}_3\text{O}_2$ 865.1787, Found 865.0500.

2.4. 6,21-Bis(4-methoxyphenyl)-6,21-di(pentafluorophenyl)-benzporphyrinato Palladium(II) (1). Dimethoxybenzporphyrin **2** (13.84 mg; 0.016 mmol) and palladium(II) acetate (9.5 mg; 0.042 mmol) in acetonitrile (10 mL) were refluxed for 3 h. The reaction mixture was allowed to cool to room temperature and then diluted to 25 mL with dichloromethane. The solution was washed with water and back-extracted with dichloromethane, organic layers were combined, and the solvent was evaporated under reduced pressure. The crude was purified by column chromatography, eluting with dichloromethane. A reddish-brown fraction was collected;

SCHEME 1: Synthesis of palladium-metal complex benziporphyrin **1**.

the solvent was evaporated using reduced pressure and residue recrystallized from chloroform/methanol mixture to obtain palladium complex porphyrin **1** in 60% as purple needles.

¹H NMR (300 MHz, CDCl₃): δ = 10.38 (s, 1H, NH), 7.36 (s, 1H, Ar-H), 7.34 (d, J = 2.0 Hz, 4H, Ar-H), 7.25 (m, 1H, Ar-H), 7.01 (m, 4H, Ar-H), 6.98 (dd, J = 2.0 Hz, 2H, Ar-H), 6.87 (d, J = 5.0 Hz, 2H, pyrrolic-H), 6.63 (s, 2H, pyrrolic-H), 6.49 (d, J = 5.0 Hz, 2H, pyrrolic-H), 3.89 (s, 6H, CH₃); MS Calcd for C₄₈H₂₃F₁₀N₃O₂Pd 969.0665, Found 968.9950.

3. Results and Discussion

Previously, various synthesis protocols towards the key intermediate dicarbinol with sequences of reactions were reported. Lash et al. reported the synthesis of dicarbinol through metal-halogen exchange reaction protocol [24, 27]. A new synthesis methodology was reported using phenyl lithium, an organometallic reagent reacted with isophthalaldehyde to afford dicarbinol [28]. Litman et al. reported sequential reactions to prepare the dicarbinol intermediate [25]. A fairly direct route to metal complex benziporphyrin was reported starting from the isophthalaldehyde and organomagnesium halide reagents. Starting from commercially available chemicals and using one pot preparation protocol, dicarbinol intermediate **3** was synthesized (Figures S1–S3 in the Supplementary Materials). The isophthalaldehyde subjected to the round bottom flask with diethyl ether solvent was stirred with 4-methoxyphenylmagnesium bromide; the reaction was quenched

using the addition of 1% sulfuric acid. To this crude, gradual addition of Na₂CO₃ solution develops carbon dioxide gases; the addition was continued until bubbling of the gas ceased. The organic layer was extracted and the crude was purified by column chromatography. Recrystallization using hexane/dichloromethane solvent mixture was conducted. The reaction of dicarbinol intermediate **3** with pyrrole and pentafluorobenzaldehyde in dry DCM in the presence of TFA, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), gave the benziporphyrin **2** as depicted in Scheme 1 (Figures S4–S6 in Supplementary Materials).

The crude was purified using column chromatography and further recrystallized from methanol-chloroform solvent mixture to obtain benziporphyrin **2** with a 15% yield. This approach has been adopted to prepare the free base more easily and with improved yields relative to previously reported works. Compound **2** was reacted with palladium(II) acetate in refluxing acetonitrile and followed by purification by column chromatography. The organometallic products **1** were isolated as deep red color (Figures S9–S11 in Supplementary Materials). In the proton NMR spectrum for **1** in CDCl₃, the meso protons afforded a 2H singlet at 7.15 ppm which is pyrrolic protons between the two pentafluorobenzene moieties, while the other pyrrolic protons gave rise to a 2H doublet at 6.90 ppm and 7.79 ppm, respectively. The methoxy protons are depicted at 3.99 ppm. The methyl-substituted system is too sterically crowded to easily allow the methoxy units to take on the required geometry, and palladium complex possesses a symmetrical

FIGURE 2: UV-Vis absorption spectral changes of benziporphyrin **2** (2.85×10^{-5} M, in CH_2Cl_2) upon titration with TFA.

FIGURE 3: ^1H NMR of benziporphyrin **2** and its Pd complex benziporphyrin **1** in CDCl_3 .

arrangement where the coordinated palladium(II) draws the individual rings together [27, 29, 30].

Here, the metal ion is located in the CNNN plane where tetracoordinated complex contains a metal-carbon bond which forces a coplanar position of the benzene ring. The free base and palladium-metal complex were titrated with trifluoroacetic acid using UV-Vis spectroscopy (Figure S12 in Supplementary Materials). The UV-Vis spectra for the free base (benziporphyrin **2**) of Soret-band absorption in chloroform gave λ_{max} at 425 nm; the *meso*-aryl substituents play a role for the significant bathochromic shift effect on the absorption properties [26]. The UV-Vis absorption of the dimethoxybenziporphyrin **2** was recorded with a black line, followed by the addition of 1% TFA in DCM with a red line

and regenerated free base **2** through the addition of base 1% TEA in DCM shown with a blue line (Figure S7 in Soret-band absorption). Here, the original spectrum is fully recovered by the addition of a qualitative equivalent of a triethylamine base.

Titration of porphyrin gave an essential chemical change, which is more noticeable when acid was added; proton goes to the substituent or to the core nitrogen atom to generate the conjugated acid species. The phenomena observed such as optical, solubility, and spectroscopy properties of the benziporphyrins were well investigated and briefly discussed [26]. Acid titration of porphyrin **2** leads to a redshift (71 nm) of the Soret band; in the meantime, its absorption intensity gradually decreased with further addition of acid. Finally, the

Soret band at 448 nm disappeared with the new band appearing at 519 nm (Figure 2 and Figure S8 in Supplementary Materials).

Further, the Q band at 649 nm is broadened and its intensity is gradually decreased while increasing the acid titration. In the course of acid titration, a new and strong absorption band was observed at 849 nm. The absorption intensity of this band is progressively strengthening. Here, the substituents role revealed that remarkable absorption properties of the synthesized free base were observed compared to tetraphenyl benziporphyrin [26, 27]. Methoxy groups at *meso*-positions of the synthesized porphyrin interacted with the ring through the delocalization of the lone pair electrons. Nowadays, metal-based drugs have tremendous attention in the recent decades due to their advanced properties and benefits in biomedical therapeutic and diagnostic systems. Porphyrin-metal complexes have potential applications as photodynamic therapy (PDT) [29]. The proton NMR spectra for palladium(II) benziporphyrin **1** recorded in CDCl₃ gave resonances for the pyrrolic protons further downfield than the corresponding free bases benziporphyrin **2** (Figure 3). In addition, the internal pyrrolic proton disappeared due to the coordination formed with the Pd-metal.

4. Conclusions

Bis(*meso*-4-methoxyphenyl)-benziporphyrin and its palladium-metal complex were synthesized using three components in the one-pot method. Their proton NMR spectroscopic properties and UV-Vis absorption pattern were studied. The key intermediate dicarbinol was prepared easily from commercially available materials in excellent yields. This specific study will be further strengthened and be additional evidence to the researchers how the substituents play a significant role to affect the optical and spectroscopic properties of the synthesized porphyrin. Furthermore, from the UV-Vis acid titration spectrum, we confirmed that the palladium complex exhibited strong metal-CNNN coordination in the system. This property will provide additional information and input where the synthesized benziporphyrin could become a good candidate for organometal catalyst. Last but not least, from this study, we found that benziporphyrins are still a potential unexplored territory in porphyrin chemistry.

Data Availability

The data used to support the findings of this study are included within the article and also submitted as Supplementary Materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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Supplementary Materials

See supplementary data for the following information: (1) HRMS, MALDI-TOF ¹H NMR, and ¹³C NMR spectra of all compounds (Figures S1–S6, S9, and S10). (2) UV-Vis spectra of all compounds (Figures S7, S8, S11, and S12). (*Supplementary Materials*)

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