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Synthesis, Characterization and Electrochemical Behavior of Zinc(II) 5,10,15,20-(tetra-2-naphthalenyl)porphyrin in Presence of Triphenylphosphine (PPh₃) and Triphenylphosphine Oxide (OPPh₃)

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Citation: Sarr M.M., Dimé A.K.D., Diouf G. and Boye M. B. (2025) Synthesis, Characterization and Electrochemical Behavior of Zinc(II) 5,10,15,20-(tetra-2naphthalenyl)porphyrin in Presence of Triphenylphosphine (PPh3) and Triphenylphosphine Oxide (OPPh3), J. Mater. Environ. Sci., 16(6), 982-994 Abstract: The metallation of 5,10,15,20-(tetra-2-naphthalenyl)porphyrin (H2P) in the presence of Zn(OAc)₂.2H₂O leads to the zinc(II) 5,10,15,20-(tetra-2-naphthalenyl)porphyrin **ZnP** as attested by MALDI-TOF mass spectrometry, UV-vis absorption spectroscopy and NMR analyses. The yield of 90% obtained at the end of reaction. The electrochemical behaviour of **ZnP** in presence of triphenylphosphine (PPh₃) and triphenylphosphine oxide (OPPh₃) was examined by means of cyclic voltammetry (CV). In presence of 20 eq of PPh₃, the voltammogram of **ZnP** exhibits an irreversible and more intense peak. Accordingly, the presence of PPh₃ can favor the substitution in β position. The electrochemical behaviours of **ZnP** were also investigated in the presence of OPPh₃. Interestingly, the peak remains reversible but is shifted towards less positive potential.

Keywords: Zinc, Porphyrin; Cyclic voltammetry, Triphenylphosphine, Oxide

1. Introduction

Porphyrins have been the subject of intense researches in numerous research fields due to their essential role in natural processes such as photosynthesis and oxygen transport in blood (Paske *et al.*, 2011; Ishihara *et al.*, 2014; Kazemi *et al.*, 2015; Schnetz *et al.*, 2025; Swoboda *et al.*, 2025). This macrocycle finds applications in material science, (electro)catalysis and energy converting devices (Huang *et al.*, 2015; Xue *et al.*, 2025; Zhuang *et al.*, 2025; Yong *et al.*, 2025). These properties can be easily adapted to specific applications by introducing new metal ions in the center of the porphyrin ring or by chemical chain functionalization (Jurow *et al.*, 2010; Verma *et al.*, 2025). The zinc porphyrins have also attracted much attention, both because the zinc is easy to introduce into the macrocycle and the porphyrins can generally stabilize for several years (Dimé *et al.*, 2012; Devillers *et al.*, 2013). Nucleophilic substitution of porphyrins in the β and/or *meso* positions is much studied in the literature (Padilla *et al.*, 1976; Smith *et al.*, 1979; Bhardwaj *et al.*, 2025). Numerous examples are known of reaction with nucleophiles after

the electrochemical generation of porphyrins cation radicals (Shine *et al.*, 1979; Malek *et al.*, 1991; Dimé *et al.*, 2018).

Porphyrins are strongly studied to find more than 80,000 articles on Scopus from 1890 to present. >56,000 articles from 2000 to 2024 traduce the high concern of researchers. This high production incited us to launch a bibliometric analysis based on Scopus to show the most published authors, their countries and the collaboration (José de Oliveira et al., 2019; N'diaye *et al.*, 2022; Chakir *et al.*, 2023; Duan, 2024; Öztürk *et al.*, 2024; Kachbou *et al.*, 2025). Figure 1 indicated the results of the Scopus search by yearly publication for the dataset period of 2000–2024. During this period of more than 25 years, scientific production increased, to reach the pic in 2009 (over 2900 articles) and in 2024, 2700 articles which are These articles are divided between chemistry and different applications, the majority of which are in pharmacy and medicine (Figure 2).



Figure 1. Yearly publications using Porphyrins (2000–2024).



Figure 2. Distribution of articles by domains and Fields

The study also shows that China is the most productive country, followed by the United States, Japan, Germany, India as shown in Figure 3. China exceeded 12,600 articles while the US <12,000. We notice that there is dominance in many scientific fields in recent years. Figure 4 shows the 10 most prominent authors in the research area on Porphyrins. The Japanese Osuka published more than 500 papers on Porphyrins among 864 articles on Scopus and an H-index of 97 and around 41,000 citations by 15,440 documents. The second author is Kim with more than 300 articles, and followed by Kadish, Karl M. University of Houston, United States Scopus ID: 7004463259, having 352 articles (total 666 articles, H-index= 81 and 26,700 citations). We observe that the most published (>5,700 citations) in Science (Yella *et al.*, 2011).



Figure 3. The 10 ranked countries in the research area on Porphyrins



Figure 4. The 10 most prominent authors in the research area on Porphyrins

Researchers pointed out that the complexation with transition metals can enhance the physiological effect of a molecule, modify its safety profile, and even imbue it with novel attributes of interest in the fields of medicine and pharmacy (Sadiki *et al.*, 2015; Jalal *et al.*, 2020; Todorov & Kostova, 2024). The bibliometric analysis can be completed by associating complex to porphyrin, to see the evolution of the wide application of this kind of compounds in medicine and others fields. More

than 20,000 articles were gathered using Scopus. VOS viewer mapping can be used to show more visibility in the 2000-2024 period, where 14,950 articles were published. This analysis enables the mapping and expansion of knowledge on porphyrin complex domain, to show connections between the main publications, authors, institutions. The authors are presented by colored nodes indicating that Osuka A. with largest red node and interconnecting with other collaborators as shown in Figures 5 & 6. Figure 7 indicates that the US is the most profiler in using complexes of porphyrin compounds for various applications, followed by China, Japan and Germany.



Figure 5. VOS viewer mapping of authors in the 2000-2024 period







Figure 7. VOS viewer mapping of Countries and Regions in the 2000-2024 period

Some nucleophile can have a double role namely substitution and coordination such as triphenylphosphine and pyridine (Devillers *et al.*, 2011; Dimé *et al.*, 2014). Triphenylphosphine and pyridine are considered good ligands on the magnesium(II) and zinc(II) metals of porphyrins (Devillers *et al.*, 2013; Dimé *et al.*, 2018). The resulting porphyrins exhibit good solubility in common organic solvents contrary to the free bases of porphyrins. This coordinated porphyrin opens the way to the application of a large variety of metalloporphyrins. This possibility of coordination may be the key advantage of allowing the design of organic pollutants sensors. More recently, we reported the coordination of PPh₃ on the trisubstituted porphyrin, comprising only one free *meso*-position (Dimé *et al.*, 2018). Phosphine oxidation can easily lead to the formation of phosphine oxide which is widely use in pesticides (Pei *et al.*, 2023). Therefore, its presence in water can cause environmental pollution and affect human health (Guo *et al.*, 2024).

In this context, this work focuses on the behavior in cyclic voltammetry of zinc(II) 5,10,15,20-(tetra-2-naphthalenyl)porphyrin **ZnP** comprising none free *meso*-position in presence of triphenylphosphine (PPh₃) and triphenylphosphine oxide (OPPh₃).

2. Experimental section

2.1. Materials

5,10,15,20-(tetra-2-naphthalenyl)porphyrin (**H2P**) is a commercially available compound. Tetraethylammonium hexafluorophosphate (TEAPF₆, Fluka puriss, electrochemical grade, \geq 99.0%), triphenylphosphine (PPh₃) (Sigma-Aldrich, 99%) and triphenylphosphine oxide (OPPh₃) (Sigma-Aldrich, 99%) and triphenylphosphine oxide (OPPh₃) (Sigma-Aldrich, 98%) were used as received. CH₂Cl₂ (Carlo Erba 99.5%) and CH₃CN (SDS, Carlo Erba, HPLC gradient 99.9%) were distilled from P₂O₅ and CaH₂ respectively.

2.2. Instruments and Methods

Mass spectra were obtained on a Bruker ProFLEX III spectrometer (MALDI-TOF) using dithranol as a matrix.

NMR spectra were measured on a BRUKER 300, 500 or 600 MHz spectrometer (Avance III Nanobay, Avance III, Avance II, respectively). The reference was the residual non-deuterated solvent.

All electrochemical manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon at room temperature (T = $20^{\circ}C \pm 3^{\circ}C$). The supporting electrolyte was degassed under vacuum before use and then dissolved to a concentration of 0.1 mol L⁻¹. Voltammetric analyses were carried out in a standard three-electrode cell, with an Autolab PGSTAT 302 N potentiostat, connected to an interfaced computer that employed Electrochemistry Nova software. The reference electrode was a saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk filled with the background solution. The auxiliary electrode was a platinum wire separated from the analyzed solution by a sintered glass disk filled with the background solution. For all voltammetric measurements, the working electrode was a platinum disk electrode ($\emptyset = 2 \text{ mm}$). In these conditions, when operating in a mixture of CH₂Cl₂/CH₃CN 4/1 (0.1 M TEAPF₆) the formal potential for the Fc⁺/Fc couple was found to be +0.40 V vs. SCE.

3. Results and discussion

3.1. Synthesis of zinc(II) 5,10,15,20-(tetra-2-naphthalenyl)porphyrin

According to known procedures (Berthelot *et al.*, 2022), zinc(II) *5,10,15,20*-(tetra-2-naphthalenyl)porphyrin **ZnP** was synthesized as described in Scheme 1.



Scheme 1. Synthesis of ZnP

A solution of **H2P** (120.00 mg, 1.47×10^{-1} mmol, 1.0 eq.) and Zn(OAc)₂.2H₂O (64.54 mg, 2.94×10^{-1} mmol, 2.0 eq.) in CHCl₃ (17.5 mL) and CH₃OH (6.4 mL) was stirred at 60 °C for 1.5 h, monitoring the progress of the reaction by TLC (SiO₂, CH₂Cl₂). The solvent was then removed by rotary evaporation and the crude product was recrystallized in a CH₂Cl₂/CH₃OH mixture. The resulting precipitate was washed with CH₃OH and dried at 150 °C under vacuum for 1 h giving **ZnP** in 90% yield (117.0 mg, 1.33×10^{-1} mmol).

3.2. UV-Visible absorption spectrum of ZnP

The UV-visible absorption spectrum of ZnP in CH₂Cl₂ exhibits an intense Soret band at 426 nm (solid line, Figure 8) and weaker Q bands at 551 and 594 nm.



3.3. NMR characterization of ZnP

The ¹H NMR spectrum of **ZnP** (Figure 9) in CDCl₃ exhibits one singlet (¹H) at 8.97 ppm corresponding to the eight β -pyrrolic proton signals Ha (see attribution on Figure 9). In particular, the presence of only singlet is in agreement with the high symmetry of the molecule. Indeed, on the ¹H NMR spectrum, the naphthalenyl groups proton signals (Hb, Hc, Hd, He, Hf, Hg) are located between 8.69 and 7.70 ppm. The full attribution of this NMR spectrum was performed using 2D NMR techniques (COSY and NOESY experiments).



Figure 9. Partial ¹H NMR spectrum of **ZnP** (500 MHz, 298 K, CDCl₃).

3.4. MALDI-TOF characterization of ZnP

The MALDI-TOF mass spectrum of this crude solution exhibits a nearly exclusive and intense peak at m/z = 877 which is consistent with 5,10,15,20-(tetra-2-naphthalenyl)porphyrin incorpored by a zinc (II) metal and seems to indicate a nearly quantitative reaction with one very major product.

3.4. Electrochemical investigations by cyclic voltammetry

The cyclic voltammogram (CV) of **ZnP** in CH₂Cl₂/CH₃CN mixture (4/1 v/v) 0.1 M TEAPF₆ (black line, **Figure 4**) exhibits one monoelectronic reversible oxidation leading to the cation-radical at *E*p (O1) = 0.80 V. Indeed, when an one to 20 molar equivalents of triphenylphosphine (PPh₃) as a nucleophilic are added to the solution, the first oxidation process (peak O1') becomes gradualy irreversible with a more intense peak current. This result indicates that the initially generated cation radical **ZnP**⁺ undergoes a fast chemical reaction with triphenylphosphine followed by a subsequent one electron uptake (ECE-type mechanism) (Devillers *et al.*, 2011; Giraudeau *et al.*, 1996). Contrary to Zn(II) *5*, *15*-bis(p-tolyl)-*10*-phenylporphyrin (**1-Zn**) (Dimé *et al.*, 2012) which has only one available free *meso* position (**Figure 5**) whose peak O1' is shifted towards less positive potential (*E*pa(O1)-*E*pa(O1') = -0.23 V), the first oxidation peak of **ZnP** is located at the same potential. This behaviour is in agreement with the no axial coordination of PPh₃ on the zinc (II) *5*, *15*-bis(p-tolyl)-*10*-phenylporphyrin (**1-Zn**). The decrease of the peak current of Ox1 reveals a low reactivity of PPh₃ on the β position.





To gain insight into the electrochemical behaviour of **ZnP**, triphenylphosphine oxide (OPPh₃) was also put under scrutiny. To the best of our knowledge, a coordinated phosphine oxide has never been studied in presence of zinc porphyrin. The cyclic voltammogram (CV) of **ZnP** (Figure 12) reveals that the first oxidation peak is located at a potential less positive than that of **ZnP** without OPPh₃ (peak O1', Ep(O1') = -20 mV) which indicates an axial coordination of OPPh₃ on the zinc (II) atom. Clearly, at the first oxidation stage, the addition of triphenylphosphine oxide (OPPh₃) don't modify the electrode reaction, where the peak remains reversible. This result is in agreement with the non-nucleophilic character of OPPh₃.



Figure 11. Cyclic voltammograms of **ZnP** (7×10⁻⁴ M) with (red, blue, purple and brown lines) or without (black line) PPh₃ in CH₂Cl₂/CH₃CN (4/1 v/v) 0.1 M TEAPF₆. Working electrode: Pt disk (Ø=2 mm); sweep rate: 100 mV s⁻¹; initial potential: 0.00 V versus SCE.



Figure 12. Cyclic voltammograms of **1-Zn** (5×10⁻⁴ M) with (solid red line) or without (solid black line) 20 eq. of PPh₃ in CH₂Cl₂/CH₃CN (4/1 v/v) 0.1 M TEAPF₆. Working electrode: Pt disk (Ø=2 mm); sweep rate: 100 mV s⁻¹; initial potential: 0.00 V versus SCE.



Figure 13. Cyclic voltammograms of **ZnP** (4×10^{-4} M) with (red, blue and green lines) or without (black line) OPPh₃ in CH₂Cl₂/CH₃CN (4/1 v/v) 0.1 M TEAPF₆. Working electrode: Pt disk (\emptyset =2 mm); sweep rate: 100 mV s⁻¹; initial potential: 0.00 V versus SCE.

Conclusion

In summary, the metallation of *5*, *10*, *15*, *20*-(tetra-2-naphthalenyl)porphyrin (**1-H2**) in the presence of Zn(OAc)₂.2H₂O affords, in good yield, zinc(II) *5*, *10*, *15*, *20*-(tetra-2-naphthalenyl)porphyrin (**ZnP**). The electrochemical oxidative reactivity of **ZnP** in the presence of triphenylphosphine (PPh₃) has been studied. Analytical electrochemical investigations showed that intermediate generated at the first mono-electronic oxidation reacts with phosphine. This work echoes our recently reported results on the redox reactivity of porphyrin comprising only one free *meso*-position **1-Zn**. Contrary to **1-Zn**, coordination of PPh₃ molecule for **ZnP** was not observed despite the fact that PPh₃ is known to strongly coordinate zinc(II) porphyrin complexes. In this study, addition of a coordinating solvent (OPPh₃) allows the axial coordination on the zinc (II) atom.

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