Axially Ligated Zirconium(IV) Tetraphenylporphyrin: Synthesis, Characterization, and Biological Activity

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A series of 5,10,15,20-tetraphenylporphinatozirconium(IV) acetylacetonatophenolates containing different phenols as axial ligands \([\text{Zr}(\text{TPP})(\text{Y})(\text{X})]\) (TPP = 5,10,15,20-tetraphenyl-21H, 23H-porphine; \(\text{Y} = \text{acac}; \text{X} = \text{different phenolates}\)) have been synthesized and characterized by various spectrochemical studies. The complexes were also screened for antimicrobial activities. Antifungal activity of some adducts has been carried out against the fungal strain Sclerotium rolfsii. Most of the complexes have shown good antibacterial activity.

1. Introduction

The present work is a continuation of our earlier work [1] where we have reported the synthesis of zirconium(IV) porphyrin complexes with salicylic acid and 5-sulfosalicylic acid which were made by replacing the two \(\text{Cl}^−\) by the organic ligands and this was followed by a biological study on some of these compounds and in view of the interesting results obtained from such axially substituted zirconium(IV) porphyrin it is considered worthwhile to make a study of axially substituted zirconium(IV) porphyrin with phenol and its derivatives. The ability of numerous chemical modifications and the large number of different mechanisms by which porphyrins affect microbial and viral pathogens place porphyrins into a group of compounds with an outstanding potential for discovery of novel agents, procedures, and materials active against pathogenic microorganisms [2]. A variety of biological activities exhibited by porphyrins are due to the fact that natural and synthetic porphyrins have relatively low toxicity \(\text{in vitro}\) and \(\text{in vivo}\) and they possess antitumor [3, 4] and antioxidant effects [4, 5] and have a good potential for metal ions complexation. Metalloporphyrins are the basis of new antifungal, antiparasitic, and anticancer drugs because modification of the porphyrin periphery confers qualitatively a new spectrum of activities to metalloporphyrins [6–8]. Zirconium(IV) porphyrins have gained attention from global researchers due to the peculiar characteristics of this class of compounds. The peculiarity of these complexes lies in the fact that metal ion in the complexes, that is, \(\text{Zr}^{4+}\), has large ionic radius (72 pm for most Zr(IV) 6-coordinate complexes), which fits partly into the core of porphyrin ligand and hence shows “out of plane” geometry with additional ligands always in cis position relative to the porphyrin plane [9]. The metal ion in these complexes is oxophilic [10] and thus may show preference for carboxylate and other oxygen-bearing anionic ligands. A lot of work is reported on the complexes of zirconium(IV) phthalocyanines [11–13] but comparatively less work has been done on zirconium(IV) porphyrin complexes with phenol as axial ligand [14, 15]. With this background in mind we reported herein the synthesis, spectroscopic characterization, and biological studies of a series of new axially substituted zirconium(IV) porphyrin with phenol and its derivatives as axial ligands.

2. Experiment

2.1. Materials and Instruments. All the chemicals were of analytical grade and used as received unless otherwise noted.
Pyrrole was distilled over potassium hydroxide pellets under vacuum prior to use. All the organic solvents that were used for the synthesis and for chromatographic separations were dried before use. UV-vis spectra were recorded on a T90+ UV/VIS spectrophotometer in the range of 350–700 nm. The oscillator strength \( f \) of the transitions in absorption spectra was calculated from the expression

\[
f = 4.33 \times 10^{-9} \varepsilon \Delta \nu_{1/2},
\]

where \( \varepsilon \) is the molar absorption coefficient in dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) and \( \Delta \nu_{1/2} \) is the full width at half maximum in cm\(^{-1}\). Infrared spectra were recorded on a PerkinElmer spectrum 400 FTIR spectrophotometer using KBr pellets in the range of 4000–400 cm\(^{-1}\). The elemental analysis was performed on Elemental Analyser CHNS-932, LECO, USA, at a temperature of about 1000°C using helium as carrier gas and oxygen for combustion. The ESI mass spectroscopy was recorded at room temperature and methanol was used as solvent. The \(^1\)H NMR spectra were recorded on a Bruker Avance II 500 (500 MHz) using tetramethylsilane as internal standard and CDCl\(_3\) as solvent. Fluorescence measurements were performed on Synergy MX BIOTEK multimode reader. The solution of porphyrins prepared in DMSO was 10\(^{-6}\) M.

2.2. Biological Studies

2.2.1. Antibacterial Studies. Qualitative analysis for screening of antibacterial activity was carried out by agar-well diffusion method [16] with modifications. By measuring the inhibition zone in mm, the test compounds were taken at a concentration of 0.1 \( \mu \)M using dimethyl sulfoxide (DMSO) as solvent. Chloramphenicol was used as positive control for antibacterial activity. The compound was tested against four gram positive bacteria (Bacillus subtilis, Bacillus cereus, Staphylococcus aureus, and Enterococcus faecalis) and four gram negative bacteria (Klebsiella pneumoniae, Alcaligenes denitrificans, Campylobacter, and Micrococcus luteus) in control, and then it was filtered through anhydrous Na\(_2\)SO\(_4\) in order to remove water and chromatographed through basic alumina using chloroform as an eluent and recrystallized from dichloromethane-hexane solution (1:1) with modification.

2.2.2. Antifungal Study. The antifungal activity of some adducts was tested against the pathogenic fungus Sclerotium rolfsii by poisoned food technique using potato dextrose agar (PDA) nutrient as the medium [17]. The linear growth of the fungus in controlled manner was recorded at different concentration of the adducts. The growth inhibition of Sclerotium rolfsii over control was calculated (Table 7). The growth inhibition of fungus over control was calculated as

\[
\text{%inhibition} (I) = \frac{C - T}{C} \times 100,
\]

where \( I \) is percent inhibition, \( C \) is mean growth of fungus (in mm) in control, and \( T \) is mean growth of fungus (in mm) in treatment.

2.3. Synthesis of Axially Ligated Zirconium(IV) Porphyrins Complexes

2.3.1. Meso-5,10,15,20-tetraphenylporphyrin \([H_4TPP]\). The \( H_4TPP \) was prepared by refluxing benzaldehyde and pyrrole in propionic acid by following reported literature method [18] with modification.

2.3.2. Synthesis of Axially Ligated Zr(IV) Porphyrins: \([Zr(TPP)(Y)(X)]\). A mixture of \( Zr(acac)_4 \) (1.87 mmol), meso-tetraphenylporphyrin (3.74 mmol), and respective phenol (0.12 mmol) with constant stirring refluxed for about 50–60 minutes (Scheme 1). The reaction course was monitored by absorption spectra of the reaction mixture. After concentration, the mixture was dissolved in minimum quantity of CHCl\(_3\) and extracted with 2N NaOH solution to remove excess phenols. The lower layer containing compound in CHCl\(_3\) was collected and then it was filtered through anhydrous Na\(_2\)SO\(_4\) in order to remove water and chromatographed through basic alumina using chloroform as an eluent and recrystallized from dichloromethane-hexane solution (1:1).

The same procedure was applied for the synthesis of all axially ligated zirconium porphyrin complexes as described above. The purified axially ligated zirconium porphyrin complexes were obtained in yields of 35–40%.

\(Zr(TPP)(acac)(Oph)\). Red solid; Anal. Calcd. for C\(_{55}\)H\(_{42}\)N\(_{2}\)O\(_{2}\)Zr: C 73.71, H 4.50, N 6.25; found: C 73.26, H 4.45, N 6.83; MS (CH\(_3\)OH): \( m/z \) calcd. for C\(_{55}\)H\(_{40}\)N\(_{4}\)O\(_{3}\)Zr: 896.16; found 897.31 ([M+H]\(^+\)); IR (KBr)\( \nu_{\text{max}} \): 473 cm\(^{-1}\) (\( \nu_{Zr-N} \)).

\(Zr(TPP)(acac)(p-NH\(_{2}\)phO)\). Yellow solid; Anal. Calcd. for C\(_{55}\)H\(_{41}\)N\(_{5}\)O\(_{3}\)Zr: C 72.50, H 4.54, N 7.69; found: C 72.62, H 4.52, N 7.62; MS (CH\(_3\)OH): \( m/z \) calcd. for C\(_{55}\)H\(_{41}\)N\(_{5}\)O\(_{3}\)Zr: 911.17; found 912.01 ([M+H]\(^+\)); IR (KBr)\( \nu_{\text{max}} \): 460 cm\(^{-1}\) (\( \nu_{Zr-N} \)).

\(Zr(TPP)(acac)(p-OCH\(_{3}\)phO)\). Red solid; Anal. Calcd. for C\(_{55}\)H\(_{42}\)N\(_{2}\)O\(_{4}\)Zr: C 72.62, H 4.57, N 6.05; found: C 71.23, H 4.96, N 5.62; ESI-MS (CH\(_3\)OH): \( m/z \) calcd. for C\(_{55}\)H\(_{42}\)N\(_{2}\)O\(_{4}\)Zr: 926.18; found 927.34 ([M+H]\(^+\)); IR (KBr)\( \nu_{\text{max}} \): 481 cm\(^{-1}\) (\( \nu_{Zr-N} \)).

\(Zr(TPP)(acac)(p-CH\(_{3}\)phO)\). Red solid; Anal. Calcd. for C\(_{55}\)H\(_{42}\)N\(_{2}\)O\(_{4}\)Zr: C 73.90, H 4.65, N 6.16; found: C 73.65, H 4.88, N 5.42; ESI-MS (CH\(_3\)OH): \( m/z \) calcd. for C\(_{55}\)H\(_{42}\)N\(_{2}\)O\(_{4}\)Zr: 910.18; found 911.25 ([M+H]\(^+\)); IR (KBr)\( \nu_{\text{max}} \): 468 cm\(^{-1}\) (\( \nu_{Zr-N} \)).

\(Zr(TPP)(acac)(p-ClphO)\). Brown solid; Anal. Calcd. for C\(_{55}\)H\(_{42}\)ClN\(_{2}\)O\(_{4}\)Zr: C 70.99, H 4.22, N 5.62; found: C 71.66, H 4.81, N 5.64; ESI-MS (CH\(_3\)OH): \( m/z \) calcd.
for C_{55}H_{39}ClN_{4}O_{3}Zr: 930.61; found 931.52 ([M+H]^+); IR (KBr)υ_{max}^\text{IR} = 475 \text{ cm}^{-1} (\nu_{Zr-N})

Zr(TPP)(acac)(p-NO_{2}phO). Brown solid; Anal. Calcd. for C_{55}H_{39}N_{5}O_{2}Zr: C 70.19, H 4.18, N 7.44; found: C 70.23, H 4.12, N 7.56; ESI-MS (CH_{3}OH): m/z calcd. for C_{55}H_{39}N_{5}O_{2}Zr: 941.15; found 942.05 ([M+H]^+); IR (KBr)υ_{max}^\text{IR} = 484 \text{ cm}^{-1} (\nu_{Zr-N})

Zr(TPP)(acac)(o,p-Cl_{2}phO). Yellow solid; Anal. Calcd. for C_{55}H_{39}N_{5}O_{3}Cl_{2}Zr: C 68.45, H 3.97, N 5.81; found: C 68.31, H 3.52, N 5.43; ESI-MS (CH_{3}OH): m/z calcd. For C_{55}H_{39}N_{5}O_{3}Cl_{2}Zr: 965.05; found 966.19 ([M+H]^+); IR (KBr)υ_{max}^\text{IR} = 480 \text{ cm}^{-1} (\nu_{Zr-N})

Zr(TPP)(acac)(o,p-(NO_{2})_{2}phO). Red solid; Anal. Calcd. for C_{55}H_{39}N_{6}O_{7}Zr: C 66.99, H 3.88, N 8.52; found:
Table 1: Optical absorption data of Zr(TPP)(Y)(X) complexes in CHCl₃.

| Compounds                              | B-bands $\lambda_{\text{max}}$ (nm), (log $\epsilon$) | Q-bands $\lambda_{\text{max}}$ (nm), (log $\epsilon$) |
|----------------------------------------|--------------------------------------------------------|-------------------------------------------------------|
| Zr(TPP)(acac)(Oph)                     | 413.1, (5.074)                                          | 500.5, (4.183)                                        |
|                                        |                                                        | 535.7, (4.796)                                        |
|                                        |                                                        | 579.9, (5.009)                                        |
| Zr(TPP)(acac)(p-OCH₃phO)               | 414.2, (5.101)                                          | 501.5, (4.197)                                        |
|                                        |                                                        | 536.8, (4.812)                                        |
|                                        |                                                        | 580.9, (5.031)                                        |
| Zr(TPP)(acac)(p-CH₃phO)                | 413.9, (5.104)                                          | 501.7, (4.200)                                        |
|                                        |                                                        | 537.4, (4.814)                                        |
|                                        |                                                        | 581.4, (5.033)                                        |
| Zr(TPP)(acac)(p-NO₂phO)                | 412.9, (5.056)                                          | 501.4, (4.168)                                        |
|                                        |                                                        | 535.1, (4.788)                                        |
|                                        |                                                        | 580.8, (4.990)                                        |
| Zr(TPP)(acac)(p-ClphO)                 | 413.3, (5.068)                                          | 500.8, (4.177)                                        |
|                                        |                                                        | 536.1, (4.795)                                        |
|                                        |                                                        | 580.2, (5.005)                                        |
| Zr(TPP)(acac)(p-NH₂phO)                | 415.1, (5.119)                                          | 502.9, (4.214)                                        |
|                                        |                                                        | 538.9, (4.828)                                        |
|                                        |                                                        | 583.5, (5.049)                                        |
| Zr(TPP)(acac)(o,p-Cl₂phO)              | 411.8, (5.061)                                          | 499.2, (4.172)                                        |
|                                        |                                                        | 534.3, (4.793)                                        |
|                                        |                                                        | 578.8, (4.997)                                        |
| Zr(TPP)(acac)(o,p-(NO₂)₂phO)           | 410.9, (5.049)                                          | 498.5, (4.159)                                        |
|                                        |                                                        | 532.9, (4.781)                                        |
|                                        |                                                        | 578.3, (4.472)                                        |
| Zr(TPP)(acac)(α-naphtholate)           | 412.8, (5.068)                                          | 500.3, (4.178)                                        |
|                                        |                                                        | 535.4, (4.795)                                        |
|                                        |                                                        | 579.7, (5.007)                                        |

3. Results and Discussion

3.1. Synthesis and Characterization. The general synthetic route to axially ligated zirconium(IV) porphyrins is shown in Scheme 1. All of these new zirconium(IV) porphyrins were purified by column chromatography with aluminum oxide as adsorbent and were characterized by spectral data (UV-visible spectroscopy, IR spectroscopy, $^1$H NMR spectroscopy, mass spectral data, and elemental analysis). The characterization data of the new compounds are consistent with the assigned formula. All the synthesized complexes are water insoluble.

3.1.1. Spectral Analysis of Zr(TPP)(Y)(X). The spectral data of the synthesized complexes (Table 1) revealed that the axially ligated Zr(IV) metal derivatives of porphyrin with different phenolates as an axial ligand showed hypsochromic shift (blue shift) and variation in intensities of absorption bands when compared to their respective free base porphyrin, due to incorporation of the metal ion along with phenolate in the porphyrin rings [1, 19]. The complexes with electron donating groups in phenolates have slightly red shifted B- and Q-bands while those having electron withdrawing groups in phenolates have blue shifted B and Q bands. When the optical absorption spectra of the compounds of Zr(TPP)(Y)(X) were recorded in different solvents (Figure 1) only a marginal change in $\lambda_{\text{max}}$ values, absorption coefficient ($\epsilon$), and oscillator strength ($f$) values was observed. Data revealed that a change in polarity of the solvent results in slight change in the position of transitions but there was a significant increase in $\nu_{1/2}$ and “$f$” values of transitions by increasing the polarity of the solvent (Table 2). The magnitude of change in “$f$” value in axially ligated Zr(IV) metal derivatives of porphyrin revealed the relative strength of $\pi-\pi^*$ interactions. It was also found that, with the increase in polarity of the solvents, B and Q-bands in axially ligated Zr(IV) metal derivatives showed red shift with progressive broadening of bands indicating that the magnitude of red shift of B and Q bands depends on the nature of the solvent used.

By comparing the infrared spectral data of H₂TPP and its corresponding axially ligated Zr(TPP)(Y)(X) (Table 3),
Figure 1: UV-vis spectra of Zr(TPP)(acac)(p-OCH₃-phO) in different solvent (—— Acetone, –– CHCl₃, …… CH₂Cl₂).

Figure 2: Infrared spectrum of Zr(TPP)(acac)(p-OCH₃-phO).
Table 2: Optical absorption data of Zr(TPP)(Y)(X) in different solvents.

| Compounds                  | Solvent | λ<sub>max</sub> (nm) | log ε (M<sup>-1</sup> cm<sup>-1</sup>) | v<sub>1/2</sub> (cm<sup>-1</sup>) | Q(0,0) |
|----------------------------|---------|----------------------|--------------------------------------|-------------------------------|--------|
|                            |         | B(0,0) | Q(2,0) | Q(1,0) | Q(0,0) | B(0,0) | Q(0,0) | f       |
| Zr(TPP)(acac)(phO)         | Acetone | 413.1  | 500.5  | 535.7  | 579.9  | 1309.3 | 1067.2 | 0.235877|
|                            | CH<sub>2</sub>Cl<sub>2</sub> | 409.4  | 496.3  | 532.2  | 575.8  | 1241.6 | 1020.7 | 0.197404|
|                            | CHCl<sub>3</sub> | 411.3  | 498.5  | 533.4  | 577.5  | 1278.1 | 1041.1 | 0.207468|
| Zr(TPP)(acac)(p-OCH<sub>3</sub>phO) | Acetone | 414.2  | 501.5  | 536.8  | 580.9  | 1340.2 | 1085.9 | 0.252492|
|                            | CH<sub>2</sub>Cl<sub>2</sub> | 409.8  | 496.4  | 530.6  | 574.9  | 1279.9 | 1039.3 | 0.207586|
|                            | CHCl<sub>3</sub> | 411.9  | 498.3  | 534.2  | 578.5  | 1312.6 | 1062.4 | 0.213671|
| Zr(TPP)(acac)(p-CH<sub>3</sub>phO) | Acetone | 412.9  | 501.4  | 535.1  | 580.8  | 1270.3 | 1035.2 | 0.219019|
|                            | CH<sub>2</sub>Cl<sub>2</sub> | 409.7  | 496.3  | 532.3  | 576.4  | 1218.3 | 992.6  | 0.183752|
|                            | CHCl<sub>3</sub> | 411.2  | 499.1  | 533.8  | 577.9  | 1236.8 | 1007.9 | 0.194033|
| Zr(TPP)(acac)(p-NO<sub>2</sub>phO) | Acetone | 410.9  | 500.2  | 536.1  | 582.5  | 1271.2 | 1033.2 | 0.256245|
|                            | CH<sub>2</sub>Cl<sub>2</sub> | 408.6  | 495.2  | 531.5  | 576.3  | 1218.1 | 991.3  | 0.191456|
|                            | CHCl<sub>3</sub> | 410.1  | 498.9  | 537.6  | 577.7  | 1235.9 | 1006.7 | 0.198565|
| Zr(TPP)(acac)(α-naphtholate) | Acetone | 413.5  | 500.4  | 535.2  | 581.9  | 1272.3 | 1034.2 | 0.232365|
|                            | CH<sub>2</sub>Cl<sub>2</sub> | 411.5  | 497.8  | 535.6  | 577.6  | 1217.3 | 995.6  | 0.182536|
|                            | CHCl<sub>3</sub> | 413.5  | 498.3  | 535.8  | 578.9  | 1235.8 | 1005.3 | 0.195632|

it is found that the band at 3447 cm<sup>-1</sup> in H<sub>2</sub>TPP assigned to ν(N–H) (pyrrole) stretching vibration was disappeared in metallated complexes and the characteristic ν(Zr–N) vibration frequency found at ~500–430 cm<sup>-1</sup>, which indicated the formation of zirconium(IV) porphyrin compounds [20, 21]. In the spectra of all the axially ligated zirconium(IV) porphyrin complexes the incorporation of various phenolates in Zr(IV) metal derivatives of porphyrin, that is, Zr(TPP)(Y)(X), was confirmed by the appearance of Zr–O vibrational frequencies in the range of 649–680 cm<sup>-1</sup> indicating the coordination of phenolic oxygen to the metal via deprotonation (Figure 2). Also, the incorporation of acetylacetonate (acac) in axially ligated Zr(IV) derivatives was confirmed by the appearance of C=O vibrational frequencies in the range of 1622–1641 cm<sup>-1</sup> and Zr–O in the range of 702–819 cm<sup>-1</sup> corresponding to the ligation of zirconium to oxygen of phenolic and carboxylic groups, respectively [22, 23]. Thus, the zirconium atom in the centre of porphyrin ring coordinates with the acetylacetonate and phenol group axially to form seven-coordinate complex of Zr(IV) porphyrin.

From the 1H NMR data of axially ligated zirconium(IV) porphyrin complexes in CDCl<sub>3</sub> at 298 K (Table 4), it is found that the N–H protons of H<sub>2</sub>TPP appear at ~2.77 ppm. In all the zirconium(IV) porphyrins there were absence of signal related to N–H protons and shift in other signals indicating the insertion of zirconium in porphyrin macrocycle [21]. Generally, the presence of Zr(IV) metal in the porphyrin ring shifts the resonances of the porphyrin's protons to downfield accompanied by marginal changes in the pattern. One of the important features of axially ligated Zr(IV) derivatives of porphyrins is that the metal is almost out of the plane of the porphyrin ring responsible for the production of asymmetric environment above and below the plane of the macrocycle
### Table 3: Main vibrational frequencies of axially ligated Zr(IV) porphyrin complexes.

| Porphyrin | $\nu$(N–H) (cm$^{-1}$) | $\nu$(C=C) (cm$^{-1}$) | $\nu$(Zr–N) (cm$^{-1}$) | $\nu$(Zr–O) phenolate (cm$^{-1}$) | $\nu$(CH$_3$) (cm$^{-1}$) | $\nu$(OCH$_3$) (cm$^{-1}$) | $\nu$(NH$_2$) (cm$^{-1}$) | $\nu$(NO$_2$) (cm$^{-1}$) | $\nu$(C–Cl) (cm$^{-1}$) | $\nu$(Zr–O) acac (cm$^{-1}$) | $\nu$(C=O) acac (cm$^{-1}$) |
|-----------|------------------------|------------------------|-----------------------|-----------------------------------|--------------------------|--------------------------|--------------------------|------------------------|--------------------------|-----------------------------|-----------------------------|
| Zr(TPP)(acac)(Oph) | — | 1590 | 473 | 664 | 2907 | — | — | — | — | 703 | 803 |
| Zr(TPP)(acac)(p-NH$_2$phO) | — | 1592 | 460 | 655 | 2891 | — | — | $\nu$(NH$_2$)$_{sym}$ = 3292 | $\nu$(NH$_2$)$_{asym}$ = 3366 | — | — | 712 |
| Zr(TPP)(acac)(p-OCH$_3$phO) | — | 1590 | 481 | 653 | 2894 | $\nu$(C–H) = 2817 | $\nu$(COC)$_{sym}$ = 1025 | $\nu$(COC)$_{asym}$ = 1261 | — | — | 702 |
| Zr(TPP)(acac)(p-CH$_3$phO) | — | 1584 | 468 | 651 | 2895 | — | — | — | — | 702 |
| Zr(TPP)(acac)(p-ClphO) | — | 1591 | 475 | 666 | 2906 | — | — | — | — | 704 |
| Zr(TPP)(acac)(p-NO$_2$phO) | — | 1592 | 484 | 667 | 2909 | — | — | 1342 | 1543 | — | 713 |
| Zr(TPP)(acac)(α,p-Cl$_2$phO) | — | 1595 | 480 | 669 | 2907 | — | — | — | — | 716 |
| Zr(TPP)(acac)(α,p-(NO$_2$)$_2$phO) | — | 1596 | 478 | 668 | 2905 | — | — | — | — | 705 |
| Zr(TPP)(acac)(α-naphtholate) | — | 1589 | 473 | 659 | 2897 | — | — | — | — | 709 |

Note: The values in the table represent the observed vibrational frequencies in cm$^{-1}$ for each functional group and ligand.
| Porphyrins                      | Imin protons | β-Pyrrole protons | Meso-aryl protons | acac protons | Phenolate protons |
|--------------------------------|--------------|-------------------|-------------------|--------------|------------------|
| Zr(TPP)(acac)(phO)             | —            | 8.94 (s)          | 8.26 (d, 4H, Ho)  | 1.46 (s, 6H, H<sub>CH</sub>) | 7.04 (d, 2H, Ho) |
|                               |              |                   | 7.79 (d, 4H, Ho)  | 4.56 (s, H, H<sub>CH</sub>) | 714–727 (m, 3H, Hm, p) |
| Zr(TPP)(acac)(p-NH<sub>2</sub>phO) | —            | 8.42 (s)          | 7.45 (d, 4H, Ho)  | 1.52 (s, 6H, H<sub>CH</sub>) | 6.87 (d, 2H, Ho) |
|                               |              |                   | 7.28 (d, 4H, Ho)  | 3.85 (s, H, H<sub>CH</sub>) | 6.71 (d, 2H, Hm) |
|                               |              |                   | 7.11–719 (m, 12H, Hm, p) |              | 4.85 (s, 2H, H<sub>CH</sub>) |
| Zr(TPP)(acac)(p-OCH<sub>3</sub>phO) | —            | 8.47 (s)          | 750 (d, 4H, Ho)   | 1.55 (s, 6H, H<sub>CH</sub>) | 6.98 (m, 4H, Ho, m) |
|                               |              |                   | 7.40 (d, 4H, Ho)  | 3.89 (s, H, H<sub>CH</sub>) | 3.43 (s, 3H, H<sub>CH</sub>3) |
|                               |              |                   | 7.16–7.24 (m, 12H, Hm, p) |              | |
| Zr(TPP)(acac)(p-CH<sub>3</sub>phO) | —            | 8.47 (s)          | 748 (d, 4H, Ho)   | 1.50 (s, 6H, H<sub>CH</sub>) | 6.98 (m, 4H, Ho, m) |
|                               |              |                   | 7.74 (d, 4H, Ho)  | 3.89 (s, H, H<sub>CH</sub>) | 2.18 (s, 3H, H<sub>CH</sub>3) |
|                               |              |                   | 715–723 (m, 12H, Hm, p) |              | |
| Zr(TPP)(acac)(p-ClphO)         | —            | 934 (s)           | 8.37 (d, 4H, Ho)  | 1.79 (s, 6H, H<sub>CH</sub>) | 712 (d, 2H, Ho) |
|                               |              |                   | 8.18 (d, 4H, Ho)  | 4.59 (s, H, H<sub>CH</sub>) | 736 (d, 2H, Hm) |
|                               |              |                   | 783–792 (m, 12H, Hm, p) |              | |
| Zr(TPP)(acac)(p-NO<sub>2</sub>phO) | —            | 936 (s)           | 8.49 (d, 4H, Ho)  | 1.81 (s, 6H, H<sub>CH</sub>) | 721 (d, 2H, Ho) |
|                               |              |                   | 8.21 (d, 4H, Ho)  | 4.65 (s, H, H<sub>CH</sub>) | 742 (d, 2H, Hm) |
|                               |              |                   | 788–797 (m, 12H, Hm, p) |              | |
| Zr(TPP)(acac)(o,p-Cl<sub>2</sub>phO) | —            | 8.51 (s)          | 8.48 (d, 4H, Ho)  | 1.80 (s, 6H, H<sub>CH</sub>) | 712 (s, 1H, Ho) |
|                               |              |                   | 8.21 (d, 4H, Ho)  | 4.64 (s, H, H<sub>CH</sub>) | 786–782 (m, 2H, Hm) |
|                               |              |                   | 795–8.05 (m, 12H, Hm, p) |              | |
| Zr(TPP)(acac)(o,p-(NO<sub>2</sub>)<sub>2</sub>phO) | —            | 9.57 (s)          | 8.57 (d, 4H, Ho)  | 2.11 (s, 6H, H<sub>CH</sub>) | 7.22 (s, 1H, Ho) |
|                               |              |                   | 8.29 (d, 4H, Ho)  | 4.72 (s, H, H<sub>CH</sub>) | 7.72–786 (m, 2H, Hm) |
|                               |              |                   | 8.05–8.13 (m, 12H, Hm, p) |              | |
Table 5: Summary of the fluorescence band maxima at 23 K in DMSO.

| Compound                  | B(0, 0) | \(\lambda_{\text{max}}\) nm | Q(0, 0) | Q(0, 1) |
|---------------------------|---------|-------------------------------|--------|--------|
| \(\text{H}_2\text{TPP}\)  | 450     | 653                          | 715    |        |
| \(\text{Zr(TPP)(acac)(p-OC}_3\text{H}_2\text{phO)}\) | 440     | 609                          | 660    |        |
| \(\text{Zr(TPP)(acac)(p-CH}_3\text{phO)}\) | 440     | 608                          | 657    |        |
| \(\text{Zr(TPP)(acac)(p-NO}_2\text{phO)}\) | 443     | 610                          | 663    |        |
| \(\text{Zr(TPP)(acac)(\alpha-naphtholate)}\) | 441     | 608                          | 653    |        |

which ultimately account for the pronounced no-equivalence of the orthoprotons of the phenyl rings.

The signals of axial phenol and acetylacetonate fragment protons are shifted to higher field in comparison to the protons with respect to \(\text{Zr(TPP)(acac)(Oph)}\) which have the orthoproton of the phenyl rings.

In the present investigation, the variation of emission properties in free base porphyrin \(\text{H}_2\text{TPP}\) and some of its corresponding axially ligated \(\text{Zr(IV)}\) porphyrins has been studied (Table 5). The free base porphyrin exhibits two emission bands at 653 nm and 715 nm corresponding to Q(0,0) and Q(0,1) transitions, respectively, the intensity of the Q(0,0) being higher than the Q(0,1) transition. The axially ligated zirconium(IV) porphyrin complexes are emissive and show intraligand fluorescence comparable to other regular metalloporphyrins (Table 5). However, the emission bands of axially ligated \(\text{Zr(IV)}\) porphyrins are blue shifted compared to free base porphyrin (Figure 3). This behavior is attributed to an enhanced spin–orbit coupling induced by the presence of the heavy-atom central metals in zirconium(IV) porphyrins complexes, which leads to a more efficient intersystem crossing from the lowest porphyrin singlet excited state \(1\text{S}_1(\pi, \pi^*)\) to the corresponding triplet manifold and thus reduces the probability of fluorescent emission [25]. Thus, the excitation spectrum of fluorescence is in agreement with absorption spectrum.

Mass spectrometric characterization of \(\text{Zr(TPP)(Y)(X)}\) complexes employed ESI as soft ionization technique. The mass spectra of axial ligated zirconium(IV) porphyrins are characterized by the presence of the molecular ion peak for monomeric form followed by a degree of fragmentation when employing this technique, which suggested that axial ligand was labile (Figure 4).

3.1.2. Biological Studies. Antibacterial activity of all the synthesized zirconium(IV) porphyrin complexes was tested against eight bacterial strains, namely, \(K.\) pneumonia, \(S.\) aureus, \(E.\) faecalis, \(A.\) denitrificans, \(B.\) cereus, \(M.\) luteus, \(B.\) subtilis, and \(C.\) campylobacter (Table 6). Our results demonstrated antibacterial activity against most of the zirconium(IV) porphyrin complexes and by comparing these complexes with \(\text{H}_2\text{TPP}\) we noted that introducing zirconium and axial ligand in \(\text{H}_2\text{TPP}\) increased antibacterial activity. Among all the complexes studied, \(\text{Zr(TPP)(acac)(p-NO}_2\text{phO)}\) was found to be highly potential against all the eight bacterial strains with sensitivity ranging from 1 to 2.5 mm zone of inhibition and even more than positive control in some cases (Table 6). \(\text{Zr(TPP)(acac)(\alpha-naphtholate)}\) was the only other complex after \(\text{Zr(TPP)(acac)(p-NO}_2\text{phO)}\) complex that showed antibacterial sensitivity against all the bacterial strains with zone of inhibition ranging from 1 to 1.75 mm. On comparison of the antibacterial activities of synthesized complexes, we noted that for most of the bacterial strains complexes having axial ligand with electron withdrawing group have increased antibacterial activity compared to complexes having ligand with electron donating group and also compared to complex having no substituent on axial ligand, \(\text{Zr(TPP)(acac)(phO)}\).

3.1.3. Antifungal Activity. The antifungal activity of all the synthesized zirconium porphyrin complexes was tested at different concentrations against the pathogenic fungus \(S.\) rotsii. From the results found, it has been concluded that, by increasing the concentration of the complexes \(\text{Zr(TPP)(Y)(X)}\), the colony diameter of the fungus decreases and hence percent inhibition increases. On doubling the concentration of the complexes, the percent inhibition also doubles, which shows linear relationship between concentration and percent inhibition. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to combined activity effect of the metal and the ligand.
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Table 6: *In vitro* antibacterial evaluation of free base porphyrin and the corresponding zirconium(IV) porphyrin complexes.

| PORPHYRIN                        | K. pneumoniae | S. aureus | E. faecalis | A. denitrificans | B. cereus | M. luteus | B. subtilis | Campylobacter |
|----------------------------------|---------------|-----------|-------------|-----------------|-----------|-----------|------------|--------------|
| H₂TPP                            | —             | —         | 1           | —               | —         | —         | —          | —            |
| Zr(TPP)(acac)(phO)               | —             | —         | 1.25        | —               | —         | —         | —          | —            |
| Zr(TPP)(acac)(p-NH₂phO)          | —             | —         | 1.5         | —               | —         | —         | —          | —            |
| Zr(TPP)(acac)(p-ClphO)           | —             | —         | —           | —               | —         | —         | —          | 1.5          |
| Zr(TPP)(acac)(p-OCH₃phO)         | —             | —         | 1           | —               | —         | —         | —          | —            |
| Zr(TPP)(acac)(α-naphtholate)     | 1             | 1.15      | 1.1         | 1.25            | 1.1       | 1.5       | 1.75       | 1            |
| Zr(TPP)(acac)(p-NO₂phO)          | 2             | 1         | 1.5         | 1.5             | 1.2       | 1.4       | 2.5        | 1.5          |
| Zr(TPP)(acac)(p-CH₃phO)          | 1             | 0.7       | 1.7         | —               | 0.9       | 0.7       | 0.7        | 0.7          |
| Zr(TPP)(acac)(o,p-Cl₂phO)        | —             | —         | —           | 0.9             | —         | —         | —          | 1.25         |
| Zr(TPP)(acac)(o,p-(NO₂)₂phO)     | —             | 1.25      | 1.25        | —               | 2         | —         | —          | 1.5          |
| Control chloramphenicol          | 2.5           | 2.1       | 1.4         | 2               | —         | 2.25      | 2          | 2            |

[26, 27]. It is concluded that most of the synthesized compounds showed overall good activity. However, some complexes, namely, Zr(TPP)(acac)(phO), Zr(TPP)(acac)(p,p'-Cl₂phO), and Zr(TPP)(acac)(o,p-(NO₂)₂phO), showed negligible results at given concentrations and the data for only those complexes has been provided which showed significant results (Table 7).

It is interesting to note that most of the synthesized axially ligated complexes were found to be more active (IC₅₀ = ~26-196 μg/mL) than the corresponding free base ligand (IC₅₀ = 212.24 μg/mL) with Zr(TPP)(acac)(p-CH₃phO) appearing to be the most potent. The selectivity might be resulting from the well-established structural differences between fungal and bacterial cells, although the exact reasons remain as yet unclear [28].

4. Conclusion

A detailed analysis of ultraviolet-visible (UV-vis), proton nuclear magnetic resonance (¹H NMR) spectroscopy, infrared (IR) spectroscopy, fluorescence and mass spectroscopic studies, and elemental analysis suggested the transformation from free base porphyrins to zirconium(IV) porphyrins. The spectroscopic data revealed the ligation of acetylacetonate and different phenolates at axial position on Zr(IV) metal atom in [Zr(TPP)(acac)]X. Therefore the coordination number of central metal ions is seven and the zirconium is expected to be above the porphyrin plane. Among all the complexes prepared [Zr(TPP)(acac)(p-NO₂phO)] was found to be highly potential against all the eight bacterial strains and even more than positive control...
Table 7: *In vitro* evaluation of complexes against *Sclerotium rolfsii*. Mean colony diameter of control $C = 90$ mm.

| Name of the complex                  | Concentration ($\mu$g/mL) | Colony diameter (mm) | % Inhibition $I = \frac{[C − T]/C} \times 100$ | IC$_{50}$ ($\mu$g/mL) |
|-------------------------------------|---------------------------|----------------------|-----------------------------------------------|-----------------------|
| $\text{H}_2\text{TPP}$             | 100                       | 66                   | 26.66                                         | 212.24                |
|                                     | 200                       | 48                   | 46.66                                         |                       |
|                                     | 300                       | 28                   | 68.89                                         |                       |
| $\text{Zr}(\text{TPP})(\text{acac})(p-\text{NH}_2\text{phO})$ | 100                       | 57                   | 36.66                                         | 180.61                |
|                                     | 200                       | 39                   | 56.66                                         |                       |
|                                     | 300                       | 11                   | 87.77                                         |                       |
| $\text{Zr}(\text{TPP})(\text{acac})(p-\text{ClphO})$       | 100                       | 61                   | 32.22                                         | 159.42                |
|                                     | 200                       | 43                   | 52.22                                         |                       |
|                                     | 300                       | 12                   | 86.66                                         |                       |
| $\text{Zr}(\text{TPP})(\text{acac})(p-\text{OCH}_3\text{phO})$ | 100                       | 65                   | 27.77                                         | 196.46                |
|                                     | 200                       | 41                   | 54.44                                         |                       |
|                                     | 300                       | 27                   | 70                                            |                       |
| $\text{Zr}(\text{TPP})(\text{acac})(\alpha-\text{naphtholate})$ | 100                       | 33                   | 53.33                                         | 102.75                |
|                                     | 200                       | 30                   | 66.66                                         |                       |
|                                     | 300                       | 8                    | 91.11                                         |                       |
| $\text{Zr}(\text{TPP})(\text{acac})(p-\text{NO}_2\text{phO})$ | 100                       | 35                   | 51.11                                         |                       |
|                                     | 200                       | 23                   | 73.33                                         | 91.87                 |
|                                     | 300                       | 7                    | 92.22                                         |                       |
| $\text{Zr}(\text{TPP})(\text{acac})(p-\text{CH}_3\text{phO})$ | 100                       | 35                   | 61.11                                         | 26.02                 |
|                                     | 200                       | 21                   | 77.77                                         |                       |
|                                     | 300                       | 7                    | 92.22                                         |                       |

in some cases. Also, antifungal activity of the synthesized complexes shows that these complexes have potential against fungal growth.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**References**

[1] G. D. Bajju, G. Devi, S. Katoch et al., “Synthesis, spectroscopic, and biological studies on new zirconium(IV) porphyrins with axial ligand,” *Bioinorganic Chemistry and Applications*, vol. 2013, Article ID 903616, 15 pages, 2013.

[2] I. Stojilkovic, B. D. Evavold, and V. Kumar, “Antimicrobial properties of porphyrins,” *Expert Opinion on Investigational Drugs*, vol. 10, no. 2, pp. 309–320, 2001.

[3] A. A. Fadda, R. E. El-Mekawy, A. El-Shafei, H. S. Freeman, D. Hinks, and M. El-Fedawy, “Design, synthesis, and pharmacological screening of novel porphyrin derivatives,” *Journal of Chemistry*, vol. 2013, Article ID 340230, 11 pages, 2013.

[4] Y. Ni, “Metalloporphyrins and functional analogues as MRI contrast agents,” *Current Medical Imaging Reviews*, vol. 4, no. 2, pp. 96–112, 2008.

[5] N. A. Antonova, V. P. Osipova, M. N. Kolyada, N. O. Movchan, E. R. Milaeva, and Y. T. Pimenov, “Study of the antioxidant properties of porphyrins and their complexes with metals,” *Macrocycles*, vol. 3, no. 2-3, pp. 139–144, 2010.

[6] M. Yuasa, K. Oyaizu, H. Murata, Y. Sahara, T. Hatsugai, and A. Ogata, “Antioxidant and anticancer properties of metalloporphyrins embedded in liposomes,” *Journal of Oleo Science*, vol. 56, no. 2, pp. 87–93, 2007.

[7] K. Rajesh, A. K. Rahiman, K. S. Bharathi, S. Sreedaran, V. Gangadewi, and V. Narayanan, “Spectroscopic, redox and biological studies of push-pull porphyrins and their metal complexes,” *Bulletin of the Korean Chemical Society*, vol. 31, no. 9, pp. 2656–2664, 2010.

[8] J. Bozja, J. Sherrill, S. Michaelsen, and I. Stojilkovic, “Porphyrin-based, light-activated antimicrobial materials,” *Journal of Polymer Science A: Polymer Chemistry*, vol. 41, no. 15, pp. 2297–2303, 2003.

[9] E. V. Motorina and T. N. Lomova, “Formation of supramolecular complex between imidazole and dichloro(5,10,15,20-tetraphenylporphinato)zirconium(IV),” *Russian Journal of General Chemistry*, vol. 80, no. 4, pp. 842–848, 2010.

[10] A. Falber, B. P. Burton-Pye, I. Radijovec et al., “Ternary porphyrinato HfIV and ZrIV polyoxometalate complexes,” *European Journal of Inorganic Chemistry*, no. 17, pp. 2459–2466, 2009.

[11] L. A. Tomachynski, V. Y. Chernii, H. N. Gorbenko, V. V. Filonenko, and S. V. Volkov, “Synthesis, spectral properties, and anticancer activity of a new axially substituted phthalocyanine complex of zirconium (IV) with citric acid,” *Chemistry and Biodiversity*, vol. 1, no. 6, pp. 862–867, 2004.

[12] I. N. Tretyakova, V. Y. Chernii, L. A. Tomachynski, and S. V. Volkov, “Synthesis and luminescent properties of new zirconium(IV) and hafnium(IV) phthalocyanines with various
carbonic acids as out-planed ligands,” *Dyes and Pigments*, vol. 75, no. 1, pp. 67–72, 2007.

[13] V. Kovalska, M. Losytskyy, V. Chernii et al., “Studies of anti-fibrillogenic activity of phthalocyanines of zirconium containing out-of-plane ligands,” *Bioorganic and Medicinal Chemistry*, vol. 20, no. 1, pp. 330–334, 2012.

[14] G. D. Bajju, S. K. Anand, and S. Kundan, “Synthesis and characterization of zirconium (IV) derivatives of meso-tetra(p-methylphenyl)porphyrin with acetylacetone and different phenolates at axial positions,” *Oriental Journal of Chemistry*, vol. 28, no. 1, pp. 417–432, 2012.

[15] G. D. Bajju, S. K. Anand, and S. Kundan, “Synthesis and spectroscopic studies of zirconium(IV) porphyrins with acetylacetone and phenolates at axial positions,” *Oriental Journal of Chemistry*, vol. 28, no. 1, pp. 449–462, 2012.

[16] E. Oke, B. Aslim, S. Ozturk, and S. Altundag, “Essential oil composition, antimicrobial and antioxidant activities of *Satureja cuneifolia* Ten,” *Food Chemistry*, vol. 112, no. 4, pp. 874–879, 2009.

[17] J. M. Vincent, “Distortion of fungal hyphae in the presence of certain inhibitors,” *Nature*, vol. 159, no. 4051, article 850, 1947.

[18] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, “A simplified synthesis for meso-tetraphenylporphin,” *Journal of Organic Chemistry*, vol. 32, no. 2, p. 476, 1967.

[19] E. Fagadar-Cosma, D. Vlascici, and G. Fagadar-Cosma, “Monomer and sandwich type dimer complexes of Zr (IV) with meso-tetraphenylporphin. Synthesis and comparative IR, UV-vis and HPLC behavior,” in *Proceedings of the 12th Symposium on Analytical and Environmental Problems*, Szeged, pp. 25–29, Szeged, Hungary, September 2005.

[20] Z.-C. Sun, Y.-B. She, Y. Zhou, X.-F. Song, and K. Li, “Synthesis, characterization and spectral properties of substituted tetraphenylporphyrin iron chloride complexes,” *Molecules*, vol. 16, no. 4, pp. 2960–2970, 2011.

[21] D. Vlascici, O. Bizerea-Spiridon, and E. Fagadar-Cosma, “Metalloporphyrin based fluoride-selective electrode;” in *Proceedings of the 13th Symposium on Analytical and Environmental Problems*, pp. 92–95, Szeged, Hungary, September 2006.

[22] Q. Ming-Hui, L. Guo-Ya, S. Tong-Shun, and X. Jin-Jie, “Syntheses and photo-electronic properties of lanthanide acetylacetone benzoporphyrins,” *Chemical Research in Chinese Universities*, vol. 20, no. 1, pp. 118–220, 2004.

[23] Z. Zhi-xin, L. Xiang-qing, W. Xing-quo, and L. Guo-ya, “Lanthanide complexes with acetylacetone and 5,10,15,20-tetra(para(4-chlorobenzyloxy)phenyl) porphyrin,” *Chemical Research in Chinese Universities*, vol. 16, no. 3, pp. 259–262, 2000.

[24] Y. S. Gerasymchuk, V. Y. Chernii, L. A. Tomachynskii, M. Kowalska, J. Legendziewicz, and S. Radzki, “Correlation between computer models of structure of 5-sulfosalicylato Zr(IV) phthalocyanine with results obtained by NMR, ESI-MS and UV-Vis spectra,” *Optical Materials*, vol. 32, no. 9, pp. 1193–1201, 2010.

[25] G. Knor and A. Strasser, “Coexisting intraligand fluorescence and phosphorescence of hafnium(IV) and thorium(IV) porphyrin complexes in solution,” *Inorganic Chemistry Communications*, vol. 5, no. 11, pp. 993–995, 2002.

[26] Z. Changfu, T. Xuexin, W. Dong et al., “An unsymmetrical porphyrin and its metal complexes: synthesis, spectroscopy, thermal analysis and liquid crystal properties,” *Journal of the Serbian Chemical Society*, vol. 74, no. 10, pp. 1097–1104, 2009.

[27] L. Mishra and V. K. Singh, “Synthesis, structural and antifungal studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with new Schiff bases bearing benzimidazoles,” *Indian Journal of Chemistry*, vol. 32, no. 5, pp. 446–457, 1993.

[28] B. Thati, A. Noble, R. Rowan et al., “Mechanism of action of coumarin and silver(I)-coumarin complexes against the pathogenic yeast *Candida albicans*,” *Toxicology in Vitro*, vol. 21, no. 5, pp. 801–808, 2007.