SYNTHESIS AND CHARACTERIZATION OF 5,10,15,20-TETRAKIS[3-(3,4-DICHLOROPHENOXY)]-PORPHYRIN AND SOME OF ITS METAL COMPLEXES

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Abstract: The newly prepared 5,10,15,20-Tetrakis[3-(3,4-dichlorophenoxy)] porphyrin, TDClPP, was characterized by ^{1}H NMR, ^{13}C NMR, electronic absorption spectroscopy, and MALDI-TOF mass spectrometry. The porphyrin exhibited a Soret band at 419 nm and Q bands at 515, 549, 589, 646 nm with corresponding extinction coefficients of $2x10^{5}$, $1x10^{4}$, $4x10^{3}$, $3x10^{3}$, $2x10^{3}$ $cm^{-1}M^{-1}$. Excitation at 419 nm gave an emission line at 650 nm. The quantum yield was determined to be 0.07. The zinc, copper, cobalt, and nickel complexes of this porphyrin have been synthesized and characterized by UV-Vis and MALDI-TOF mass spectroscopy. Details of these spectra are reported in this paper.

Introduction

In recent years, much research has focused on the development of appropriate materials for optical applications.[1-30] Among the types of materials studied are photothermal materials,[1-3] organic dyes,[3-10] magneto-optical materials,[10-13] phase change materials,[10,14-17] holographic materials,[18-24] and electron transfer materials,[15,25-30] such as porphyrins. Porphyrins are an attractive material because of the wealth of known photochemistry and photophysics. For example, the photosynthesis system demonstrates the ability of porphyrins to carry out fast photochemical electron transfer on a picosecond time scale.[31,32] Of equal importance is the area of the spectrum in which the material will absorb. Porphyrins absorb in the blue region of the spectrum, 380 to 500 nm, depending on the structure of the porphyrin. This absorption is observed in the intense Soret band and Q bands of the porphyrins. This makes porphyrins a desirable medium to optical devices using GaN laser diodes, which have emission lines in this region of the spectrum.[33] The advantage of such lasers is that the shorter wavelengths allow for smaller areas in a material to be targeted.

The focus of this work was the synthesis of a new chromophore in which the electron withdrawing group was covalently attached to the molecule. This would give the possibility of intramolecular transfer as well as different absorption characteristics. The desire for chromophores exhibiting qualities described lead to the synthesis of 5,10,15,20-tetrakis[3-(3, 4-dichlorophenoxy)] porphyrin, TDClPP, and some of its metal complexes.

Experimental Section

Chemicals and Reagents. Pyrrole **2**, 3-[3,4-(dichlorophenoxy)]-benzaldehyde **1**, propionic acid, octanoic acid, spectroscopic grade $CHCl_3$, nickel (II) acetate tetrahydrate, cobalt (II) acetate tetrahydrate, copper (II) acetate tetrahydrate, and zinc (II) acetate dihydrate were purchased from Aldrich Chemical Company and used as received.

Methanol purchased from Fischer Scientific was used in the synthesis and column chromatography of the metal complexes. Solvents used for synthesis or NMR measurements were used as received.

Instrumentation

Ultraviolet-visible (UV-vis) absorption spectra for the base TDClPP were recorded on a Hewlett Packard 8451A spectrophotometer. UV-Vis absorption spectra for the metallated TDClPP complexes were recorded on a Jasco V-530 spectrophotometer. All nuclear magnetic resonance (NMR) spectra for the base TDClPP were recorded on a Bruker AV500 or Bruker AV600 spectrometer at approximately 298 K with $CDCl_3$ as the solvent. The chemical shifts are reported in parts per million (δ) with respect to an internal reference peak of residual undeuterated solvent (that is, 7.26 ppm for $CHCl_3$ in $CDCl_3$). The sample **3** was analyzed using ^1H and ^{13}C NMR. The proton assignments were determined using ^1H NMR (500.13 MHz) and ROESY NMR [(AV- 500) Rotating frame Overhauser Enhancement SpectroscopY] and ge-2D-COSY NMR [(500.13 MHz) gradient enhanced correlation spectroscopy]. The numbering for ^1H and ^{13}C NMR is given in fig. (**1**). ^{13}C NMR peaks were assigned using ^{13}C NMR spectrum (125.76 MHz), ^{13}C Dept 90, HSQC ^{13}C (Heteronuclear Single Quantum Coherence), and HMBC ^{13}C (Heteronuclear Multiple Bond Correlation)[1]. A ^{13}C Dept 90 (125.76 MHz), was run to determine the set up for the HSQC ^{13}C dimensions. The HSQC [AV-600; ^1H (600.13 MHz); ^{13}C (150.92 MHz)] was run to get the '$J^1H^{13}C$ interactions and the HMBC (AV-600) was run to make assignments on the non-protonated carbons of the molecule. The mass spectra were taken using a Bruker Reflex™ III with MALDI as the ionization method. For the base porphyrin, the sample was dissolved in acetone, and then the solution was mixed with dihydroxyl benzoic acid matrix at a 1:1 ratio. For the metal complexes, the sample was dissolved in acetone, and this solution was directly applied onto MALDI stainless steel target. Fluorescence spectra were obtained using a FluoroMax-3 spectrofiuorimeter.

Synthesis of 5,10,15,20-Tetrakis[3-(3, 4-dichlorophenoxy)]porphyrin. A single necked 250 mL round bottomed flask fitted with a reflux condenser was charged with 25.0 mL of octanoic acid and 25.0 mL of propionic acid. To this solvent, 1.8 g (6.8 mmol) of 3-(3,4-dichlorophenoxy) benzaldehyde **1** and 0.5 g (6.8 mmol) of pyrrole **3** was added. This mixture was heated with stirring. The color of the solution was amber. This was brought to reflux, and allowed to reflux for 30 min. The color of the solution was dark brown to black after being heated. This solution was allowed to cool to room temperature and the electronic absorption spectrum was measured. After cooling, the solution was added to an 800 mL Erlenmeyer flask followed by a 2.0 M solution of $NaHCO_3$. The mixture was gently stirred until the acids were neutralized. The solution was then left in the flask stirring overnight to ensure complete neutralization. This solution containing crude porphyrin was filtered using vacuum filtration and the solid was allowed to dry. A column was packed with dry silica gel, 70-230 mesh, with chloroform as the eluent. The crude compound was chromatographed; 1.7 g (1.34 mmoles) pure compound was recovered. The overall reaction yield was 80%. Figure 1 shows the reaction scheme for TDClPP **1.** The structure was confirmed using ^1H NMR, ^{13}C NMR, UV-Vis and high resolution mass spectrometry. UV ($CHCl_3$) [λ,nm (ε, $cm^{-1}M^{-1}$)]: 419 ($2x10^5$), 515 ($1x10^4$), 549 ($4x10^3$), 589 ($3x10^3$), 646 ($2x10^3$). ^1H NMR (500.13 MHz, $CDCl_3$), δ (ppm): 8.91 (s, 8H, H_β), 8.04 (d, J=7.3 Hz, 4H, H_4), 7.90 (s, 4H, H_2), 7.77 (dd, J=7.3, 8.4 Hz, 4H, H_5), 7.47 (dd, J= 8.4, 2.2 Hz, 4H, H_6), 7.43 (d, J=8.7 Hz, 4H, $H_{5'}$), 7.37 (d, J=2.0 Hz, 4H, $H_{2'}$), 7.12 (dd, J=8.7, 2.0 Hz, 4H, $H_{6'}$), -2.80 (s, 2H, NH). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ (ppm): 156.47 ($C_{1'}$), 154.8 (C_1), 145.86 ($C_{\alpha\text{-pyrrole}}$), 144.02 ($C_3$), 133.40($C_{3'}$), 131.19 ($C_{5'}$), 131.1 ($C_{\beta\text{-pyrrole}}$), 130.67 ($C_4$), 128.23 ($C_5$), 126.86 ($C_{4'}$), 125.49 ($C_2$), 120.68 ($C_{2'}$), 119.14 ($C_{meso}$), 118.64 ($C_6$), 118.21 ($C_{6'}$). MALDI-TOF MS (m/z): $[M + H]^+$ calcd for $C_{68}H_{38}N_4Cl_8O_4$: 1255.04 a.m.u (monoisotopic); observed: 1255.09 a.m.u.. Mp 103 °C. Excitation at 419 nm of a 10^{-6} M solution of TDClPP gave an

emission line at 650 nm. The fluorescence quantum yield, Φ_F, was determined to be 0.07 at room temperature for chloroform solutions of TDClPP by a relative method using TPP in $CHCl_3$ as a standard having $\Phi_F = 0.11$ as reported in the literature.[34] Figure 2 gives the numbering system used in the NMR analysis.

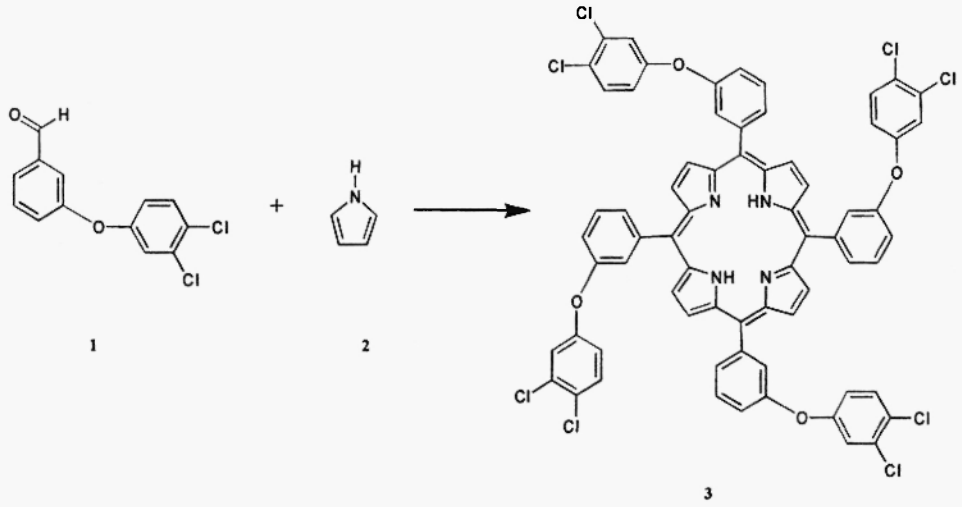

Figure-1 : Synthesis of 5,10,15,20-tetrakis[3-(3, 4-dichlorophenoxy)]porphyrin.

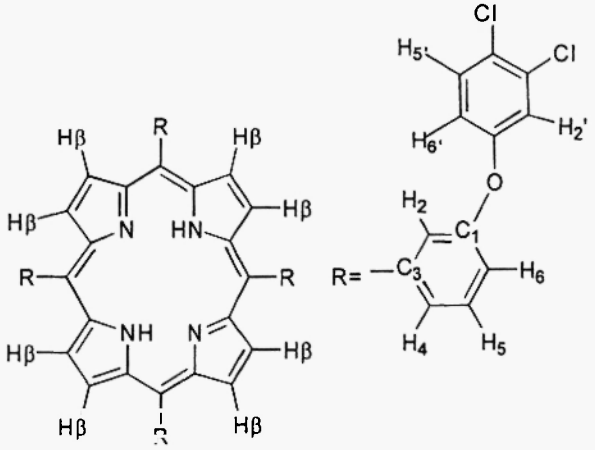

Figure-2 : Structure of TDClPP numbered for NMR analysis.

Synthesis of 5, 10, 15, 20-Tetrakis[3-(3, 4-dichlorophenoxy)]porphyrin Metal Complexes. The cobalt, nickel, copper, and zinc complexes were prepared using chromatographed 5,10,15,20-tetrakis[(3-(3,4-dichlorophenoxy)]-porphyrin **3** (0.2 g, 0.2 mmoles) in boiling chloroform (100 mL). Once the porphyrin was dissolved, 3 mL of a saturated solution of the metal acetate hydrate in methanol was added. The reaction was monitored using UV-Vis looking at the shift in the Soret band. The shift in the electronic absorption spectrum indicated the formation of the metal complex. The reaction mixture was concentrated on a rotary evaporator. The metal complexes were purified using column chromatography on silica gel with chloroform as the eluent. The yields of these reactions and other characterizations are given below.

(5,10,15,20-Tetrakis[3-(3,4-dichlorophenoxy)]porphyrinato)cobalt. Reaction time: 25 min. The overall yield of the reaction was 62%. UV ($CHCl_3$) [λ,nm (ε, $cm^{-1}M^{-1}$)]: 412 ($2x10^5$), 530 ($1x10^4$). MALDI-TOF MS (m/z): calcd for $C_{68}H_{36}N_4Cl_8O_4Co$: 1311.0 a.m.u (monoisotopic); observed: 1311.0 a.m.u.. Mp 125 °C.

(5,10,15,20-Tetrakis[3-(3,4-dichlorophenoxy)]porphyrinato)nickel. Reaction time: 3 days. The overall yield of the reaction was 65%. UV ($CHCl_3$) [λ,nm (ε, cm $^1M^{-1}$)]: 418 ($1x10^5$), 528 ($1x10^4$). MALDI-TOF MS (m/z): calcd for $C_{68}H_{36}N_4Cl_8O_4Ni$: 1310.0 a.m.u (monoisotopic); observed: 1310.2 a.m.u.. Mp 84 °C.

(5,10,15,20-Tetrakis[3-(3, 4-dichlorophenoxy)]porphyrinato)copper. Reaction time: 1 min. The overall yield of the reaction was 40%. UV ($CHCl_3$) [λ,nm (ε, $cm^{-1}M^{-1}$)]: 416 ($4x10^5$), 539 ($2x10^4$). MALDI-TOF MS (m/z): calcd for $C_{68}H_{36}N_4Cl_8O_4Cu$: 1315.0 a.m.u (monoisotopic); observed: 1315.0 a.m.u.. Mp 86 °C.

(5,10,15,20-Tetrakis[3-(3,4-dichlorophenoxy)]porphyrinato)zinc. Reaction time: 30 min. The overall yield of the reaction was 70%. UV ($CHCl_3$) [λ,nm (ε, cm $^1M^{-1}$)]: 424 ($3x10^5$), 550 ($1x10^4$). MALDI-TOF MS (m/z): calcd for $C_{68}H_{36}N_4Cl_8O_4Zn$: 1316.0 a.m.u (monoisotopic); observed: 1316.1 a.m.u.. Mp 90 °C. Excitation at 515 nm ZnTDClPP gave emission lines at 602 and 644 nm. The fluorescence quantum yield, Φ_F, was determined to be 0.11 at room temperature for chloroform solutions of ZnTDClPP by a relative method using TPP in $CHCl_3$ as a standard having Φ_F = 0.11 as reported in the literature.[34]

Results and Discussion

5,10,15,20-Tetrakis[3-(3,4 dichlorophenoxy)]porphyrin **3** was prepared from pyrrole **2** and 3-(3,4-dichlorophenoxy)benzaldehyde **1** using a 50:50 mixture of propionic and octanoic acid as the solvent. This solvent system was found by Lindsey and coworkers to work better than the normal acetic acid method used by Adler and many others in preparation of porphyrins.[35] The overall yield of the reaction was 80%. The newly prepared TDClPP was characterized by ^1H NMR, ^{13}C NMR, UV-Visible spectroscopy, and MALDI-TOF mass spectrometry. The TDClPP metal complexes were characterized using UV-Visible spectroscopy and MALDI-TOF mass spectrometry. The electronic absorption spectrum for TDClPP is similar to that of all porphyrins. There is an intense absorption at 419 nm, the Soret band and Q bands are observed at 515 nm, 549 nm, 589 nm, and 646 nm. A series of solutions were prepared of varying concentrations of TDClPP in $CHCl_3$. The concentrations ranged from 2.0×10^{-4} to 1.0×10^{-6} M. UV-vis spectra were taken for each of the solutions. The purpose of these experiments was to elucidate the extinction coefficient of the Soret band for the porphyrin as well as the different Q bands. No systematic shifts in peak positions were observed and the extinction coefficients for the Soret band and the Q bands are very high. The non-metallated porphyrin displays an extinction coefficient of 2×10^5 $cm^{-1}M^{-1}$ for the Soret band at 419 nm. Four Q bands are observed at 515 nm, 549 nm, 589 nm, and 646 nm with extinction coefficients given as 1×10^4 $cm^{-1}M^{-1}$, 4×10^3 $cm^{-1}M^{-1}$, 3×10^3 $cm^{-1}M^{-1}$, and 2×10^3 $cm^{-1}M^{-1}$ respectively. Upon metallation, a shift in the Soret band for each complex was observed. These shifts are consistent with corresponding shifts in spectral data of 5,10,15,20-tetrakisphenylporphyrin and its metal complexes.

Conclusions

In summary, we present the first report of the synthesis and characterization of 5,10,15,20-tetrakis[3-(3,4-dichlorophenoxy)]porphyrin and its cobalt, nickel, copper, and zinc complexes. This compound is of interest and will be further studied in our laboratories for potential application in many areas of interest including but not limited to optical data storage and solar energy storage.

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References

1. T.C. Gunaratne, A.V. Gusev, X. Peng, A. Rosa, G. Ricciardi, E.J. Baerends, C. Rizzoli, M.E. Kenney and M.A.J. Rodgers, *J. Phys. Chem.* A **109**, 2078 (2005)
2. K. Szacilowski, W. Macyk, A. Drzewiecka-Matuszek, M. Brindell and G. Stochel, *Chem. Rev.* **105**, 2647 (2005)
3. T.N. Gerasimova and V.V. Shelkovnikov, *Russian Chem. Rev.* **61**, 55 (1992)
4. N.A. Melosh, C.A. Steinbeck, B.J. Scott, R.C. Hayward, P. Davidson, G.D. Stucky and B.F. Chmelka, *J. Phys. Chem.* B **108**, 11909 (2004)
5. H.S. Cho, D.H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda and A. Osuka, *J. Am. Chem. Soc.* **124**, 14642 (2002)
6. D.M. Martino and H. Willigen, *J. Phys. Chem.* A **104**, 10701 (2000)
7. V. Novotny and L. Alexandru, *J. Appl. Polym. Sci.* **24**, 1321 (1979)
8. K.T. Law, P.S. Vincett, R.O. Loutfy, L. Alexandru, M.A. Hopper, J.H. Sharp and G.E. Johnson, *Appl. Phys. Lett.* **36**, 884 (1980)
9. K.T. Law, P.S. Vincett and G.E. Johnson, *Appl. Phys. Lett.* **39**, 718 (1981)
10. M. Emmelius, G. Pawlowski and H.W. Vollmann, *Angewandte Chemie* **28**, 1445 (1989)
11. X. Xu, S.A. Majetich and S.A. Asher, *J. Am. Chem. Soc.* **124**, 13864 (2002)
12. P.G. Lacroix, *Chem. Mater.* **13**, 3495 (2001)
13. T. Suzuki, *MRS Bulletin* **21**, 42 (1996)
14. M. Seredyuk, A.B. Gaspar, V. Ksenofontov, S. Reiman, Y. Galyametdinov, W. Haase, E. Rentschler and P. Gutlich, *Chem. Mater.* **18**, 2513 (2006)
15. O. Ostroverkhova and W. E. Moerner, *Chem. Rev.* **104**, 3267 (2004)
16. N. Yamada, *MRS Bulletin* **21**, 48 (1996)
17. B. Ryan, *Byte* **15**, 289 (1990)
18. A. Urbas, V. Tondiglia, L. Natarajan, R. Sutherland, H. Yu, J.-H. Li and T. Bunning, *J. Am. Chem. Soc.* **126**, 13580 (2004)
19. A. Renn, U.P. Wild and A. Rebane, *J. Phys. Chem. A*, **106**, 3045 (2002)
20. T.J. Trentler, J.E. Boyd and V.L. Colvin, *Chem. Mater.* **12**, 1431 (2000)
21. N. Hampp, *Chem. Rev.* **100**, 1755 (2000)
22. M.P. Bernel, G.W. Burr. H. Coufal, R.K. Grygier, J.A. Hoffnagle, C.M. Jefferson, R.M. Macfarlane, R.M. Shelby, G.T. Sincerbox and G. Wittmann, *MRS Bulletin* **21**, 51 (1996)
23. D. Psaltis and F. Mok, *Scientific American* **273**, 70 (1995)
24. D. Lande, S. Orlov, A. Akella, L. Hesselink and R. Neurgaonkar, *Opt. Lett.* **22**, 1722 (1997)
25. T.P.I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.* **107**, 1011 (2007)
26. S. Selvakumar, S. M. Ravi Kumar, K. Rajarajan, A.J.A. Pragasam, S.A. Rajasekar, K. Thamizharasan and P. Sagayaraj, *Crystal Growth & Design* **6**, 2607 (2006)
27. D. Pop, B. Winter, W. Freyer, R. Weber, W. Widdra and I.V. Hertel, *J. Phys. Chem. B* **108**, 9158 (2004)

28. K.D. Belfield, A.R. Morales, J.M. Hales, D.J. Hagan, E.W. Van Stryland, V.M. Chapela and J. Percino, *Chem. Mater.* **16**, 2267 (2004)

29. J. Lindmayer, P. Goldsmith and, C. Wrigley, *Laser Focus World* **25**, 119 (1989)

30. W.W. Gibbs, *Scientific American* **273**, 31 (1995)

31. J.R. Bolton, N. Mataga and G. McLendon (Eds), *Electron Transfer in Inorganic, Organic, and Biological Systems, American Chemical Society*, Washington, DC., 1991

32. R.A. Marcus, *Chem. Phys. Lett.* **133**, 471 (1986)

33. K. Niemax, A. Zybin and D. Eger, *Anal. Chem* **73**, 134A (2001)

34. M. Gouterman and G.E.Khalil, *J. Mol. Spectrosc.* **53**, 88 (1974)

35. E.C.A. Ojadi, H. Linschitz, M. Gouterman, R.I. Walter, J.S. Lindsey, R.W. Wagner, P.R. Droupadi and W.J. Wang, *Phys. Chem* 97, 13192 (1993).

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