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Synthesis and spectral evaluation of 5,10,15,20-tetrakis(3,4-dibenzyloxyphenyl) porphyrin

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Abstract: Porphyrins are of interest in many applications that involve electron transfer and absorption of light, such as solar energy and photodynamic cancer therapy. The newly synthesized 5,10,15,20-tetrakis(3,4-dibenzyloxyphenyl)porphyrin, TDBOPP, was characterized using ^{1}H NMR, ^{13}C NMR, UV-vis and fluorescence spectroscopy and MALDI-TOF/TOF high resolution mass spectrometry. Standard ^{1}H NMR and ^{13}C NMR experiments coupled with nuclear Overhauser effect (NOE) experiments confirmed the structure of the compound. The expected M^+ and $[M+H]^+$ ions are observed in the MALDI-TOF/TOF mass spectrum. The UV-vis absorption spectrum of TDBOPP shows a Soret band at 424 nm and three Q bands at 519 nm, 556 nm, and 650 nm with molar absorptivity 3.6×10^5 cm^{-1}M^{-1}, 1.6×10^4 cm^{-1}M^{-1}, 1.0×10^4 cm^{-1}M^{-1} and 5.3×10^3 cm^{-1}M^{-1}, respectively. Excitation at 424 nm gives emission at 650 nm. The quantum yield of the porphyrin is 0.11.

Keywords: fluorescence; porphyrin; spectroscopy; synthesis; UV-vis.

Introduction

To see the amazing diversity with which porphyrins are useful, one only needs to look to nature. Scientist for years have tried to mimic the roles that porphyrins play in nature to exploit their usefulness in applications such as dye sensitized solar cells [1–7], photodynamic cancer therapy [8, 9] and sensors of many kinds [10–19]. These applications utilize the property of porphyrins to undergo extraordinarily fast electron transfers. Two examples are the use of chlorophyll in plants to absorb energy from the sun and convert it to energy that can be used by the plants in the process of photosynthesis. In photosynthesis, electron transfer on the picosecond time scale has been measured [20]. If we could mimic this property and the efficiency with which it is carried out in nature in the production of dye sensitized solar cells, our energy needs would be met. Another example of porphyrins in nature is found in hemoglobin, the oxygen transport protein which binds oxygen in areas of our body where the partial pressure of oxygen is high and carries it to places in our body where the partial pressure of oxygen is low and releases it. Upon release, it can be used in respiration. Basic research in porphyrin chemistry is reported in this paper. The synthesis, purification and characterization of the new compound, 5,10,15,20-tetrakis(3,4-dibenzyloxyphenyl) porphyrin (**1**), is described. Synthesis and characterization of some of its metal complexes is currently underway in our laboratories.

Results and discussion

Synthesis of porphyrin **1**, abbreviated as TDBOPP, was carried by the reaction of pyrrole and 3,4-dibenzyloxybenzaldehyde in propionic acid as the solvent (Scheme 1) [21–23]. Porphyrins are usually produced in low yields and the synthesis of TDBOPP was no exception. The overall yield of the reaction was 31%. The composition was verified by obtaining the exact masses for M^+ and $[M+H]^+$ using MALDI-TOF/TOF high resolution mass spectrometry (Figure 1). TDBOPP was further characterized by ^{1}H NMR, ^{13}C NMR, UV-vis and fluorescence spectroscopy.

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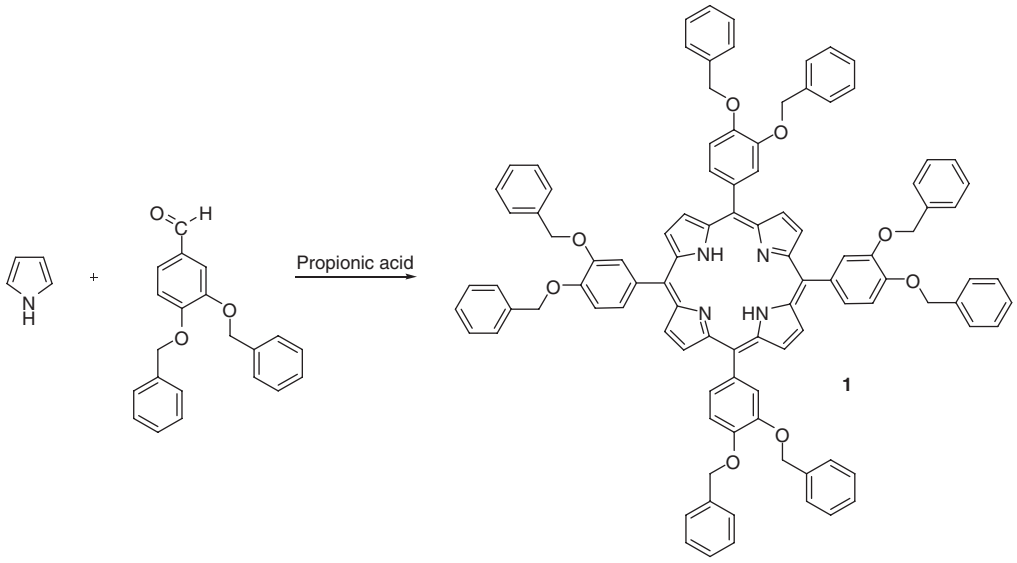

Scheme 1 Synthesis of 5,10,15,20-tetrakis(3,4-dibenzyloxyphenyl)porphyrin.

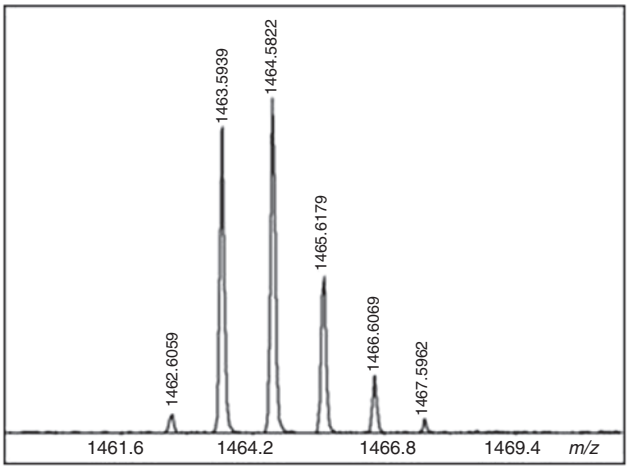

Figure 1 MALDI-TOF/TOF HRMS in the molecular ion region.

NMR experiments

From analysis of Figure 2, it can be expected that in the ^{1}H NMR spectrum of TDBOPP the hydrogens numbered 1, 2, 3, 6 and 13 will appear as singlets, the hydrogens numbered as 4, 5, 7 and 10 will appear as doublets and hydrogens numbered 8, 9, 11 and 12 will appear as triplets. Due to the diamagnetic ring current experienced by H_1 atoms, these protons show resonance at −2.80 ppm. The remaining singlets were assigned using NOE experimental data. When the resonance at 5.36 ppm is irradiated, an enhancement is observed in the resonance at 7.54 ppm which indicates that these two protons are in close proximity. This information coupled with the experiment where the signal at 7.90 ppm is irradiated causing an enhancement in the resonance at 7.54 ppm leads to the confirmation that the singlet at 5.36 is H_{13}, the doublet at 7.54 ppm is H_{10} and the peak at 7.90 ppm, resolved to a singlet when heated to 305 K, can be assigned to H_3. Additional NOE experiments gave the assignment of H_6 and H_7. Irradiation of the resonance at 5.49 ppm causes an enhancement of the resonance at 7.70 ppm and hence the singlet at 5.49 ppm is assigned to H_6 and the doublet at 7.70 ppm is assigned to H_7.

COSY experiments were done to extract more information about the assignments of the remaining hydrogens. In these experiments, coupling between the doublet at 7.70 ppm and the triplet at 7.53 ppm was observed and coupling between the triplet at 7.53 ppm and the triplet at 7.45 ppm was observed. These observations confirm the assignment of these peaks, 7.53 ppm to H_8 and 7.45 ppm to H_9. Due to coupling between the doublet at 7.54 ppm and the triplet at 7.40 ppm, the proton H_{11} is assigned to the peak at 7.40 ppm. The remaining triplet at 7.35 ppm corresponds to proton H_{12}. COSY experiments confirmed the correlation between the resonances at 7.34 ppm and 7.74 ppm and that the resonance at 7.74 ppm is correlated with the resonance at 7.90 ppm. Thus, the doublet at 7.34 ppm corresponds to H_5 and the broad peak at 7.74 ppm belongs to H_4. The remaining peak in the spectrum appeared as an imperfect doublet in the range of 8.80 ppm to 8.76 ppm. Since heating the sample to 315 K resolved this peak into a singlet, this peak must be assigned to H_2. ^{13}C NMR peaks were assigned from analysis of the spectrum, from data obtained in the ^{13}C-^{1}H correlation and from data of a heteronuclear multiple bond correlation.

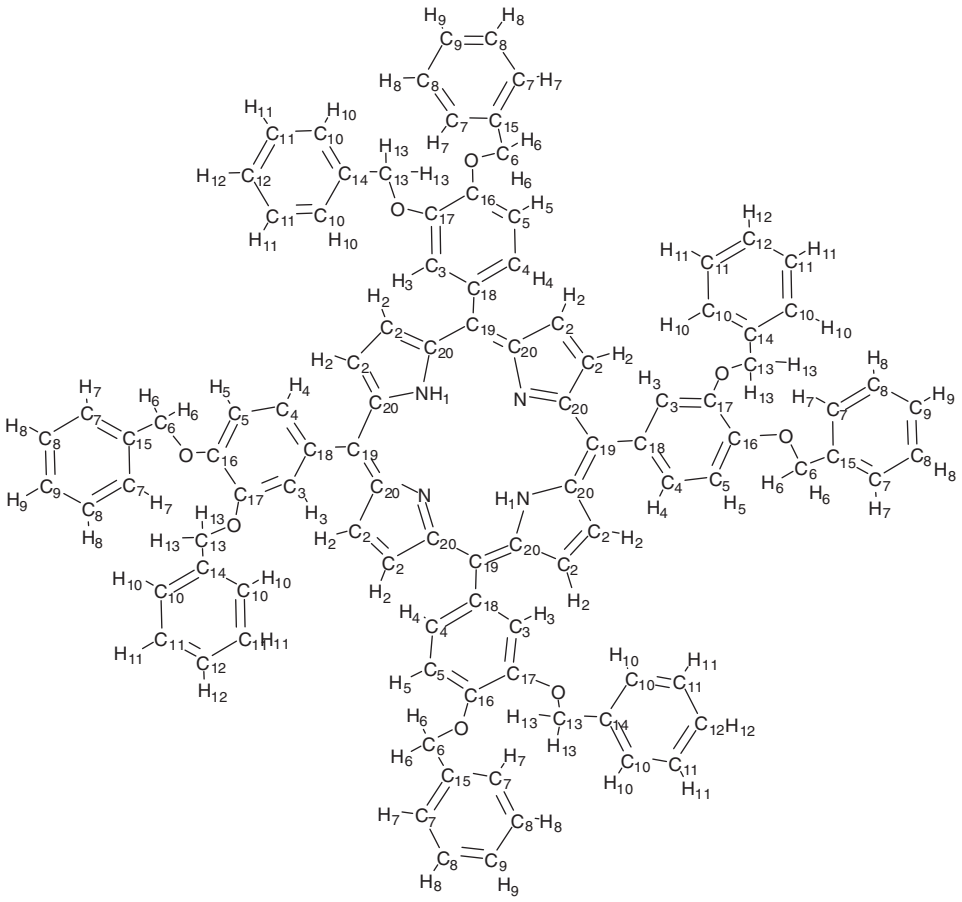

Figure 2 A numbering scheme for hydrogen and carbon atoms of 5,10,15,20-tetrakis-(3,4-dibenzyloxyphenyl)porphyrin. The hydrogens and carbons are numbered in accordance with ^{1}H and ^{13}C NMR assignments.

Electronic absorption spectra

The electronic absorption spectrum of TDBOPP is given in Figure 3. There is an intense absorption at 424 nm for the Soret band and the Q bands are observed at 519 nm, 556 nm, and 650 nm. A series of solutions of TDBOPP in $CHCl_3$ were prepared at varying concentrations ranging from 5.5×10^{-5} M to 1.7×10^{-7} M. UV-vis spectra were taken for each of the solutions. The purpose of these experiments was to elucidate the molar absorptivities of the Soret band and the Q bands and to determine if Beer's law was obeyed. The molar absorptivities for the Soret band and the Q bands are high as expected. This porphyrin displays a molar absorptivity of 3.6×10^{5} $cm^{-1}M^{-1}$ for the Soret band at 424 nm. The Q bands are observed at 519 nm, 556 nm, and 650 nm with molar absorptivities of 1.6×10^{4} $cm^{-1}M^{-1}$, 1.0×10^{4} $cm^{-1}M^{-1}$, and 5.3×10^{3} $cm^{-1}M^{-1}$, respectively.

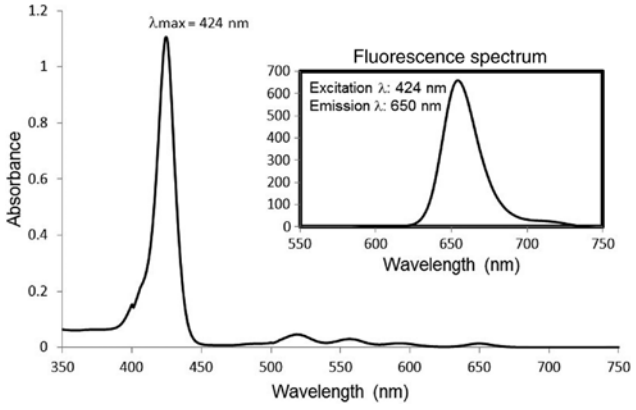

Figure 3 Electronic absorption and fluorescence spectra for TDBOPP.

Fluorescence measurements

Excitation at 424 nm gives an emission line at 650 nm. The fluorescence quantum yield, Φ_F is 0.11 at room temperature in chloroform, with an excitation wavelength of 515 nm, by a relative method using TPP in chloroform as a standard having Φ_F of 0.11 as reported in the literature [24]. The fluorescence spectrum is given in Figure 3.

Conclusions

The first report of the synthesis and characterization of 5,10,15,20-tetrakis(3,4-dibenzyloxyphenyl)porphyrin is presented. The absorption spectrum of TDBOPP shows a characteristic spectral pattern similar to those of other porphyrins. The fluorescence spectrum is also consistent with what is observed with other porphyrins. The expected M^+ and $[M+H]^+$ ions observed in the MALDI mass spectrum are in excellent agreement with the given structure. Analysis of ^{1}H NMR and ^{13}C NMR spectra confirm the structure. This compound is being studied further for usefulness in applications involving electron transfer.

Experimental

The reagents and solvents were purchased from Fisher Scientific. Ultraviolet-visible (UV-vis) absorption spectrum for the porphyrin was recorded on a Jasco V-530 spectrophotometer. The MALDI-TOF/TOF high resolution mass spectrum was acquired on a AB Sciex 4800 MALDI TOF/TOF mass spectrometer equipped with a Nd : YAG laser operating at 355 nm. The signal was averaged over 1600 scans, at laser power of 4600. The sample was prepared as following: The TDBOPP sample powder was dissolved in chloroform at 20 μg/mL and the matrix solution was α-cyano-4-hydroxycinnamic acid at 7 mg/mL in 60/40 (v/v) acrylonitrile/water. The calibration peptide mixture contained bradykinin, angiotensin and neurotensin ACTH in water. For internal calibration, 10 μL of matrix, 10 μL of calibration peptide mixture, and 2 μL of 20 μg/mL sample were mixed together and 1 μL of the mixture was spotted on target. The ^{1}H NMR (500 MHz) spectrum and ^{13}C NMR (125 MHz) spectrum were recorded in $CDCl_3$ on a Bruker AM 500 spectrometer at approximately 298 K. Fluorescence spectrum was obtained using a JascoFP-6300 spectrofluorometer.

Synthesis of 5,10,15,20-tetrakis(3,4-dibenzyloxyphenyl) porphyrin

A mixture of pyrrole (1.60 g, 5.02 mmol), 3,4-dibenzyloxybenzaldehyde (0.36 g, 5.39 mmol) and 100 mL of propionic acid was stirred and heated under reflux for 30 min, then cooled and treated with an aqueous saturated solution of sodium carbonate until propionic acid was neutralized. This mixture was then filtered and the solid material collected. The crude porphyrin was purified by silica gel column chromatography eluting with chloroform: Yield 0.56 g (0.38 mmol, 31%); UV-vis ($CHCl_3$) [λ, nm (ε, $cm^{-1}M^{-1}$)]: 424 (3.6×10^5), 519 (1.6×10^4), 556 (1.0×10^4), 650 (5.3×10^3); ^{1}H-NMR: δ – 2.80 (s, NH_1), 8.80 (s, H_2), 7.90 (s, H_3), 7.74 (d, $J=8$ Hz, H_4), 7.34 (d, $J=8$ Hz, H_5), 5.49 (s, H_6), 7.70 (d, $J=8$ Hz, H_7), 7.53 (t, $J=8$ Hz, H_8), 7.45 (t, $J=8$ Hz, H_9), 7.54 (d, $J=8$ Hz, H_{10}), 7.40 (t, $J=8$ Hz, H_{11}), 7.35 (t, $J=8$ Hz, H_{12}), 5.36 (s, H_{13}); ^{13}C-NMR: δ 149.0 (C16), 146.8 (C17), 137.4 (C15), 137.2 (C14), 135.5 (C18), 130.8 (C2), 128.7 (C8), 128.6 (C11), 128.4 (C4), 128.0 (C9), 127.9 (C12), 127.6 (C10), 127.5 (C7), 122.4 (C3), 119.7 (C19), 113.1 (C5), 71.6 (C6), 71.5 (C13). MALDI-TOF MS. Calcd for $C_{100}H_{78}N_4O_8$ (M^+): *m/z* 1463.5893. Found: *m/z* 1463.5939.

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