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Synthesis, Characterization and AC, DC conductivity of Tetramethoxy and Tetrahydroxy phenyl porphyrin.

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ABSTRACT

Porphyrins have ability to undergo fast electron transfer. The fast electron transfer reaction gives promise for much application in Optoelectronics. The compound 5,10,15,20 Tetramethoxy phenyl porphyrin (H_2TMPP) and 5,10,15,20 Tetrahydroxy phenyl porphyrin (H_2THPP) were synthesized by modified Alder procedure. These compounds are characterized by UV-Visible spectroscopy, H-NMR and Cyclic voltammetry. The DC conductivity of the compounds is measured by Keithley High Resistance Meter/Electrometer 6517B at room temperature. The AC conductivity of the compounds carried out using a Hioki 3532-50 LCR meter at room temperatures in the frequency range 50 Hz to 5MHz. Tetramethoxy and Tetrahydroxy porphyrins show some AC and DC conductivity. So it can be used for Optoelectronic applications.

Keywords: AC conductivity, DC conductivity, Cyclic Voltammetry, UV-Visible, ^{1}H-NMR.

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INTRODUCTION

Porphyrins continue to attract a great deal of attention for organic photonic devices because of their strongly light absorbing chromophores, varied molecular framework and versatile optoelectronic properties [1-4]. Porphyrins are aromatic compounds, where the molecule contains four pyrrole ring linked via methane bridges. The properties of these compounds can be systematically turned by rational utilization of substituents as well as by using different metal atoms. These modifications can change the molecular properties like geometric, electronic structure and optical properties [5-6]. Efforts are being made to study new organic materials and boosting their physical properties in order to incorporating them into all modern applications. The electronic and photophysical properties are governed by the bound, metal ion, exocyclic moites on the pyrrole ring or the meso position, the matrix surrounding the chromophore[7-8].

Porphyrins are a class of organic compounds having very alternative features with high thermal and chemical stability. They are classified as p-type semiconductor and characterized by low mobility and low carrier concentration [9-10]. Electrical conductivity is a prominent factor which reveals reliable information about the transport phenomenon in materials. Porphyrins coupled to electron donor and electron acceptors have been designed for efficient photo induced electron transfer suitable for a variety of optoelectonic applications Berezina et al [11]. El-Nahass et al [12-13] and have studied the conductivity of metallated tetraphenyl porphyrins. Conductivity was measured depending upon either frequency dependence or temperature dependence. The aim of the present work is to study the AC and DC conductivity of Tetramethoxy and Tetrahydroxy phenyl porphyrins at room temperature and in the frequency range of 50Hz to 5MHZ.

EXPERIMENTAL

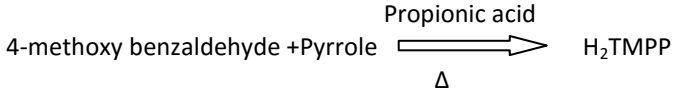
Materials

All the chemicals and reagents used were analar grade obtained from Merck, India and were used as received without further purification.

Synthesis

Synthesis of 5,10,15,20 Tetramethoxy phenyl porphyrin (H_2TMPP)

Tetramethoxy porphyrin was prepared from pyrrole and 4-methoxy benzaldehyde by Adler's method incorotporating some modifications [14]. Freshly distllled pyrrole (1.67 mL, 25 mmol) and 4-methoxy benzaldehyde (**2.**8mL, 25 mmol) were added to about 500 mL of boiling propionic acid in a 1000 mL round-bottomed flask fitted with a water condenser and refluxed carefully for 2 hour. The reacilon mixture was cooled to room temperature and stored in refrigerator for 12 h. The solid insoluble propionic acid was filtered and washed thoroughly with ethanol till the filtrate become colourless. The solid residue was then purified by column chromatography on silica gel (100-200 mesh) using toluene as the eluant. The first violet coloured fraction was collected and the solid porphyrin was obtained by the removal of the solvent .(Figure 1a)



Synthesis of 5,10,15,20 Tetrahydroxy phenyl porphyryin (H_2THPP)

The compound Tetrahydroxy phenyl porphyrin was obtained from the free base Tetramethoxy phenyl porphyrin by hydrolysis of methoxy groups using the known procedure[15] .Typically, a 250 mL round bottom flask equipped with a magnetic stirring bar was charged with Tetramethoxy phenyl porphyrin (1. 468 g, 2 mmol) and pyridine hydrochloride (50 g). The flask was fitted with a condenser and kept under gentle reflux for 3 h. The heating source was removed and the hot solution was poured into 1000 ml of water. The aqueous mixture was extracted with ethyl acetate and the combined organic layer was washed with 1% hydrochloric acid and filtered. The filtrate was concentrated to a purple solid which was dried under vacuum to give Tetrahydroxy phenyl porphyrin. The completion of the reaction was monitored through TLC. The product was

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purified by column chromatography on silica gel (100 - 200 mesh) using chloroform followed by methanol in chloroform as eluant.(Figure 1b)

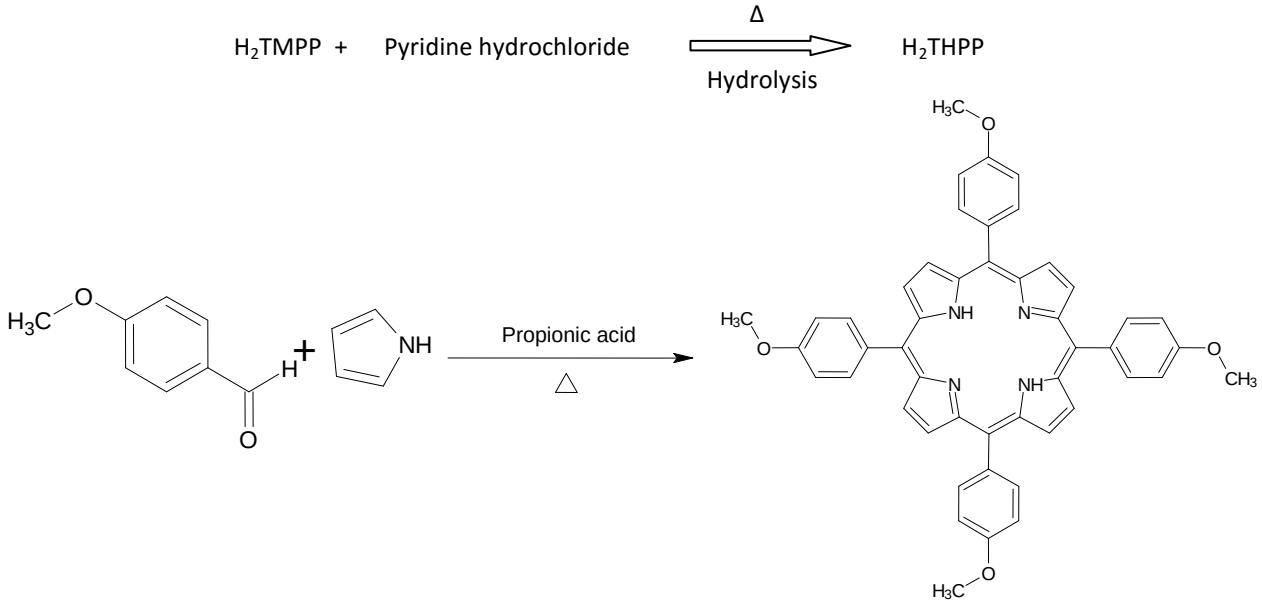

Figure 1a: Synthesis of 5,10,15,20 Tetramethoxy phenyl porphyrin

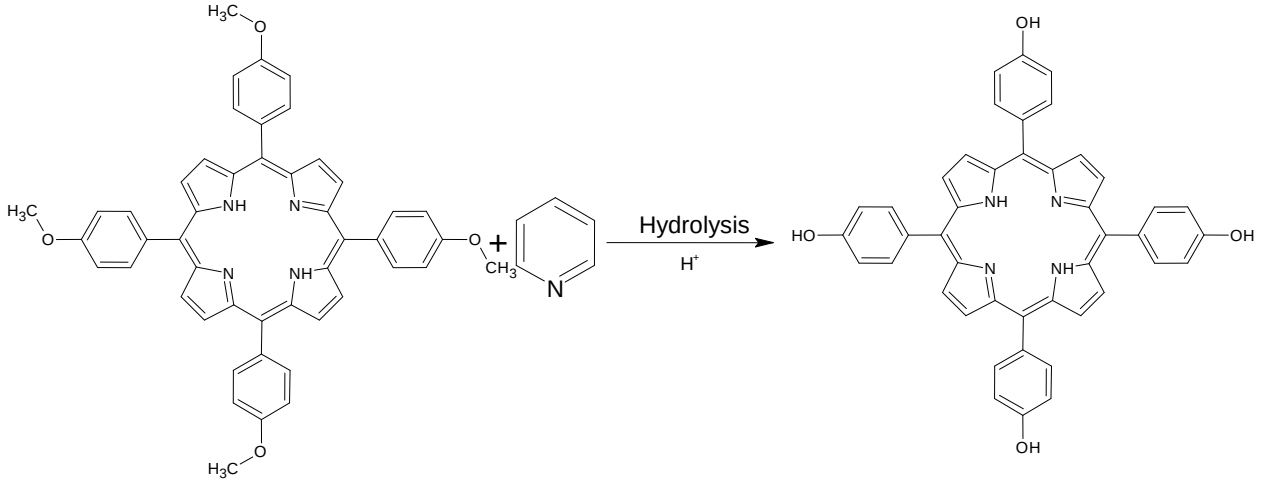

Figure 1b: Synthesis of 5,10,15,20 Tetrahydroxy phenyl porphyrin

Characterization techniques

UV-Visible Spectroscopy

UV-Visible Spectra were recorded at room temperature using Schimadzu 1501 spectrophotometer with 2 nm resolution.

NMR Spectroscopy

^{1}H NMR were run on a Bruker 400 MHz spectrometer using DMSO-D6 as solvent and TMS (Tetra Methyl Silane) as the internal standard.

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Cyclic Voltametry

Cyclic voltammograms were recorded using a one-compartment, three electrode cell, CH-Instruments, equipped with a platinum wire auxiliary electrode. The working electrode was a 2.0 mm diameter platinum disk from CH Instruments.

Electrical Studies

I-V measurement

The DC conductivity of H_2TMPP and H_2THPP particles are measured by Keithley High Resistance Meter/Electrometer 6517B at room temperature.This electrometer has an in-built capability of output independent voltage source of ±1000 V. The synthesized porphyrins filtered and extracted with ethanol are ground into fine powder. The powder is made into pellet at thickness of 2.434mm by hydraulic pressure pelletizer[16]. The thickness of the pellets is measured using a screw gauge. The circuit diagram used for this study is shown in the figure 1c. To ensure the proper connection to the sample, the self-made sample holder with copper electrodes is used. The pellet is mounted between two copper electrodes of the sample holder for I-V measurement.

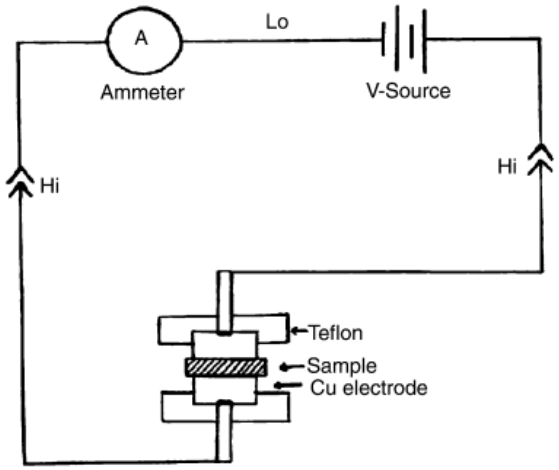

Figure 1c: The circuit diagram used for I-V measurements

Measurement of AC conductivity

The AC conductivity of the samples was carried out using a Hioki 3532-50 LCR meter at room temperatures in the frequency range 50 Hz to 5 MHz [17]. The prepared Tetramethoxy and Tetrahydroxy phenyl porphyrin pellets were treated with good quality silver paste to obtain good ohmic conduct when placed between the copper electrodes for the measurements

RESULT AND DISCUSSION

Characterization

UV- Visible Spectroscopy

The electronic absorption spectrum of porphyrin consists of two regions.The first one involves the transition from ground sate to excited state and the corresponding peak is called as Soret band or B band.The second one consists of weak transitions to the first excited state and the corresponding peak is called Q bands. Methoxy substituted tetra phenyl porphyrin shows Soret band at 415nm and Q bands exhibits peak at 510 nm, 544nm, 589 nm,640 nm.(Figure 2a). Tetrahydroxy phenyl porphyrin exhibits Soret band around 420 nm and Q band appears at 513 nm, 550nm, 593nm, 680 nm (Figure 2b)

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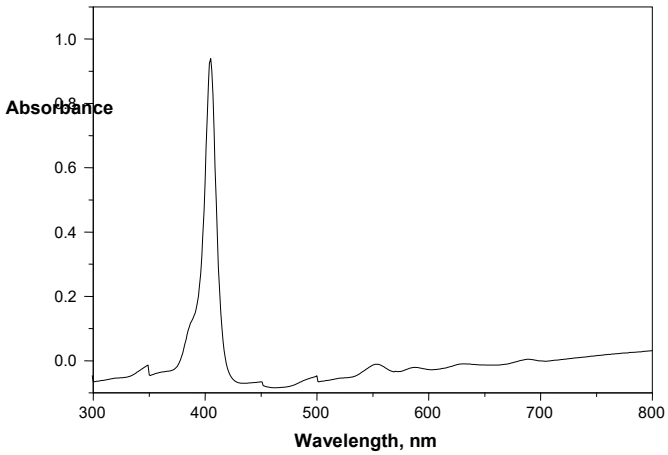

Fig 2a: UV-Visible sprectrum of 5, 10, 15, 20 Tetramethoxy phenyl porphyrin

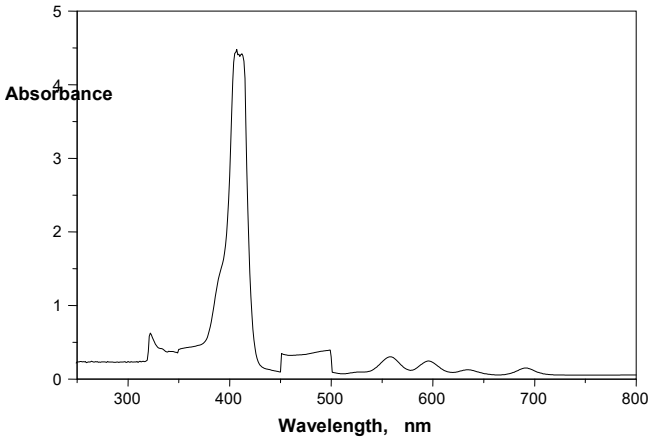

Fig 2b: UV-Visible spectrum of Tetrahydroxy phenyl porphyrin

Meso substituted porphyrins display a red shift in the soret band. This shift is observed because the addition of electron donating groups to the porphyrin results in an extension of conjucation. The energy required for π-π* transistion is less. Red shift increases with increasing electron donating nature of meso substituents [18].

Cyclic voltammetry

When the complex H_2TMPP cycled in the anodic direction there is a two oxidation potential associated with 0.09V and 1.1V due to oxidation of porphyrin. In the cathodic direction redox couple with -1.62V and -1.27V associated with reduction.Cyclic voltagram of H_2TMPP is shown in Figure.3a

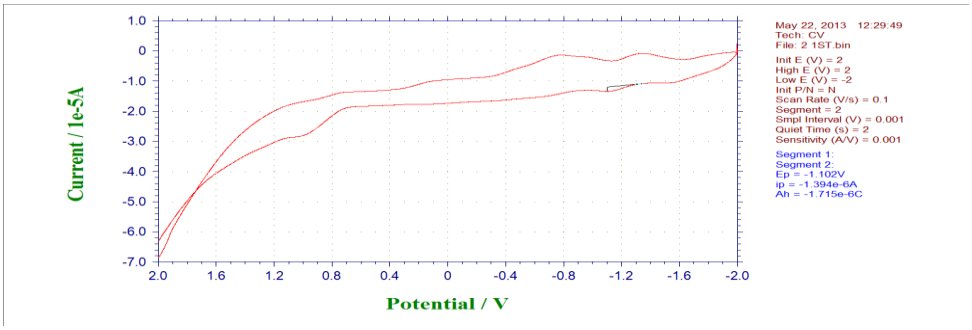

Fig 3a: Cyclic Voltammogram of 5,10,15,20 Tetramethoxy phenyl porphyrin

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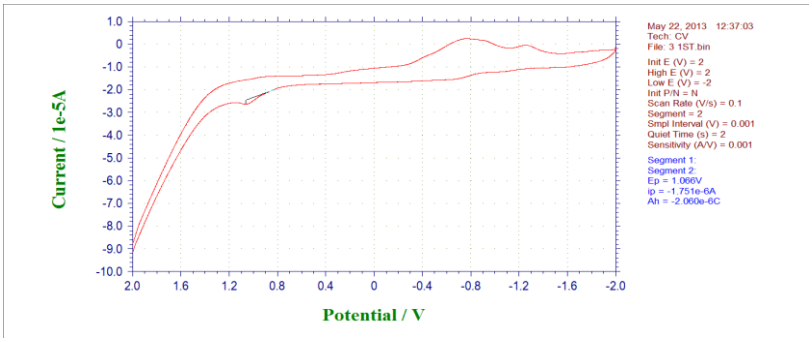

Fig 3b: Cyclic Volatammogram of 5,10,15,20 Tetrahydroxy phenyl porphyrin

When H_2THPP is cycled in the anodic direction, the oxidation wave observed at 0.7V and 1.2V associated with porphyrin oxidation. The reduction potentials appeared at -1.62V and -1.27V when cycled in cathodic direction to form anion.cyclic voltagarm of H_2THPP is shown in Figure.3b

Substitution at the meso position with electron donating group is expected to shift the potential value. It shows slightly more negative value than the corresponding analogue of H_2TPP. [19]

NMR studies

The authenticities of the complexes were ascertained through ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopy of porphyrins reveals the aromatic nature of porphyrin molecule. The Proton NMR spectrum of the compound tetramethoxy and tetrahydroxy phenyl porphyrins have been reported already.The ^{1}H NMR spectrum of H_2TMPP shows signal at -2.7ppm for inner N-H proton and for H_2THPP the inner N-H proton signals appear at -2.8ppm [20]

Electrical studies

The complexes H_2TMPP and H_2THPP shows some electrical conductivity due to suitable substituent's on meso position.The properties of porphyrin compounds can be systematically turned by rational utilization of substituents as well as by using different metal atoms.These modification can change the molecular properties like geometric, electronic structure and optical properties.

DC conducivity

The powder samples are pressed to form pellets of thickness 2.434 mm and are sandwiched between copper electrodes with the help of a pressure contact to measure the DC conductivity. The current is measured with respect to the voltage applied across the sample at room temperatures using Keithley 6517B electro meter interfaced with a Probe-Setup (DFP.2 model). The current was measured with respect to the applied voltage across the sample at room temperature. The room temperature conductivity values at different voltages were calculated using the relation.

$$\sigma = (I \times L)/ (V \times A)$$

Where, I is the current, V is the voltage, L is the thickness and A is the cross sectional area of the sample respectively. From Fig. 4a, it is noted that current linearly increases with voltage and temperature, which confirms the ohmic behavior.

AC Conductivity

Generally, AC Conductivities are done to study the charge transport mechanism of a material. In the present work the dielectric studies of sample are carried out using Hioki 3532-50 LCR meter at various temperatures, in the frequency range 50 Hz to 5 MHz. The accuracy of this instrument is ±0.01%. Pellets

sample are treated with good quality silver paste in order to obtain good ohmic conduct when placed between the copper electrodes for the measurements.

The dielectric constant of the material is calculated by using the following equation

$$\varepsilon_r = Cd/\varepsilon_o A$$

where, C is the capacitance, d is the sample thickness, A is the cross sectional area of the sample and ε_0 is the free space permittivity ($8.85x10^{-12}$ F m^{-1}).

The AC conductivity of the samples is calculated by the following equation

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta$$

where, ε_0 is the permittivity of the free space, ε_r is the dielectric constant of the sample, tan δ is the dielectric loss and ω is the angular frequency (ω=2πf). It is also observed that AC conductivity decreases with increase frequency in the same is represented in the Fig.4b. In that sample 1 is H_2TMPP and sample 2 is H_2THPP.

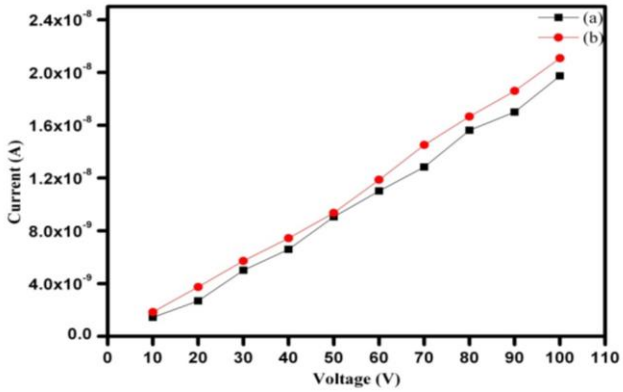

Figure 4a: I-V characteristics of (a) H_2TMPP and (b) H_2THPP

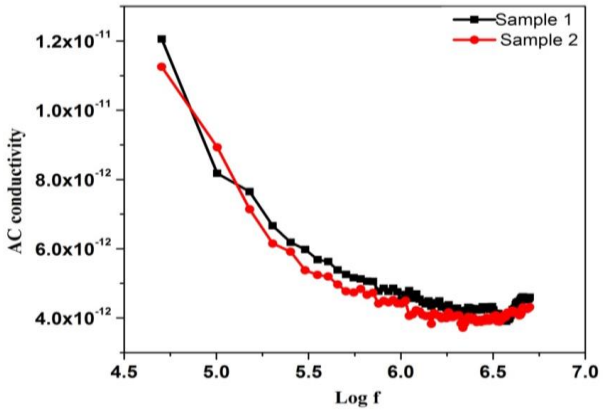

Figure 4b: A Plot log f vs. AC Conductivity

The average DC and AC conductivity values are listed in the Table 1

Samples	DC Conductivity S/cm)	AC Conductivity (S/cm)
H_2TMPP	1.84E-09	4.63E-12
H_2THPP	1.92E-09	4.36E-12

Table 1: Electrical conductivity Values

This may be due to the presence of the four polarizations namely electronic, ionic, orientation and space charge polarization.

CONCLUSION

Tetramethoxy and tetrahydroxy porphyrins show some AC and DC conductivity.So it can be used for Optoelectronic applications.Optical and electrical properties of porphyrins can be varied by changing the molecular structure, including the size, metal centre, ligands, specific side groups and conjucation.By introducing different metals in the hydroxyl and methoxy phenyl porphyrins we can enhance the Optoelectronic properties of porphyrins.

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