A MAJOR PROJECT REPORT

ON

Acid Base pH Sensing Polymer-Porphyrin Based Film

Submitted in Partial Fulfillment of the Requirement for the

Degree of

M.TECH POLYMER TECHNOLOGY

Under the supervision of

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Submitted by

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(2K11/PTE/16)

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CERTIFICATE

This is to certify that this is a bonafide record of project work based on topic

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By

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This project was carried under my supervision in year 2012-2013 and being submitted in partial fulfillment for the award of degree of Master of Technology at Delhi Technological University.

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ABSTRACT

This work presents a simple way to prepare a polymer (PMMA) Porphyrin based film for optical gas sensor. Porphyrin nanoparticle was also synthesized for this study. The dip-dry coating method that was employed in this work and resulted film shows a strong absorption band at 418 nm. A simple method by change in color of film gave qualitative analysis of hydrochloric acid (HCl) and ammonia (NH_3) molecules adsorbed on the film by their absorption bands. The Polymer (PMMA) Porhyrin film was prepared on glass substrate and spectrometer was used to obtain the spectra as sensing the vapor molecules.

Objective & Purpose of Study:

1. To synthesize the Porphyrin.

2. To synthesize the Porphyrin nanoparticle

3. To synthesize the acid-base pH sensing polymer (PMMA) porphyrin based films.

4. To investigate the sensing property towards HCl gas and NH_3 gas.

CHAPTER-1
# SYNTHESIS OF PORPHYRIN AND ITS CHARACTERIZATION

1.2 Introduction

Porphyrin have always been an attention seeker for researchers due to their diverse properties specially photoelectron and biochemical properties[1]. First produced by Fischer in 1920s; but with the passage of time, different methods have been developed for the synthesis of porphyrin with better yield and properties. Rothemund first synthesized tetra phenyl porphyrin in late 1930s and then Alder-Longo gave a simplified synthesis of meso-tetraphenyl porphyrin[2]. The synthesis of porphyrin using pyrrole with two different aldehydes, i.e. benzaldehyde and paratolualdehyde. Both these products are then characterized by using Ultraviolet- Visible spectroscopy (UV-Visible spectroscopy).

1.2 Porphyrin

A porphyrin is an organic compound that contains four pyrrole rings. A pyrrole is a pentagon-shaped ring of four carbon atoms with a nitrogen atom at one corner (C_4H_5N)[3].
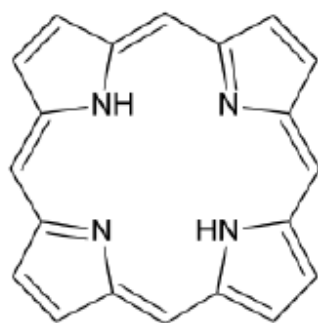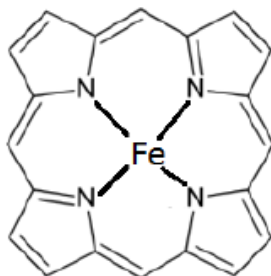

Structure of porphine,
the simplest porphyrin
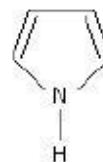
Pyrrole

Figure 1: Structure of porphyrin

Porphyrin is not a single compound but a group of organic compounds. The special thing about porphyrin is that they bind metals. The four nitrogen in the middle of the porphyrin molecule act

as teeth: they can grab and hold metal ions such as magnesium (Mg), iron (Fe), zinc (Zn), nickel (Ni), cobalt (Co), copper (Cu), and silver (Ag). When a porphyrin molecule grabs a metal, it acquires different properties and gets a different name.[1] For e.g. if the central metal is iron (Fe), the porphyrin complex is called ferroporphyrin, or *heme*.

Chemical structure of ferroporphyrin, a porphyrin molecule that has an iron ion in the middle.

Figure 2: Iron porphyrin

1.3 Natural Sources of Porphyrin

Porphyrin rings are biological molecules used in a variety of essential chemical processes. The two most well-known porphyrins are heme and chlorophyll[4].

Heme :-

 It is a cross-coupled porphyrin used in the larger molecule hemoglobin. As the basic building block of hemoglobin, and as a hemoglobin modeling molecule.
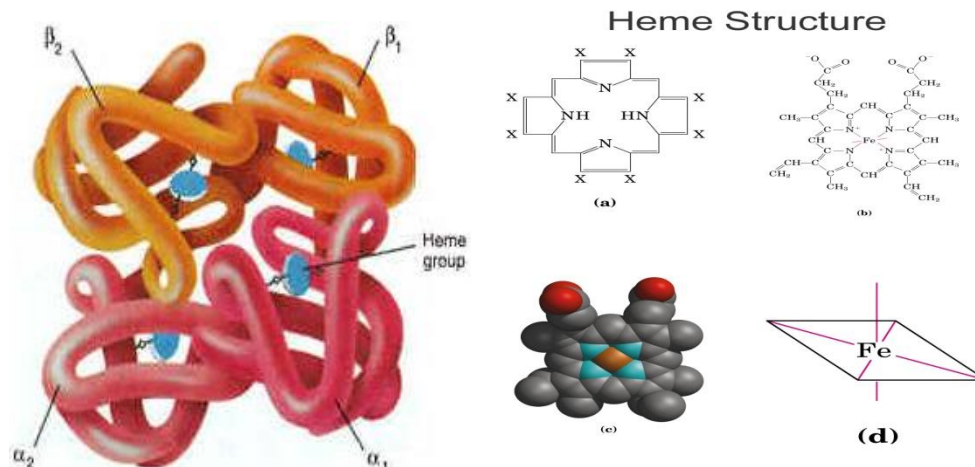
Figure:3

Chlorophyll:-

Chlorophyll is the molecule that traps this 'most elusive of all powers' - and is called a photoreceptor. The basic structure of a chlorophyll molecule is a porphyrin ring, coordinated to a central atom.

The vitamin B_{12} consists of a porphyrin molecule with a cobalt ion in the middle. So, porphyrins are an extremely important group of organic compounds. They are universal, found in most living cells of animals and plants, where they perform a wide variety of functions.

1.4 Polymeric Porphyrins

The importance in heterogeneous catalysis, immobilized enzyme models, organic semiconductors, etc. has led to the synthesis of porphyrin containing polymers. They may be classified as coordination polymers, polymer attached porphyrins and polyporphyrins. Coordination polymers are those in which the polymer coordinately binds to the porphyrin through a metal ion. e.g., coordination of iron porphyrins to polystyrene.

Naturally occurring porphyrins contain pendant functions, has been used in the synthesis of the polymer attached porphyrins. These polymers have been prepared by the reaction of a prepolymer with porphyrin derivatives. Porphyrins with carboxylic acid functions through amide linkages to preformed polymers. Polyporphyrins include condensation polymers. This group would further include synthetic materials wherein the polymerization reaction is the formation of porphyrin.

These polymers were prepared by the condensation polymerization of esters and amines containing porphyrin moiety or by the copolymerization of their vinyl monomers Polymers containing paramagnetic species in their side chains are potentially new magnetic materials, because a magnetic ordering of the paramagnetic species through an exchange interaction of unpaired electrons The magnetic susceptibility measurements and ESR study supported the presence of an exchange interaction between the side groups in a polymer chain. Also the visible spectra showed a stacking between the porphyrin rings in the polymer, which is considered unfavorable in monomeric porphyrins.

1.5   Synthesis of Porphyrins:

a) Synthesis of meso-tetraphenylporphyrin

600 mL of propionic acid was taken in a 1 L round bottom flask. Then pumice stone was added to the flask which acted as a heat absorber and provided stability to the solution during reflux. This propionic acid was then heated to 50^0C. After this 0.75 mL of benzaldehyde along with equimolar amount of pyrrole (0.509 mL) was added to it. This solution was then refluxed for about 30 minutes at about 60^0C. The resulting solution was then cooled to room temperature and

kept in refrigerator overnight. The cooled solution was filtered out and residue was washed with warm water followed by cold methanol. Purple crystal was dried and kept at low temperature.
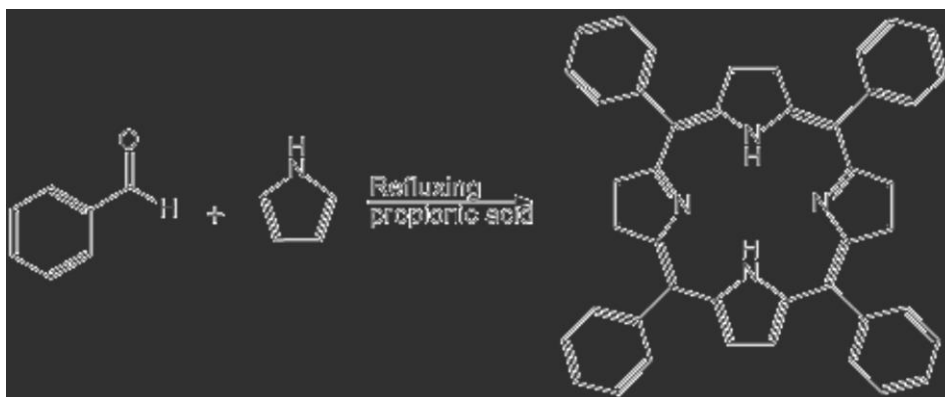
Figure:4

(b) Synthesis of meso-tetratoluylporphyrin

600 mL of propionic acid was taken in a 1 L round bottom flask. Then pumice stone was added to the flask which acted as a heat absorber and provided stability to the solution during reflux. This propionic acid was then heated to 50^0C. After this 0.75 mL of p-tolualdehyde along with equimolar amount of pyrrole (0.50 mL) was added to it. This solution was then refluxed for about 30 minutes at about 60^0C. The resulting sol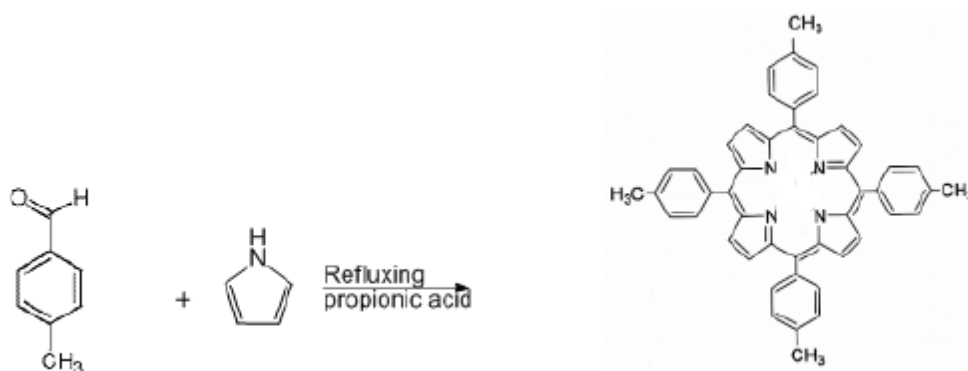ution was then cooled to room temperature and kept in refrigerator overnight. The cooled solution was filtered out and residue was washed with warm water followed by cold methanol. Purple crystal was dried and kept at low temperature
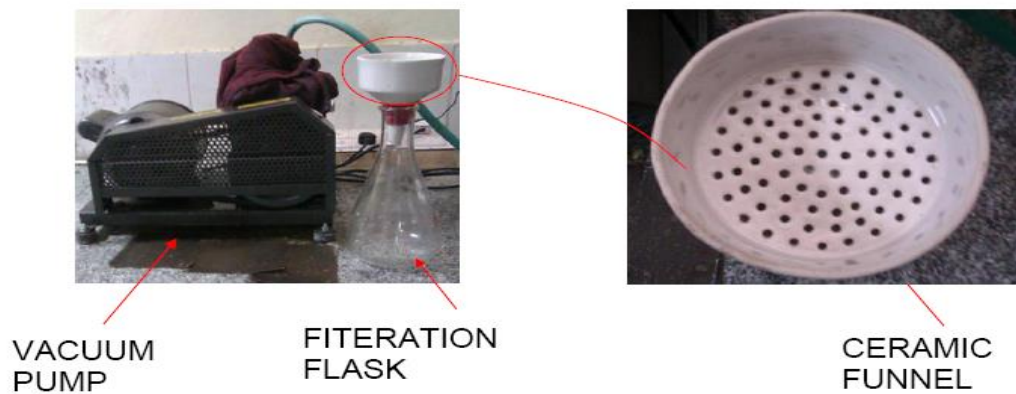

Figure:5

Figure:6 Assembly for preparation of porphyrin

1.6 Filtration of porphyrin products

A ceramic funnel on a conical flask with the help of a vacuum pump to drain the porphyrin in the propionic acid. The porphyrin product is collected as residue on the wattman paper.

Figure:7

Figure:8 Shiny dark blue crystals of porphyrin

1.7   Characterization of Porphyrin

UV-Visible Spectroscopy

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry refers to absorption spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbital. The more easily excited the electrons (i.e. lower energy gap), the longer the wavelength of light it can absorb.
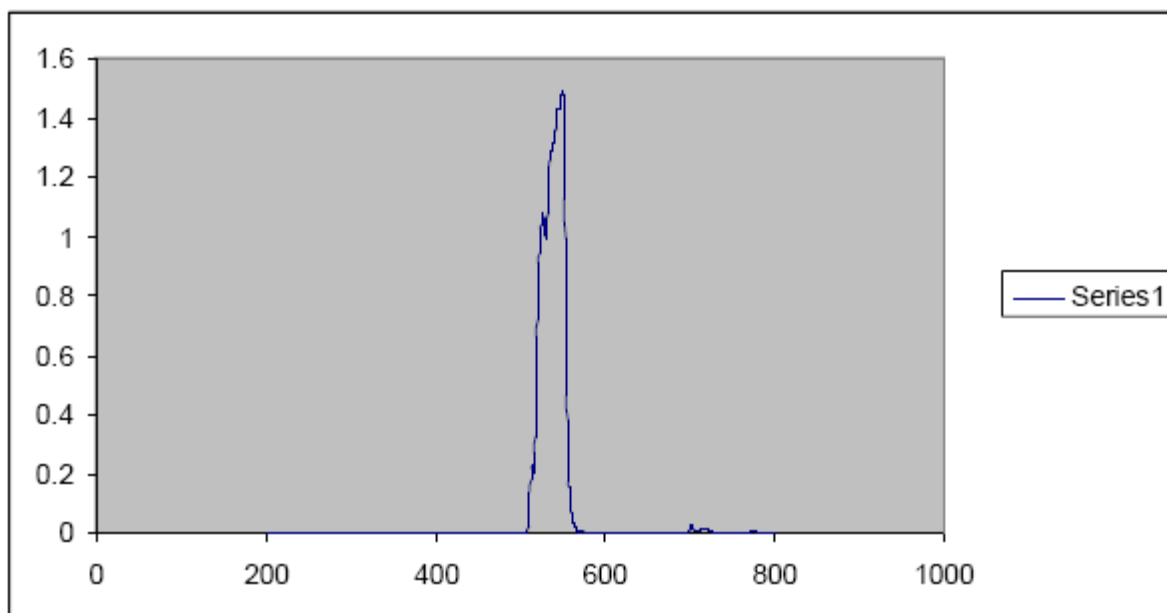
Concentrated solution   *Level of dilution required*
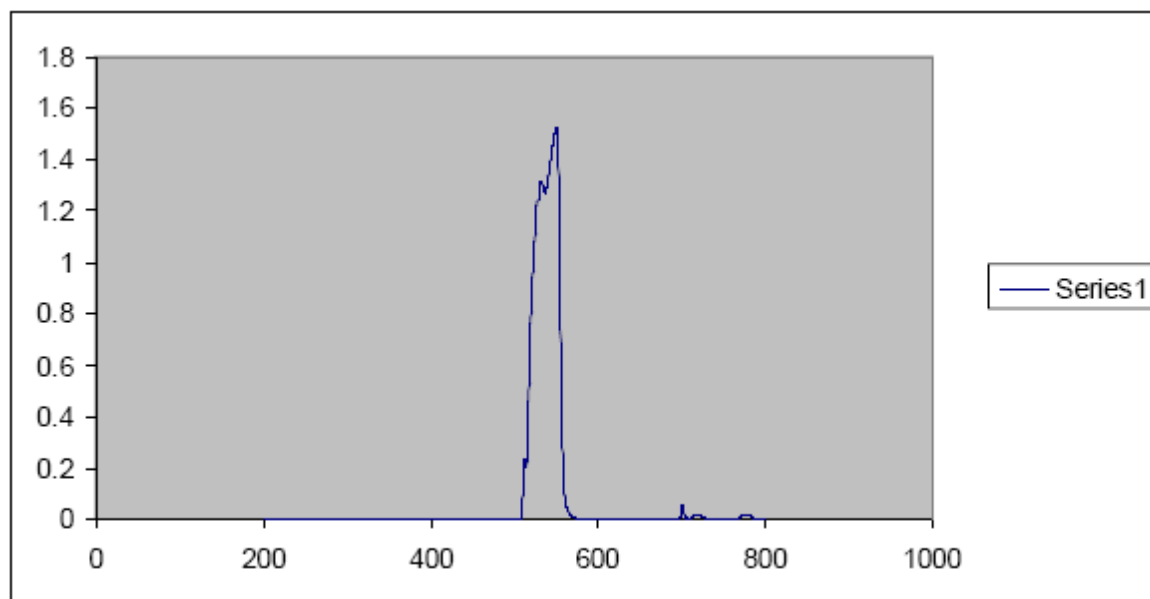
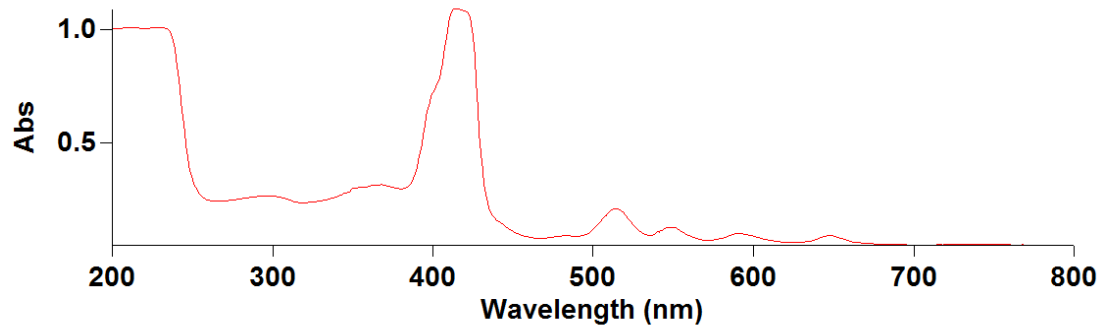*Figure:9*

GRAPH-1: Porphyrin with Benzaldehyde

Figure:10

GRAPH-2: Porphyrin with p-tolualdehyde

Figure:11

Figure:12 UV-vis spectrum of porphyrin

CHAPTER-2
SYNTHESIS OF PORPHYRIN NANOPARTICLE

2.1 Introduction

Many of the unique properties of nanoscaled materials, especially their electronic, photonic and magnetic properties cannot be achieved using the corresponding atomic, molecular, polymeric or macroscopic materials. Porphyrins are representative of photofunctional organics, and they show remarkable photo-, electro- and biochemical properties that contribute to light harvesting.[5] Hence, meso/nano-scaled porphyrin assemblies or particles are expected to be promising candidates for use in photonic devices[6].

To fabricate organic nano-architectures composed of porphyrins, it should be recognized that van der Waals intermolecular and hydrogen-bonding interactions as well as the electrostatic attraction areresponsible for the specific electronic/optical properties that are fundamentally different from those of inorganic metals or semiconductors[7].

The formation of nanoscaled colloidal particles of porphyrins can be accomplished by adding water to a solution of a hydrophobic porphyrin in water-miscible organic solvents such as THF, DMSO, DMF, or CH_3CN with a few percent of a low molecular weight polyethylene glycol (PEG). This mixed solvent approach is an efficient means to make large quantities of nanoparticle colloids (20–500 nm diameter) of a variety of porphyrins[8-9].

2.2. Preparation of Nanoparticle of Porphyrin

The porphyrin nanoparticles have been synthesized using mixing solvent technique. In addition, it was that discovered poly ethylene glycol as a stabilizer of the porphyrin nanoparticle. In this process they have chosen the good solvent either DMSO or pyridine and poor solvent as water. However, the DMSO or pyridine cannot be a good solvent for preparing pure organic

nanoparticles by 'reprecipitation' method because they are highly non-volatile. It is true, porphyrin is desolved in both DMSO and pyridine and both the solvents are easily misicible in water but these solvents are having boiling point with 189° and 115°C respectively. Furthermore, those solvents easily form moderately strong hydrogen bonding with porphyrin molecules irrespective of hydrogen bonding with water. Hence, removal of the good solvent from poor solvent is highly unlikely even through the boiling of poor solvent (water). As a result, presumed nanoparticles formed .As a result, presumed nanoparticles formed in this method is not pure porphyrin nanoparticles rather it is a nanoparticle of porphyrin-DMSO or porphyrinpyridine cluster. Formation of hydrogen bonding of porphyrin with DMSO or pyridine does not change the photophysical properties (absorption and fluorescence) of porphyrin except little decrease in absorbance in Soret band. Furthermore, they have used poly ethylene glycol (PEG) as stabilizer for porphyrin nanoparticle, which could make hydrogen bonding complex with pyrrole N-atom in porphyrin macrocycle leading to give nanocomposite of porphyrin/DMSO/PEG or porphyrin/pyridine/PEG, rather than only pure porphyrin nanoparticles.

2.3 Experimental

Chemicals and instruments

DMF used as a solvent was purchased from chemical company used as received. Triethylene glycol monomethyl ether was used as a stabilizer and also purchased from chemical company UV–vis absorption spectra were recorded on a Agilent make spectrophotometer. The surface morphology and size of porphyrin nanoparticles were observed with a Hitachi S-3700nN scanning electron microscope (SEM) using voltage of 15KV coating with Au.

Synthesis of Porphyrin Nanoparticle

Porphyrin was prepared according to the Adler-Longo method. A typical preparation procedure as follows: stabilizer (triethylene glycol monomethyl ether, 100 µL) was added to stock solution of TClPP in DMF (1.22 mM for TClPP, 200 µL), followed by addition of water (20 mL with vigorous mixing. In this research, the effect of different variables on the size of nanoparticles was examined via UV-vis spectroscopy.

Figure 1. Preparation of porphyrin nanoparticles.
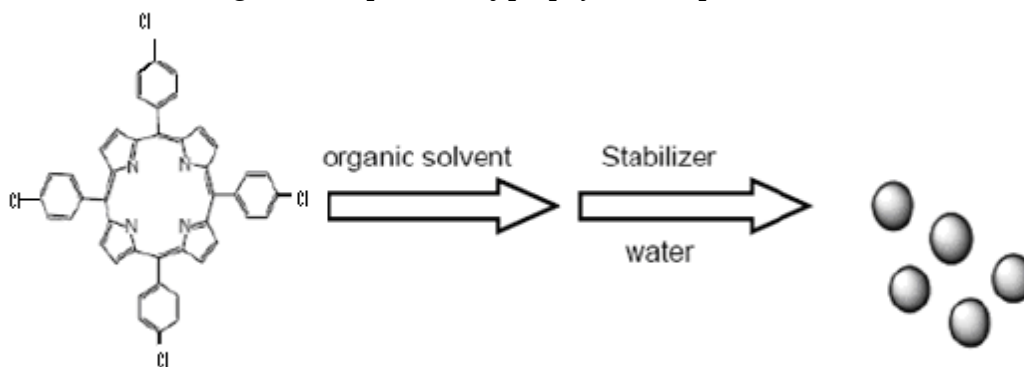
Figure:2 Porphyrin nanoparticles prepared in lab
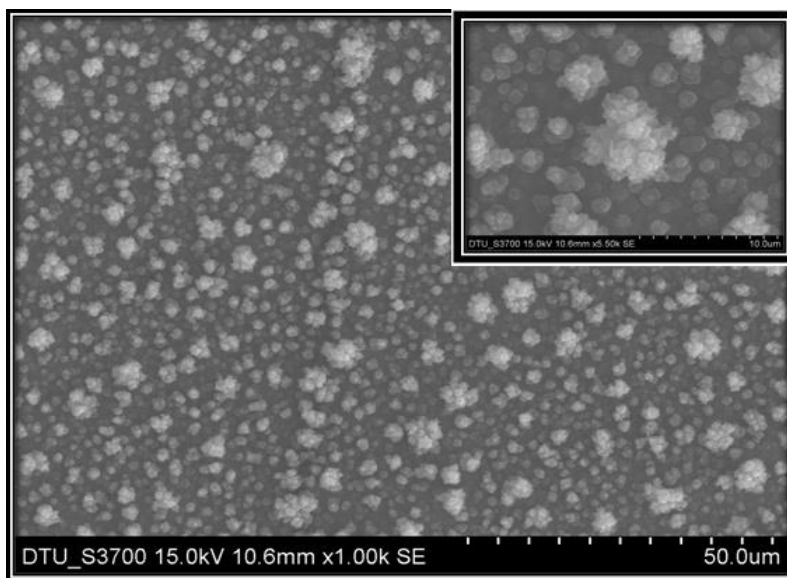
2.4 Characterization of Porphyrin Nanoparticles

2.4.1 Scanning electron microscopy

Scanning electron microscopy was performed on a Hitachi S-3700nN scanning electron microscope operating at 15 kV. The samples for SEM imaging were coated with electrolyte.

Figure:3
**Hitachi S-3700nN scanning electron microscope**

Figure : 4 SEM images of porphyrin nanoparticles.

The SEM images of the porphyrin nanoparticles are shown in above Figure. The particles are spherical in shape and the average size is 200 nm. These nanoparticles were stable in solution without precipitation stored under dark at room temperature for at least 30 days. The porphyrin nanoparticles are held together by hydrophobic and π-stacking effects and hydrogen bonds.

2.4.2 UV-visible spectra

The UV-vis spectra of porphyrin nanoparticles are significantly different compared to the spectra of the corresponding porphyrin solutions. Soret bands are found to be broadened and/or split. The arrangement of macrocycles in aggregates generally fall into two types, "J"(edge-to-edge) interactions are characterized by red shifts and "H" (face-to-face) interactions are characterized by blue shifts. The spectra suggest both types of interactions in the nanoparticles and are well understood to be indicative of electronic coupling of the chromophores. The extent of J versus H aggregation depends on the specific porphyrin used. The difference between porphyrins in solution and nanoTClPP is clearly shown by the spectra of the nanoTClPP.

UV-visible spectra
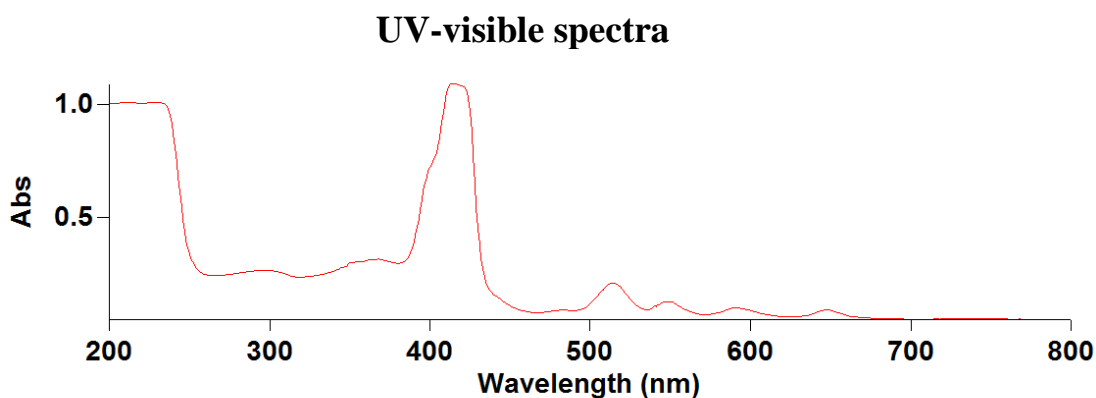
Figure : 5 UV-vis spectra of porphyrin in chloroform
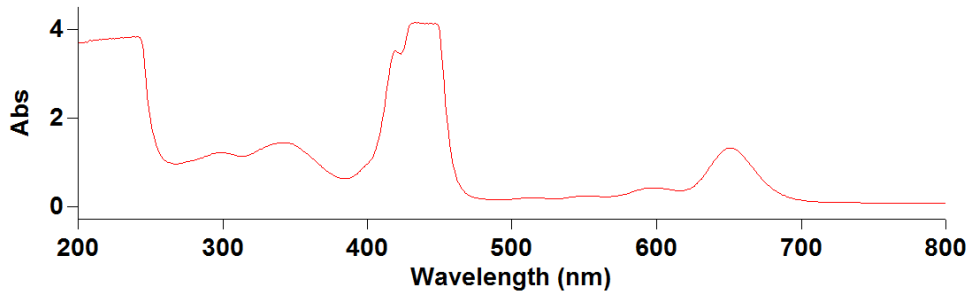
Figure : 6 UV-vis spectra of porphyrin nanoparticle

2.4.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.. The goal of any absorptionspectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength

Figure:7 Fourier transforms Infrared Spectroscopy (FTIR)
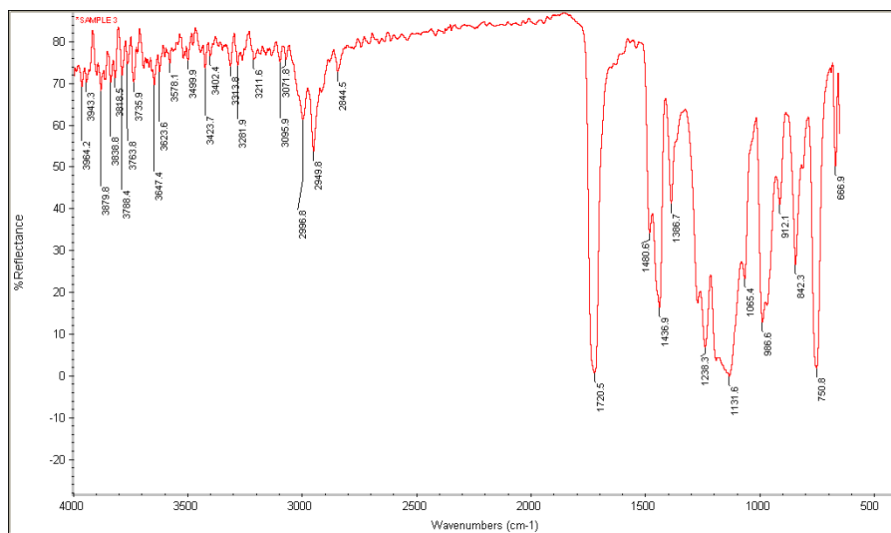
Figure:8

Wavenumber (in cm⁻¹)	Remarks
3050-2990	CH Stretching vibration
1730	CO double bond Stretching vibration
1395-1450	CH_3 and CH_2 deformation vibration
1260-1040	COC single bond stretching vibration
880-960	COC single bond deformation vibration

2.5 Results and discussions

In a typical preparation of porphyrin nanoparticles, in dichloromethane(DCM) was rapidly injected into 5 mL of distilled water by high precision A light yellow transparent colloid-like solution was obtained after centrifugation for approximately 15 min. Casting a drop of colloidal porphyrin solution directly onto cleaned stub and using scanning electron microscopy (SEM) as well as putting the colloidal porphyrin particles prepared were observed to be a collection of nanoparticlesof ~ 50–250 nm diameter.

2.6 Conclusion

In conclusion, a simple and convenient method for preparation of absolutely pure andstable porphyrin nanoparticles with ~ 50–250 nm and 30–200 nm diameter respectively. The possibility of tuning the size and photophysical properties of the nanoparticles using this process on changing the substituents on the porphyrins or introduction of the metal ions inside the macrocycle along with judicial selection of other organic solvents will open the way to synthesize not only verities of porphyrin nanoparticles but also other organic nanoparticles with potential applications. Self-aggregation of the constituent porphyrins was observed in the nanoparticles. This method provides a useful way to prepare porphyrin nanoparticles. These nanoparticles can be used as catalytsts for oxidative reactions as well as optical sensors.

CHAPTER-3
SYNTHESIS OF ACID-BASE pH SENSING POLYMER (PMMA)PORPHYRIN BASED FILMS

3.1 Acid

An acid is a substance which reacts with a base. Commonly, acids can be identified as tasting sour, reacting with metals such as calcium, and reacting with bases such as sodium carbonate. Common examples of acids include acetic acid (vinegar is a dilute solution of this liquid), sulfuric acid (used in car batteries), hydrochloric acid (a solution of this gas is used in the stomach for enzymes) and tartaric acid (a solid used in baking)[10].

Acid common features are:-

- React with zinc, magnesium, or aluminum and form hydrogen ($H_{2(g)}$)
- React with compounds containing CO_3^{2-} and form carbon dioxide and water
- Turn litmus red
- Taste sour
- Aqueous acids have a pH under 7
- Solutions with higher acidity have lower pH.

3.2 Base

A base is a substance that, in aqueous solution, is slippery to the touch, tastes bitter, changes the colour of indicators (e.g., turns red litmus paper blue), reacts with acids to form salts, and promotes certain chemical reactions (base catalysis). Examples of bases are the hydroxides of the alkali and alkaline earth metals (NaOH, $Ca(OH)_2$, etc)[11].

BASE common features are:-

- Slimy or soapy feel on fingers, due to saponification of the lipids in human skin.

- Concentrated or strong bases are caustic on organic matter and react violently with acidic substances.

- Aqueous solutions or molten bases dissociate in ions and conduct electricity.

- Reactions with indicators: bases turn red litmus paper blue, phenolphthalein pink, keep bromothymol blue in its natural colour of blue, and turn methyl orange yellow.

- The pH level of a basic solution is higher than 7.

- Bases are bitter in taste.

3.3 pH

pH is defined as the negative logarithm of theactivity of the (solvated) hydronium ion, more often expressed as the measure of the hydronium ion concentration. Pure water has a pH very close to 7 at 25 °C. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 arebasic or alkaline. The pH scale is traceable to a set of standard solutions whose pH is established by international agreement. Primary pH standard values are determined using aconcentration cell with transference, by measuring the potential difference between a hydrogen electrode and a standard electrode such as the silver chloride electrode. Measurement of pH for aqueous solutions can be done with a glass electrode and a pH meter, or using indicators.

pH measurements are important in medicine, biology, chemistry,agriculture, forestry, food science, environmental science, oceanography, civil engineering, chemical engineering, nutrition, water treatment & water purification, and many other applications[12].

pH indicator

Figure:1
Chart showing the variation of color of universal indicator paper with pH

Indicators may be used to measure pH, by making use of the fact that their color changes with pH. Visual comparison of the color of a test solution with a standard color chart provides a means to measure pH accurate to the nearest whole number. More precise measurements are possible if the color is measured spectrophotometrically, using a colorimeter of spectrophotometer. Universal indicator consists of a mixture of indicators such that there is a continuous color change from about pH 2 to pH 10. Universal indicator paper is made from absorbent paper that has been impregnated with universal indicator.

3.4 PMMA

Poly(methyl methacrylate) (PMMA) is a transparent thermoplastic, often used as a lightweight or shatter-resistant alternative to glass. Although it is not technically a type of glass, the substance

has sometimes historically been called acrylic glass. Chemically, it is the synthetic polymer of methyl methacrylate. The material was developed in 1928 in various laboratories by many chemists such as William Chalmers, Otto Röhm and Walter Bauer.

PMMA is an economical alternative to polycarbonate (PC) when extreme strength is not necessary. Additionally, PMMA does not contain the potentially harmful bisphenol-A subunits found in polycarbonate. It is often preferred because of its moderate properties, easy handling and processing, and low cost. The non-modified PMMA behaves in a brittle manner when loaded, especially under an impact force, and is more prone to scratching than conventional inorganic glass. However, the modified PMMA achieves very high scratch and impact resistance[13].
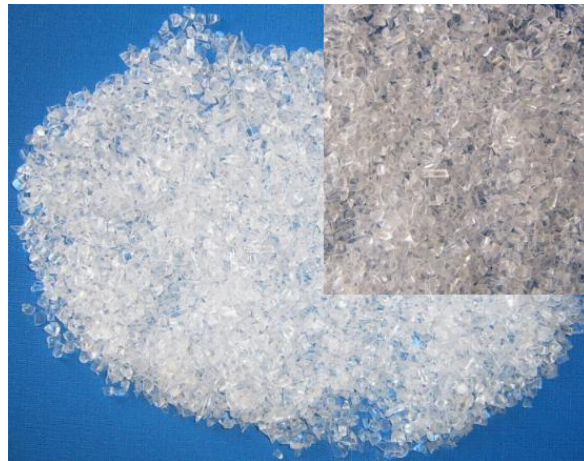
Figure :2 Poly(methyl methacrylate) (PMMA)

Uses

1. **Transparent glass substitute**

- PMMA acrylic glass is commonly used for constructing residential and commercial aquariums.

- Acrylic is used for viewing ports and even complete pressure hulls of submersibles, such as the Alicia submarine's.

- PMMA is used in the lenses of exterior lights of automobile

- The spectator protection in ice hockey rinks is made from PMMA.

- PMMA was an important improvement in the design of aircraft windows, making possible such iconic designs as the bombardier's transparent nose compartment in the Boeing B-17 Flying Fortress.

- Police vehicles for riot control often have the regular glass replaced with acrylic to protect the occupants from thrown objects.

- Acrylic is an important material in the making of certain lighthouse lenses.

2. **Medical technologies and implants**

- PMMA has a good degree of compatibility with human tissue, and it is used in the manufacture of rigid intraocular lenses in the eye when the original lens has been removed in the treatment of cataracts.

- Historically, hard contact lenses were frequently made of this material. Soft contact lenses are often made of a related polymer, where acrylate monomers containing one or more hydroxyl groups make them hydrophilic.

- In orthopedic surgery, PMMA bone cement is used to affix implants and to remodel lost bone. It is supplied as a powder with liquid methyl methacrylate (MMA). When mixed these yield dough-like cement that gradually hardens. Surgeons can judge the curing of the PMMA bone cement by pressing their thumb on it. Although PMMA is biologically compatible

- PMMA has also been linked to cardiopulmonary events in the operating room due to hypotension.. Bone cement acts like a grout and not so much like glue in arthroplasty mechanical signals to continue bone remodeling and so resorption will occur.

- Dentures are often made of PMMA, and can be color-matched to the patient's teeth & gum tissue. PMMA is also used in the production of ocular prostheses, such as the osteo-odonto-keratoprosthesis.

- In cosmetic surgery, tiny PMMA microspheres suspended in some biological fluid are injected under the skin to reduce wrinkles or scars permanently.

3.5 Porphyrin-Polymer Film

Poly Methyl Methacrylate (PMMA) is a versatile polymeric material that is well suited for many microelectronic applications. It is often preferred because of its moderate properties, easy handling and processing ,and low cost. It is melting point it $160^{o}C$.The experiments carried out on PMMA porphyrin film shows that there is a significant improvement in the the polymer industry.

 The optical properties of porphyrins would change as specific gases combined with porphyrin molecules, like NO_2, NO, CO, HCl, which are based on a rich π-electron system[14].Hence, some optical methods, such as the ultraviolet, infrared, fluorescence, phosphorescence and Raman spectroscopy could be used to detect the changes of optical properties of porphyrins. Therefore, porphyrin complexes become an ideal sensing model to study the porphyrin-based sensors. Various techniques have been proposed to prepare the porphyrin films, such as

[1] Self-assembled monolayer[15]

[2] Langmuir-Blodgett Technique[16]

[3] Vacuum deposition[17]

But these techniques are so complicated for practical application since it takes a lot of time. At same time, these techniques require expensive equipment, which lead to higher costs. Additionally, the optical gas sensors also suffer the problem of drifting baselines, which is also the problems for most optical sensors

To solve the above problems, a simple method for preparing the Polymer (PMMA) Porphyrin thin film which called dip-dry method was proposed. Then the UV-VIS spectrometer was used to obtain their characteristics of absorption spectra of the film as sensing NH_3 and HCl molecules.

3.5.1 Materials and Method

Materials required:- Dichloromethane (DCM), PMMA, porphyrin particle and polyethyleneglycol

3.5.2 Procedure

The step by step procedure for the synthesis of PMMA porphyrin based film is as follows:

1. 10 mg Porphyrin is dissolved in 50 ml DCM.

2. 1mg of Polyethylene glycol (PEG) is added to it.

3. Different weight percentage of percentage of (1%, 3% and 5%) PMMA are added and the solution is vigorously stirred using magnetic stirrer.

4. Then it is heated until the solution comes to the boiling stage and is allowed to cool for an hour.

5. Pour the solution into the petridish.

6. Allow the film to be dried at room temperature for 24 hours.

7. PMMA porphyrin film and formation of coordinated bond between nano-fillers and PMMA. The PMMA porphyrin films are prepared as of 1.3mm diameter and 5mm thickness to carry out experiments.
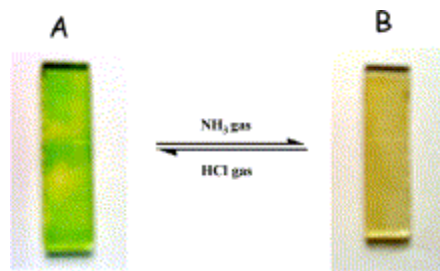

Figure :3 PMMA porphyrin film

3.6 Sensing procedure of Polymer (PMMA) Porphyrin Film

At first, the 25% NH_3 and 37% HCl liquid without dilution was individually put in a beaker with a volume of 30 cm^3 and then sealed the cell in the measurement process. The optical absorption of the polymer (PMMA) porphyrin film ranged from 370 to 500 nm was continuously measured until the vapour pressure of the cell reached to dynamic equilibrium state at room temperature. The absorption spectra of Polymer (PMMA) Porphyrin based films were also investigated by static measurement after adding 5drops of HCl, and NH_3 with the lower concentration of 3M to a cell . The detection time was over 20 minutes.

The Polymer (PMMA) Porphyrin film when expose to NH_3 gas the green colour of the film change to brown. On the exposure of HCl gas the brown colour of the film changes to green again as shown in the below figure.
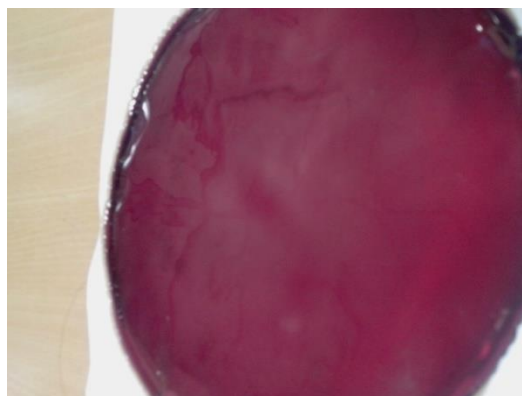
Figure : 4

Colour Change Observed The Polymer (PMMA) Porphyrin Films

Sample :-1

Sample :-2

Sample :-3

Figure :5

3.7 Characterization of Samples

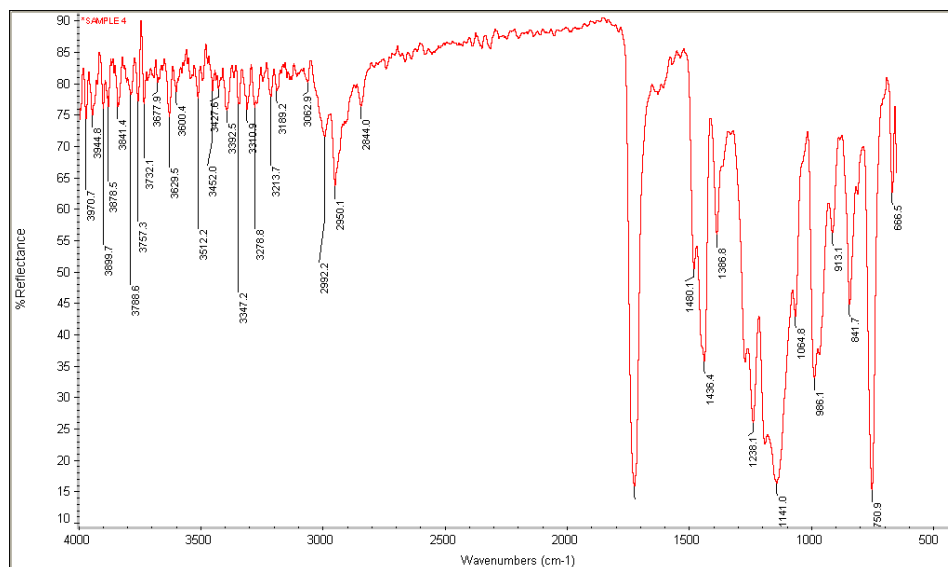## 3.7.1 Fourier Transform Infrared (FTIR) Spectrograph

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy. The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength

Figure : 6

**Fourier transforms infrared spectroscopy (FTIR)**

..

Figure : 7

Fourier Transform Infrared (FTIR) Spectrograph of Polymer (PMMA) porphyrin film

The FTIR spectrum shows that there is strong interaction between the nano – filler and polymer that enhances the property of the material. The FTIR spectra scan of Porphyrin largely reflects the presence of the C-O bonds within the polymer. These C-O bonds dominate the majority of the vibrational peaks shown within the scans Some important bands are :-

Wavenumber (in cm^{-1})	Remarks
1600	C=C
1300-1000	C—H
500-100	Substituted benzene
1700	--CONH

3.7.2 Scanning Electron Microscopy (SEM)

The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about analysis. The sample's surface topography, composition and other properties. The images show the structure of the polymer matrix and the nano filler are distributed homogeneously.
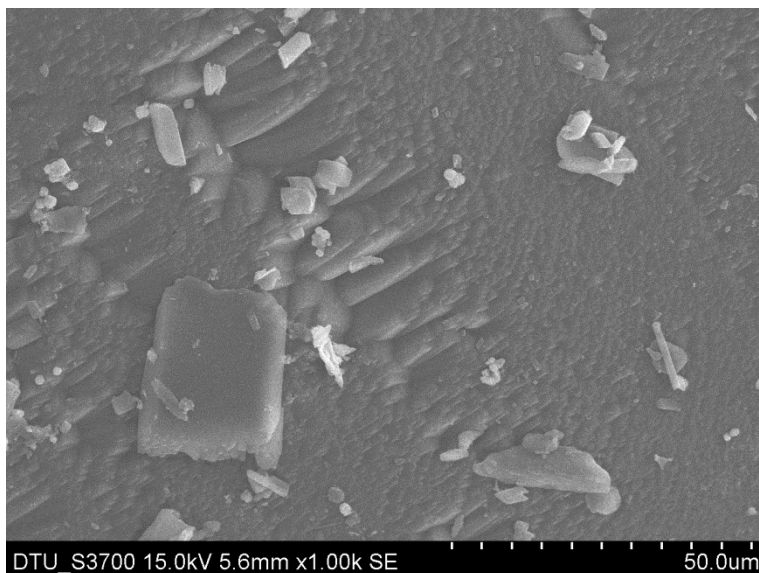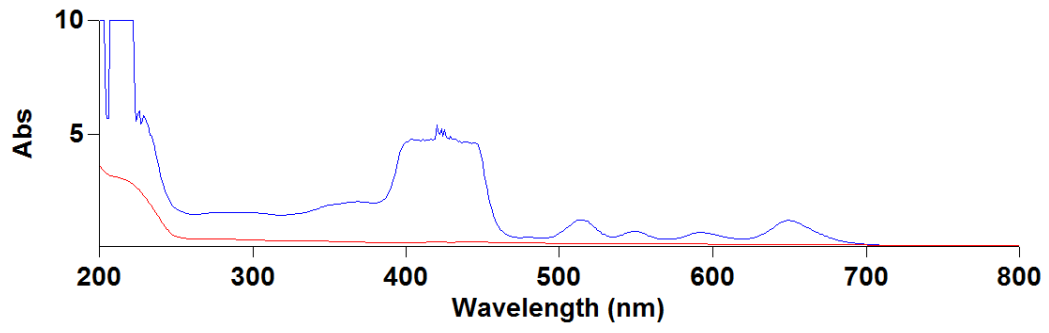
Figure : 8

Scanning Electron Microscopy (SEM) of Polymer (PMMA) porphyrin film

3.7.3 UV-vis spectra of Polymer (PMMA) Porphyrin based film

The UV-vis spectra of   Polymer(PMMA) Porphyrin based film are significantly different compared to the spectra of the corresponding porphyrin solutions. Soret bands are found to be broadened and/or split. The spectra suggest both types of interactions in the PMMA are well understood to be indicative of electronic coupling of the chromophores. Due to higher concentration of porphyrin, the Soret band are not shown clearly but the Q-bands are clearly shown in the spectra.

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Figure : 9 UV-vis spectra of Polymer(PMMA) Porphyrin based film

3.8 Results and Discussions

Porphyrin derivatives containing electron donating groups such as alkyl (-CH$_3$) and alkoxy (-OCH$_3$) groups are tested for their response to HCl gas. Freebase porphyrin shows the colour change for an exposure of of HCl gas. The decrease in the response time arises due to increase in the basicity of the pyrrole nitrogen with an increase in the electron donating strength.This indicates an increase in the hue of green colour and shows change in the colour pattern for an exposure time of low concentration of HCl gas.

3.9 Conclusion

The present work comprises of a device having freebase porphyrin as a sensing material, embedded on a thin layer of PMMA polymer film which responds to HCl and NH_3 gas (acid and base) which can be monitored either by naked human eye or using spectrophotometer. Polymer(PMMA) which incorporate in free base porphyrins comprise an embodiment of the present invention which is economical,disposable or can be stored as record for the long time and can be utilized to provide quantitative identification of the HCl and NH_3gas in low concentration level. Further, the scope of this work can be utilized in fabricating a device to sense HCl and ammonia gas in environment.

3.10 Advantages over earlier methods

The main advantage of the present acid base ph sensing Polymer (PMMA) Porphyrin based film is quite stable, simple, economical and can detect of low concentration levels of HCl and NH_3gas. This method overcomes many shortcomings in the existing methods like expensive instrumentation facilities and elaborate preparation procedures. The method has superior advantage in terms of physical stability and easy recognition of colour variation pattern of the sensor both qualitatively and quantitatively. Also, these films can be re-used after appropriate treatment for fewer more cycles

CHAPTER 4
REFERENCES

1. K. M. Kadish, K. M. Smith, R. Guilard, *The Porphyrin Handbook*. (Academic Press: San Diego, 2000).

2. Adler, A.D.; Longo, F.R.; Finarelli, J.D.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, 32, 476.

3. http://en.wikipedia.org/wiki/Porphyrin

4. Paul Goodland, Kim Fields, Peter Zhang University of South Florida: - Porphyrins Super-molecules of the Future and the Sinister Molecules of the Past.

5. Nielsen, K.T.; Spanggaard, H.; Krebs, F.C. Synthesis, Light Harvesting, and Energy Transfer Properties of a Zinc Porphyrin Linked Poly(phenyleneethynylene). *Macromolecules* **2005**, *38*, 1180–1189.

6. Rotomskis, R.; Augulis, R.; Snitka, V.; Valiokas, R.; Liedberg, B. Hierarchical Structure of TPPS4 J-Aggregates on Substrate Revealed by Atomic Force Microscopy. *J. Phys.Chem. B* **2004**,*108*, 2833– 2838.

7. Uemura, T.; Kitagawa, S. Prussian Blue Nanoparticles Protected by Poly (vinylpyrrolidone). *J. Am. Chem. Soc.* **2003**, *125*, 7814–7815.

8. Gong, X.; Milic, T.; Xu, C.; Batteas, J.D.; Drain, C.M. Preparation and Characterization of Porphyrin Nanoparticles. *J. Am. Chem. Soc.* **2002**, *124*, 14290–14291.

9. Nitschke, C.; O'Flaherty, S.M.; Kroll, M.; Blau, W.J. Material Investigations and Optical Properties of Phthalocyanine Nanoparticles. *J. Phys. Chem. B* **2004**, *108*, 1287–1295.

10. http://en.wikipedia.org/wiki/Acid

11. http://en.wikipedia.org/wiki/Base_(chemistry)

12. http://en.wikipedia.org/wiki/PH

13. http://en.wikipedia.org/wiki/Poly(methyl_methacrylate)

14. D.B. Papkovsky, Luminescent porphyrins as probes for optical (bio)sensors, Sens. Actuators B, vol. 11, pp. 293–300 (1993).

15. Z.Zang, S.Hou, Z.Zhu, Z.Liu, Preparation and characterization of a porphyrinself-assembled monolayer with a controlled orientation on gold, Langmuir 16, 537–540, 2000.

16. A.Ulman, An introduction to ultrathin organic films from langmuir–blodgett films to selfassembly, AcademicPress, San Diego, CA (1991); doi: 10.1002/ange.19921040445

17. K.Nakamura, M.Watanabe, M.Zhou, M.Fujishima, M.Tsuchiya, T.Handa, S.Ishii, H.Noguchi, K.Kashiwagi, and Y.Yoshida, vol.345, issue 1, pp. 99-103 (1999); doi: 10.1016/S0040-6090(99)00093-0