SPECTROSCOPIC STUDIES OF PORPHYRIN AND PHTHALOCYANINE INTERACTIONS WITH CHEMICAL ANALYTES

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Porphyrin and phthalocyanine compounds are promising materials for the production of sensors for selective molecular recognition. These have potential applications in the areas of sensing, information storage devices, light emitting diodes, transistors, catalysts, and solar cells. Much of the work on these materials has been realized or anticipated but a lot of work is still needed for a complete understanding of these compounds.

Thin films of porphyrins/ phthalocyanines, under study, have been deposited by vacuum evaporation and spin coating techniques. Interactions of various chemical analytes with porphyrins/phthalocyanines thin films and powder have been studied. Sites of the interaction (metal ion or ring) have been identified. The effects of chemical analytes on the structures and vibrations of metal phthalocyanines (ZnPc, NiPc and CoPc) and zinc tetraphenylporphine (ZnTPP) have been studied by monitoring the changes in bonding arrangements at the molecular level. The entire work, presented in this thesis, has been divided into five chapters, each of which is a self explanatory unit in itself.

Chapter 1 begins with introduction of porphyrin/phthalocyanine compounds and their biological importance. Description and structural relationship of these compounds have been included in this chapter. Natural and synthetic availability of these compounds and their ligands have been discussed. Ligand interactions, absorption spectrum and sensing behaviour at the molecular level have also been discussed. Vibrational transitions due to absorption/scattering of electromagnetic radiations by these macromolecular structures are explained. This Chapter ends with definition of the research problem.

Chapter 2 focuses on theoretical aspects of the study undertaken. Molecular vibrations and vibrational modes have been discussed. Vibrational spectroscopy processes namely infrared, Raman spectroscopy, resonance Raman and their selection rules are described. Brief accounts of other characterization techniques such as electronic transitions – UV-visible absorption spectroscopy, and density functional theory (DFT) are also given in this chapter.

Chapter 3 deals with experimental techniques used in the present study. In this chapter details regarding preparation of samples (thin films) of metal phthalocyanines (ZnPc, NiPc and CoPc) and zinc tetraphenylporphine (ZnTPP) by vacuum evaporation and spin coating techniques are given. Arrangement for thin films exposure with chemical analytes has also been given in this chapter. This chapter also provides concise account of different methods used for film

characterization [scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) technique, UV visible and vibrational spectroscopy] in this work. Vibrational spectroscopic techniques namely infrared and Raman spectroscopic are explained in this chapter.

Chapter 4 presents the study of the effect of pyridine on zinc phthalocyanine. In the presence of pyridine, phase of the crystalline zinc phthalocyanine changes from β to α. Some infrared bands show changes in the positions and/or intensities in the presence of pyridine. These changes have been interpreted on the basis of coordination of the pyridine molecule with the central zinc ion. Density functional theory calculations have been carried out to determine the probable geometric structures of the complexes of vapour and phthalocyanine molecules. Effects of chemical vapours (pyridine, methanol, dimethylsulfoxide, formamide and bromine) on the vibrational spectra of nickel phthalocyanine thin films have also been presented in this chapter. Some vibrational bands show changes in their positions and /or intensities on exposure of thin films with these chemical vapours. The changes have been interpreted on the basis of interactions of the vapour molecules with the central nickel ion and other peripheral atoms of phthalocyanine ring. Effect of pyridine on cobalt phthalocyanine has also been presented in this chapter. The observed changes in the Raman spectrum of cobalt phthalocyanine on exposure with the pyridine vapours have been explained on the basis of displacement of bridge bonds of phthalocyanine ring and weakening of bonds due to change in charge density.

Chapter 5 presents the effects of methanol, pyridine, diethylamine, dichloromethane, acetonitrile, bromine and NO_2 vapours on the Raman and infrared absorption spectra of zinc tetraphenylporphine thin films. Changes in the zinc tetraphenylporphine vibrations have been understood by recording their spectra before and after exposure with chemical vapours. Positions and intensities of some vibrational bands show detectable change on exposure. Coordination of vapours with the zinc ion and subsequent charge transfer are responsible for the shift in the vibrational bands. Density functional theory calculations have been carried out to determine the probable geometric structures of the porphyrins vapour complexes. Calculated geometric structures show in-plane and out-of-plane distortions in the porphyrin macrocycle. Calculations also result in charge transfer between vapour and porphyrin molecules. The thesis ends with a brief conclusion and future plans.