SYNTHESIS AND ELECTRICAL PROPERTIES OF PHTHALOCYANINES

by

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CERTIFICATE

This is to certify that the thesis entitled "**SYNTHESI AND ELECTRICAL PROPERTIES OF PHTHALOCYANINES**, being submitted by Mr. Rama Shankar to the Indian Institute of Technology, Delhi, for the award of the degree of **DOCTOR O PHILOSOPHY** in Chemistry is a record of bonafide research work carried out by him. Mr. Rama Shankar has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other university or Institute for the award of any degree or diploma.

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ABSTRACT

The thesis comprises a report on the synthesis, characterization and electrical properties of a few tetra substituted soluble phthalocyanines and their transition metal derivatives. A series of aryloxy groups has been used as peripheral substitutents. The aryloxy groups selected are: p-methyl-, p-ethyl-, p-tert.butyl-, 2,4-dimethyl- and p-chlorophenoxy. Both metal-free and metallophthalocyanines have been synthesized. The metal ions used as cavity metal were Fe, Co, Ni, Cu & Zn. All the phthalocyanines were characterized by elemental analysis, IR, far IR, UV-visible, ^{1}H and ^{13}C NMR spectroscopy. Magnetic suceptibility measurements and thermogravimetric analysis were also carried out for the phthalocyanines.

The aryloxy substituted phthalonitriles which are used as precursors for the synthesis of phthalocyanines were prepared from 4-nitro phthalonitrile and were characterised by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy.

The molecular association in solution of metal-free and metallo phthalocyanines were studied by molecular weight determination, UV-visible and ^{1}H NMR spectroscopy to evaluate the effect of central metal ion and peripheral substituent on the association. Effect of concentration and nature of solvent on association was also studied. The assoication was found dependent upon concentration of

solution, solvent polarity and cavity metal ion, however the effect of peripheral substituent was not significant.

The electrical conductivity and dielectric and poyroelectric behaviour of the phthalocyanines were studied to evaluate the effect of various chemical modifications as effect of substituent and the cavity metal on the electrical properties of these phtyalocyanines. Dielectric constant, electrical conductivity and pyrocurrent were measured as a function of temperature. The dielectric constant was determined at variable frequency to find out any possible transition. The values of activativion energy were obtained from Arrhenius plot of conductivity vs. temperature. The dielectric constant as well as the electrical conductivity were found to be dependent on the nature of the cavity metal ion and the peripheral end groups, however, there is no marked effect on the magnitude of the pyrocurrent with the change of substituent end group. The pyrocurrent was shown by the iron, cobalt and copper phthalocyanines, but not by metal-free, nickel and zinc phthalocyanines.

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CHAPTER 2 SYNTHESIS AND CHARACTERISATION OF PATHALONITRILE DERIVATIVES

CHAPTER 3 SYNTHESIS AND CHARACTERIZATION OF PHTHALOCYANINES