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DEGREE REGISTERED: Ph D

TITLE OF THE THESIS: SYNTHESIS STRUCTURE AND PHOTO PHYSICAL PROPERTIES OF BETA-PYRROLE SUBSTITUTED TETRAPHENYLPOPHRIN S

ABSTRACT

Substituted porphyrins are widely studied for mimicking various biological reactions. Various properties of porphyrin-like structure, stability and photoreactivity can be controlled by varying the substituents at the core of porphyrin ring. Here we have undertaken a detailed study of tetraphenylporphyrin (TPP) molecule substituted with two and three nitro groups at the β-pyrrole position. Novel synthetic approach using fuming HNO₃ as the nitrating agent yielded five isomers of di and three isomers of trinitro porphyrin which were successfully separated by TLC. The ground state electronic structure, crystal structural data, electrochemical redox activity and photoexcited properties of these derivatives are described.

The nitro derivatives were characterised using FAB-mass spectroscopy IR and dynamic ¹H NMR studies. The single crystal X-ray diffraction studies of a few isomers revealed interesting 'saddle' conformation of the porphyrin ring with the nitro groups disposed by ca. 40° to the plane of the pyrrole rings. The imino proton tautomerism of the porphyrin derivatives is found to be a sensitive function of the deposition of the nitro groups at the various pyrrole carbons indicating the dynamic equilibrium. A M1 calculations performed on these derivatives support the importance of number and the position of nitro group in governing the various properties of the macrocycle.

Emission studies of the free-base and zinc(II) derivatives of the nitro porphyrins reveal polar nature of the emitting state and structural change on photoexcitation. The large value of excited state dipole moment (μₑ) indicates considerable amount of charge transfer from the donor porphyrin to the acceptor nitro group. The solvent dependent kₑ and M values suggest a change in the geometry of the excited state. The different magnitude of μₑ amongst the various isomers is analysed in terms of spatial conformation of the nitro group. The CT emission is accompanied by rotation of nitro group to stabilised CT state. These isomer specific ground state and excited state properties are of importance in arriving at the reactivity of these derivatives.