



# The renaissance in optical spectroscopy of phthalocyanines and other tetraazaporphyrins

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**ABSTRACT:** Spectral properties of metallophthalocyanines and other tetraazaporphyrins are governed mainly by the Q band which originates from the  $\pi$ - $\pi^*$  transitions within the ring. The position and intensity of the Q band is important in tailoring new phthalocyanine derivatives for particular applications. Aggregation, the nature of the central metal,  $\pi$  conjugation, symmetry of the molecules, and axial, peripheral or non-peripheral substitutions affect the spectra and hence the properties of the phthalocyanine molecule. This review gives a brief outline on how optical spectroscopy provides useful informations on molecular and electronic structures, chemistry and physics of phthalocyanines and other tetraazaporphyrins. Copyright © 2004 Society of Porphyrins & Phthalocyanines.

**KEYWORDS:** phthalocyanine, absorption spectra, emission spectra, magnetic circular dichroism.

## INTRODUCTION

Phthalocyanines (Pc) and its derivatives contain an extended  $\pi$  conjugated system with unique electronic properties, resulting in a diverse number of applications ranging from industrial (catalysts, photoconductors) to biomedical (photodynamic therapy, PDT) [1]. Specificity in the applications of phthalocyanines can be introduced by modification of the phthalocyanine ring or by changes in the central metal or axial ligands. Spectral properties of phthalocyanines are central to their chemical and electronic properties and are governed by the 18  $\pi$  system of the most inner 16-membered ring. The spectra consist of an intense absorption band in the visible region near 670 nm called the Q band and a generally weak band near 340 nm called the Soret or B band. Charge transfer bands between the central metal and the ring are also observed for some phthalocyanine complexes. The color of the phthalocyanine molecules is in general determined by the Q band. A diverse number of species can be formed following oxidation or

reduction of the phthalocyanine ring. Each oxidation or reduction product has a distinct spectra which may be used for its characterization.

Reviews on the absorption and magnetic circular dichroism spectra of phthalocyanine (Pc(-2)) molecules by Stillman and Nyokong [2] and of the cationic and anionic phthalocyanine species by Stillman [3] provide a good background on the spectral properties of these molecules. Theoretical aspects of the phthalocyanine spectra have been reviewed by Kobayashi, Stillman and their coworkers [4, 5].

The positions of the absorption bands in phthalocyanines, particularly the Q band, are affected to a varying degree by the central metal, axial ligation, solvents, peripheral and non-peripheral substitution, aggregation and by extension of the conjugation. A change in the shape of the Q band occurs with a change in symmetry. Phthalocyanines are now being tailor-made to have specific absorption spectral characteristics. For example long wavelength absorbing phthalocyanine molecules are useful as photosensitizers in photodynamic therapy. Aggregation is disadvantageous for molecules to be used in photodynamic therapy since it diminishes

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