



## MOLECULAR SYMMETRY PROGRESSION IN TETRAPYRIDYL PORPHYRINS: EFFECTS OF CENTRAL SUBSTITUENT

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Light-matter interaction, under certain conditions, produces some effects known as photophysical effects, which are directly related to the perturbation exerted by the electromagnetic field of light on the electronic structure and on the states of vibronic couplings of a molecular system. Optical absorption and photoluminescence are the main examples of this type of interaction. The aim of this work is to investigate the occurrence of such effects on tetrapyrrolyl porphyrins, stabilized by different central ions with different electron distributions and ionic radii. Besides two hydrogen atoms ( $2H^+$ ), which form the free base tetrapyrrolyl porphyrin, the ions  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Co^{2+}$  are employed as central substituents. Taking into account that most of the photophysical processes in porphyrin molecules depend on a set of  $\pi$  orbitals, the evaluation of optical absorption spectra of these molecules can reveal the effects of central substituents on the tetrapyrrolyl porphyrin ring. Considerable changes are observed in the dipole strengths, sub-bands structuration, bands broadening and shifts. The analysis of these spectroscopic signatures by means of Gaussian deconvolution allowed us to evaluate with more precision the positions and widths of the sub-bands belonging to optical absorption and the results suggest a new interpretation for the vibronic couplings of these molecules, extending the conclusions available in the literature. It has been found that ions with semi-filled shells favor electronic effects of charge transfer and beyond that, the ionic radii of the ligands are fundamental for the appearance of steric effects in these porphyrins. Based on the observation of the influence of the central ion on the increase of the energy degenerescence for the vibronic transitions of these molecules, here, it is proposed the existence of a progression in the molecular symmetry of the tetrapyrrolyl porphyrins as a function of the electronic distribution of the ions and its ionic radii.

**Keywords:** metalloporphyrins; symmetry; degenerated transitions; photophysics