

## Synthesis, spectroscopic, and cellular properties of $\alpha$ -pegylated *cis*-A<sub>2</sub>B<sub>2</sub>- and A<sub>3</sub>B-types ZnPcs

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Dedicated to Professor Nagao Kobayashi on the occasion of his 65th birthday

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**ABSTRACT:** A series of pegylated *cis*-A<sub>2</sub>B<sub>2</sub>- or A<sub>3</sub>B-type ZnPcs, substituted on the  $\alpha$ -positions with tri(ethylene glycol) and hydroxyl groups, were synthesized from a new bis-phthalonitrile. A clamshell-type bis-phthalocyanine was also obtained as a byproduct. The hydroxyl group of one ZnPc was alkylated with 3-dimethylaminopropyl chloride to afford a pegylated ZnPc functionalized with an amine group. All mononuclear ZnPcs were soluble in polar organic solvents, showed intense Q absorptions in DMF, and had fluorescence quantum yields in the range 0.10–0.23. The clamshell-type bis-phthalocyanine adopts mainly open shell conformations in DMF, and closed clamshell conformations in chloroform. All ZnPcs were highly phototoxic to human carcinoma HEP2 cells, particularly the amino-ZnPc mainly protonated under physiological conditions, which showed the highest phototoxicity (IC<sub>50</sub> = 0.5  $\mu$ M at 1.5 J/cm<sup>2</sup>) and dark cytotoxicity (IC<sub>50</sub> = 22  $\mu$ M), in part due to its high cellular uptake. The ZnPcs localized in multiple organelles, including mitochondria, lysosomes, Golgi and ER.

**KEYWORDS:** phthalocyanine, PEG, photosensitizer, cytotoxicity, cellular uptake.

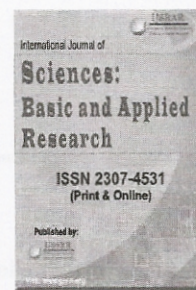
### INTRODUCTION

Phthalocyanines (Pcs) are a class of tetrapyrrolic macrocycles related to the naturally occurring porphyrins; compared with the porphyrin ring, Pcs exhibit an extended 18  $\pi$ -electron system with four benzene units fused onto the  $\beta$ -pyrrolic positions and nitrogen atoms at the *meso*-positions instead of the methine bridges in porphyrins [1, 2]. These structural features confer to Pcs a number of properties that make them highly desirable for a variety of applications in biology, medicine and materials science, including strong absorptions and emissions in the near-IR, high stability and easy macrocycle derivatization. Among their many current applications, Pcs have been used as blue-green colorant dyes, bioimaging agents, and as

photosensitizers for the photodynamic therapy (PDT) or for the photothermal therapy (PTT) of cancers [3–6]. PDT and PTT are minimally-invasive tumor treatments that involve activation of a tumor-localized photosensitizer with red light; in PTT the photoexcited molecules relax non-radiatively producing heat which induces cellular hyperthermia, whereas in PDT an excited triplet state sensitizer produces reactive oxygen species (ROS), such as <sup>1</sup>O<sub>2</sub>, which destroy cells *via* necrosis and/or apoptosis. Photofrin, a derivative of hematoporphyrin IX, has been used for nearly two decades for the PDT treatment of various cancers, including lung, skin, cervical and bladder [7–9]. Nevertheless, photofrin has some drawbacks because porphyrins typically absorb weakly in the red region of the spectrum, where light can penetrate deeper into tissues, and it tends to persist for long periods of time in healthy tissues, causing patient photosensitivity [10]. On the other hand, Pcs have been shown to be promising second-generation photosensitizers for PDT

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## Finite Difference Analysis on Magnetohydrodynamic Fluid Flow Past an Infinite Continuous Moving Surface Embedded in Porous Medium.

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### Abstract

An analysis has been carried out on the effects of variable viscosity on the problem of Magnetohydrodynamic fluid flow past an infinite continuous moving sheet embedded in porous media. The fluid viscosity is assumed to vary as an inverse linear function of temperature. The  $x$  – axis runs along the permeable continuous moving surface in the direction of the motion and the  $y$  – axis is perpendicular to it. The magnetic field is applied along the  $y$  axis. The governing equations have been reduced to the coupled non linear partial differential equations. The system of transformed non linear partial differential equations is solved numerically using the finite difference method. The effects of the various parameters on the flow are analyzed and discussed through graphs.

**Keywords:** Variable viscosity; MHD; porous surface; infinite plate.

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