

# The synthesis, fluorescence behaviour and singlet oxygen studies of new water-soluble cationic gallium(III) phthalocyanines

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Received 20 September 2006; accepted 26 November 2006

Available online 1 December 2006

## Abstract

The preparation of cationic water-soluble gallium phthalocyanine derivatives are described for the first time. Peripheral and non-peripheral 3-hydroxypyridine tetrasubstituted gallium(III)phthalocyanines (**5a**, **6a**) and their quaternarized derivatives (**5b** and **6b**) have been synthesized and characterized by elemental analysis, IR, <sup>1</sup>H NMR spectroscopy, electronic spectroscopy and mass spectra. The quaternarized compounds (**5b** and **6b**) are soluble in water and not aggregated (in water and in organic solvents) within a wide concentration range. General trends are described for singlet oxygen quantum yields, fluorescence quantum yields and fluorescence lifetimes of these compounds. These complexes showed better singlet oxygen quantum yields in water than the related quaternarized porphyrine complexes.

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**Keywords:** Gallium; Phthalocyanine; Amphiphilic; Quaternization; Fluorescence; Singlet oxygen

Phthalocyanines exhibit a number of unique properties that make them of great interest in different scientific and technological areas. Recently, they have also found applications in many fields in materials science, especially in nonlinear optical (NLO) devices, liquid crystals, Langmuir–Blodgett films, electrochromic devices, gas sensors, and photosensitizers, among others [1,2].

One of the most important characteristic of a photosensitizing drug is the perfect balance between its hydrophobic and hydrophilic properties. Phthalocyanine skeletons are essentially hydrophobic due to intermolecular interactions between the macrocycles. The solubility of phthalocyanines can be improved by introduction of substituents on the periphery of the molecule, which increase the  $\pi$ -electron density and make solvation easier [3]. Some water-soluble phthalocyanine compounds have potential for use as photosensitizers in photodynamic therapy (PDT) since they

can be injected directly into the bloodstream. The water solubility of these photosensitizers is an additional advantage despite the fact that the aggregation tendency in such polar medium, in particular, is very high [4].

Hydrophilic and non-aggregated phthalocyanines are therefore important and potentially useful materials. A substantial number of water-soluble tetra- and octasubstituted phthalocyanines have been reported. The hydrophilic moieties which have been incorporated on the peripheral of phthalocyanine ring include sulfonates [5], carboxylates [6], phosphonates [7], and quaternarized amino groups [8]. Another type of water-soluble phthalocyanines contains hydrophilic groups as axial ligands coordinated to the central metal ion [9].

The PDT properties of the phthalocyanine dyes are strongly influenced by the presence and nature of the central metal ion. Complexation of phthalocyanine with transition metals gives dyes with short lifetimes. Closed shell, diamagnetic ions, such as Zn<sup>2+</sup>, Al<sup>3+</sup> and Ga<sup>3+</sup>, give phthalocyanine complexes with both high triplet quantum yields and long triplet lifetimes [10]. MPC complexes containing metals

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