



## The first comparison of photophysical and photochemical properties of non-ionic, ionic and zwitterionic gallium (III) and indium (III) phthalocyanines

Meryem Çamur<sup>a</sup>, Vefa Ahsen<sup>a,b</sup>, Mahmut Durmuş<sup>a,\*</sup>

<sup>a</sup> Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, Gebze 41400, Kocaeli, Turkey

<sup>b</sup> Materials Institute, TUBITAK-Marmara Research Center, P.O. Box 21, Gebze 41470, Turkey

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### ABSTRACT

The spectroscopic, aggregation properties, photophysical and photochemical behaviour of 3-hydroxypyridine substituted gallium (III) and indium (III) phthalocyanine complexes and their quaternized ionic and zwitterionic derivatives are investigated and compared for the first time. The quaternized ionic and zwitterionic phthalocyanine complexes show excellent solubility in water, which makes them potential photosensitizer for use in photodynamic therapy (PDT) of cancer. Photophysical and photochemical properties of photosensitizers are very important for determination of these complexes as PDT agents. Especially, the singlet oxygen quantum yields give an indication of the efficiency of potential photosensitizers in PDT applications. The studied phthalocyanine complexes (3–8) have good singlet oxygen quantum yields. This study also presented the water soluble gallium (III) and indium (III) phthalocyanines strongly bind to blood plasma proteins such as bovine serum albumin (BSA).

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### 1. Introduction

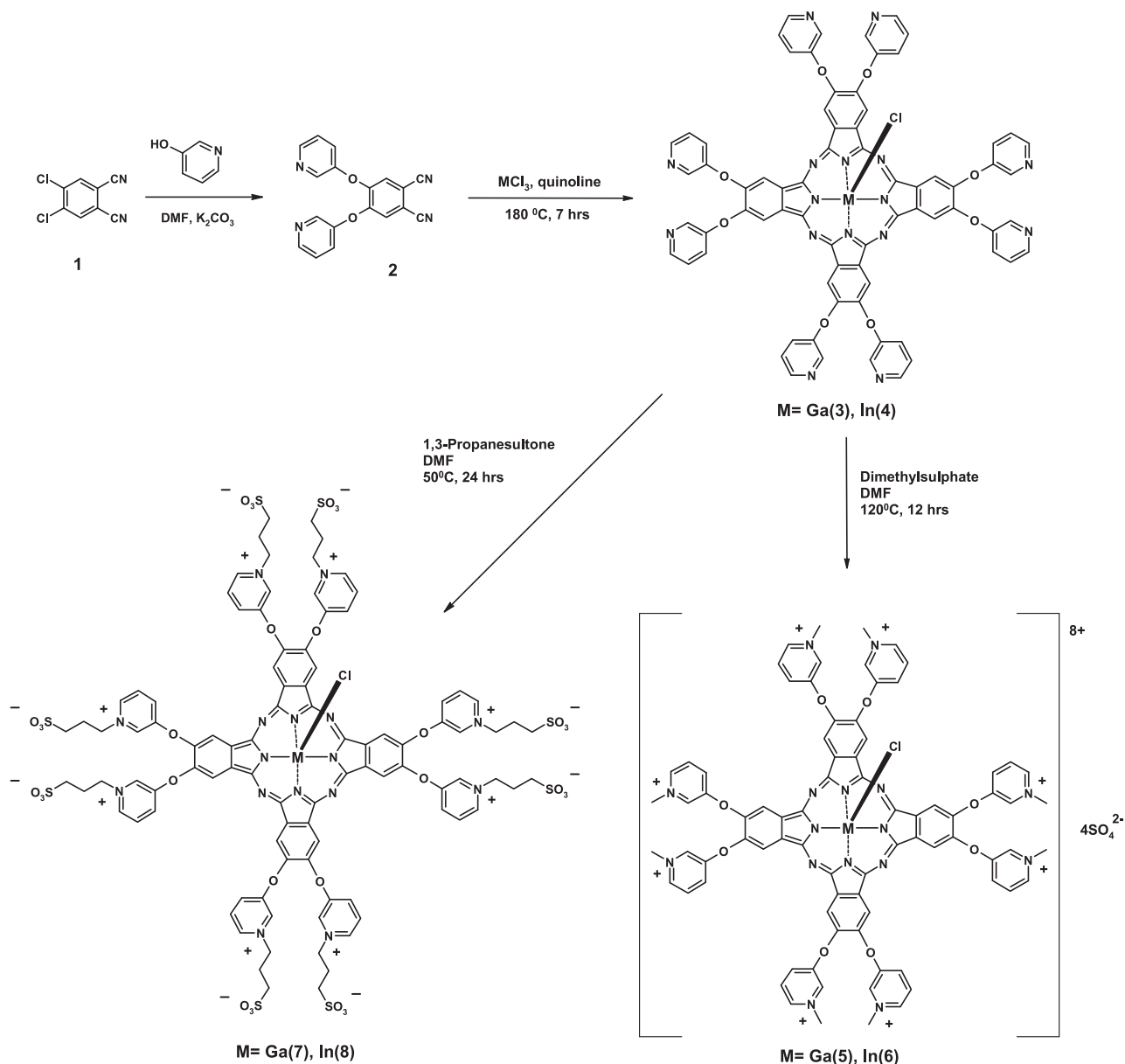
Photodynamic therapy (PDT) is an alternative cancer treatment which is a combination of a photosensitizing drug and light in the presence of molecular oxygen. PDT has been used to obtain a therapeutic effect, and proposed as an alternative treatment to complement conventional protocols in the management of malignant tumours and many other nononcologic diseases [1]. The use of photosensitizing agents for inactivation of several cancer cells has been widely studied [2]. An ideal photosensitizer should be chemically pure, have high efficiency of singlet oxygen generation and significant absorption at far-red and near infrared wavelengths, respectively. In addition, it should have preferential tumour localization, exhibiting good phototoxicity and low dark toxicity, and soluble in the injectable solvents such as water. The drug properties deemed favorable for PDT include synthetic purity, effectiveness at far-red and near infrared wavelengths where tissues are more transparent, and short-term photosensitization of the patient's skin [3].

The first photosensitizers are hematoporphyrin derivatives and have already been described in detail in several articles [4,5]. Second generation photosensitizers such as phthalocyanines have also been introduced for PDT in research and clinical trials [6]. To date, several phthalocyanine systems such as the silicon (IV) phthalocya-

nine Pc4 and a liposomal preparation of zinc (II) phthalocyanine have been in clinical trials. Photosens<sup>®</sup>, which is a mixture of sulphonated aluminium (III) phthalocyanines, is clinically used in Russia for the treatment of a range of cancers [7]. Due to their high molar absorption coefficient in the red part of the spectrum, photostability and long lifetimes of the photoexcited triplet states, phthalocyanines (Pcs) are known to be useful photosensitizers [8–10]. A decisive disadvantage of phthalocyanines is their low solubility in organic solvents or water. Altering the peripheral substitution of the macrocyclic ring is one way of tailoring the solubility properties of the Pc material. Water-soluble Pcs include sulphonates [11,12], carboxylates [13–15], phosphonates [16], and quaternized amino groups [17] on the peripheral positions. Another type of water-soluble Pcs contains hydrophilic groups as axial ligands coordinated to the central metal ion [18,19]. The methylation of the nitrogen atoms using appropriate agents (such as methylbromide, methyl iodide or dimethylsulphate) is the best way for quaternization of the compounds. 1,3-Propanesultone [20] is also used for quaternization of the nitrogen atoms. This quaternization reagent bears a hidden sulphonate group that appears after the opening of the ring during the quaternization [21]. Only a few Pc molecules bearing anionic and cationic charges on the same molecule (zwitterionic) are reported [22–24]. They are generally a result of the quaternization of substituent nitrogen by 1,3-propanesultone. The advantages of Pcs bearing cationic substituents over those with neutral and anionic substituents are numerous and the cation-substituted MPcs are too noticeable to overlook [25], hence our interest in these complexes.

\* Corresponding author. Tel.: +90 262 6053077; fax: +90 262 6053101.

E-mail address: [durmus@gyte.edu.tr](mailto:durmus@gyte.edu.tr) (M. Durmuş).



**Scheme 1.** Synthesis route of 3-pyridyloxy substituted gallium (III) and indium (III) Pc complexes and their quaternized ionic and zwitterionic derivatives.

The PDT properties of the Pc dyes are strongly influenced by the presence and nature of the central metal ion. Complex structure of Pc with transition metals gives short triplet lifetimes to these dyes. Closed shell and diamagnetic ions, such as  $Zn^{2+}$ ,  $Ga^{3+}$  and  $Si^{4+}$ , give Pc complexes with both high triplet yields and long lifetimes [8]. Diamagnetic gallium and indium metals were selected as central metals in this study. The photophysics and photochemistry of gallium (III) and indium (III) Pc complexes are well documented [26–29].

This study is the first report on comparison of the photophysical and photochemical properties of non-ionic, quaternized ionic and zwitterionic water-soluble gallium (III) and indium (III) Pc complexes. Only a few studies on the photochemical and photophysical properties of water-soluble gallium (III) and indium (III) Pc complexes are reported [25,30,31]. The aim of our ongoing research is to synthesize water-soluble gallium (III) and indium (III) Pc complexes as potential PDT agents. In this work, the synthesis, characterization and spectroscopic behaviour as well as photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet

oxygen and photodegradation quantum yields) properties of new octapyridyloxy substituted non-ionic (3 and 4), quaternized ionic (5 and 6) and zwitterionic (7 and 8) gallium (III) and indium (III) Pc complexes (Scheme 1) are presented. Quaternized ionic and zwitterionic compounds were shown to be excellent water soluble.

BSA and human serum albumin (HSA) are major plasma proteins, which contribute significantly to physiological functions and display effective drug delivery roles [32,33], hence the investigation of binding of drugs with albumin is of interest. A spectroscopic investigation of the binding of the water-soluble gallium (III) and indium (III) Pc complexes (5–8) to BSA is also presented in this work.

## 2. Experimental

### 2.1. Materials

Zinc (II) phthalocyanine (ZnPc) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aldrich. Anhydrous indium (III) chlo-

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