

# Water soluble quarternizable gallium and indium phthalocyanines bearing quinoline 5-sulfonic acid: Synthesis, aggregation, photophysical and electrochemical studies



Armağan Günsel<sup>a</sup>, Ahmet T. Bilgiçli<sup>a</sup>, Erkan Kırbaç<sup>b</sup>, Sevgi Güney<sup>c</sup>, Mehmet Kandaz<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Sakarya University, 54140 Esentepe, Sakarya, Turkey

<sup>b</sup> Department of Chemistry, Yıldız Technical University, 34210 Istanbul, Turkey

<sup>c</sup> Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

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## ABSTRACT

In this work, we have presented the synthesis, characterization, photophysical properties and electrochemical characterization of new tetra  $\alpha$  and  $\beta$ -substituted indium and gallium phthalocyanines  $\text{MPcX}(\alpha\text{- or } \beta\text{-HQSA})_4$  ( $\text{M} = \text{Ga(III)}$  (**3**) (**4**) and  $\text{In(III)}$  (**5**) (**6**);  $\text{X} = \text{Cl}$ ) attached with 1-hydroxy quinoline-5-sulfonic acid groups on non-periphery and their water-soluble quarternized counterpart. The non-periphery substituted phthalocyanines with axially counter chlorine anion exhibit high solubility and low aggregation tendency owing to bulky HQSA steric hindrance moieties. The novel phthalocyanine precursors, **3**, **4**, **5**, **6** synthesis, characterization, photochemical properties (singlet oxygen quantum yields and photodegradation quantum yields) and photophysical properties (fluorescence quantum yields and fluorescence behavior) of their peripherally tetra substituted gallium and indium phthalocyanines are reported in this study. The new compounds (**3**, **4**, **5**, **6**) have been characterized by using spectroscopic methods, FT-IR,  $^1\text{H}$  NMR spectroscopy, electronic spectroscopy and Maldi-TOF spectra in addition to elemental analysis. General trends focus on fluorescence, photodegradation and singlet oxygen quantum yields of these compounds in dimethylsulfoxide (DMSO), water ( $\text{H}_2\text{O}$ ). The nature of the substituent and solvent effect on the photophysical and photochemical parameters of the substituted phthalocyanines (**3**, **4**, **5**, **6**) are also reported. The effect of point of substitution on the electrochemical properties of newly synthesized phthalocyanine compounds, periphery ( $\beta$ -) and non-periphery ( $\alpha$ -) substituted with 8-hydroxyquinoline-5-sulfonic acid group were evaluated.

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## 1. Introduction

Metal phthalocyanine (Pc) is a kind of promising complex which has high technological application fields with various metal ions in its central cavity [1–3]. In recent years, many efforts to make the best specified molecular materials are devoted on chemical sensors [4–6], semiconductors [7], electrochromic display devices [8–10], liquid crystals [11,12], solar cells [13], photovoltaics [14] various catalytic processes [15,16] and photosensitizers [17,18]. Phthalocyanines well known to possess the photosensitizer activity are commonly used in PDT (photodynamic cancer therapy) because of their absorptions in the red region [19].

Unsubstituted phthalocyanines behave in a particular way as to create aggregate ( $\pi$ - $\pi$  stacking interactions) in polar and aqueous

media. Nevertheless, their solubility can be made better by adding suitable organic groups to phthalocyanine ring in common organic solvents [20–22]. In addition, tendency to aggregation can be reduced with attaching suitable substituent [23]. These kinds of attractive approaches to increase water solubility, reduce aggregation so that its excited state lifetimes start to enhance and develop its cellular uptake in aqueous media [24] are of extremely importance in PDT studies. It has been indicated that this molecular aggregation greatly effects photosensitizing efficiency and besides, the main nature of phthalocyanines with the inclusion of their spectroscopic, electrochemical, photophysical, and non-linear optical properties [25,26]. However, to increase the solubility of phthalocyanine (Pc) complexes in common organic solvents it is necessary to make peripheral and/or nonperipheral suitable substitution by changing the aggregation behavior [27–29]. If Pcs are modified with suitable special ligands, such as 8-hydroxy quinoline-5-sulfonic acid in  $\alpha$  or  $\beta$  positions, it could be induced to disaggregate by their bulky structure and, therefore,

\* Corresponding author. Tel.: +90 264 295 60 42; fax: +90 264 295 59 50.

E-mail addresses: [mkandaz@sakarya.edu.tr](mailto:mkandaz@sakarya.edu.tr), [mkandaz@yahoo.com](mailto:mkandaz@yahoo.com) (M. Kandaz).

major changes carry out in their optical properties. Controlling the aggregation is thought to be crucially important [30,31].

Moreover, the complete understanding of essential features of the MPcs with or without redox-active metal center is necessary to investigate the redox behaviour of MPcs which is nearly with regard to put into practice technologically, such as electrocatalysis [21–23] and electrochromism [32].

In this study, we have reported the synthesis and characterization of new tetra  $\alpha$ -substituted indium and gallium phthalocyanines MPcX( $\alpha$ - or  $\beta$ -HQSA)<sub>4</sub> {M = Ga(III) (3) (4) and In(III) (5) (6); X = Cl}. Their redox behaviour was measured by voltammetry and in situ spectroelectrochemistry. The nature of the substituent and solvent effect on the photophysical and photochemical parameters of the substituted phthalocyanines (3, 4, 5, 6) are also reported. The effect of binding position on the electrochemical properties of newly synthesized phthalocyanine compounds, periphery ( $\beta$ -) and non-periphery ( $\alpha$ -) substituted with 8-hydroxyquinoline-5-sulfonic acid group were evaluated.

## 2. Experimental

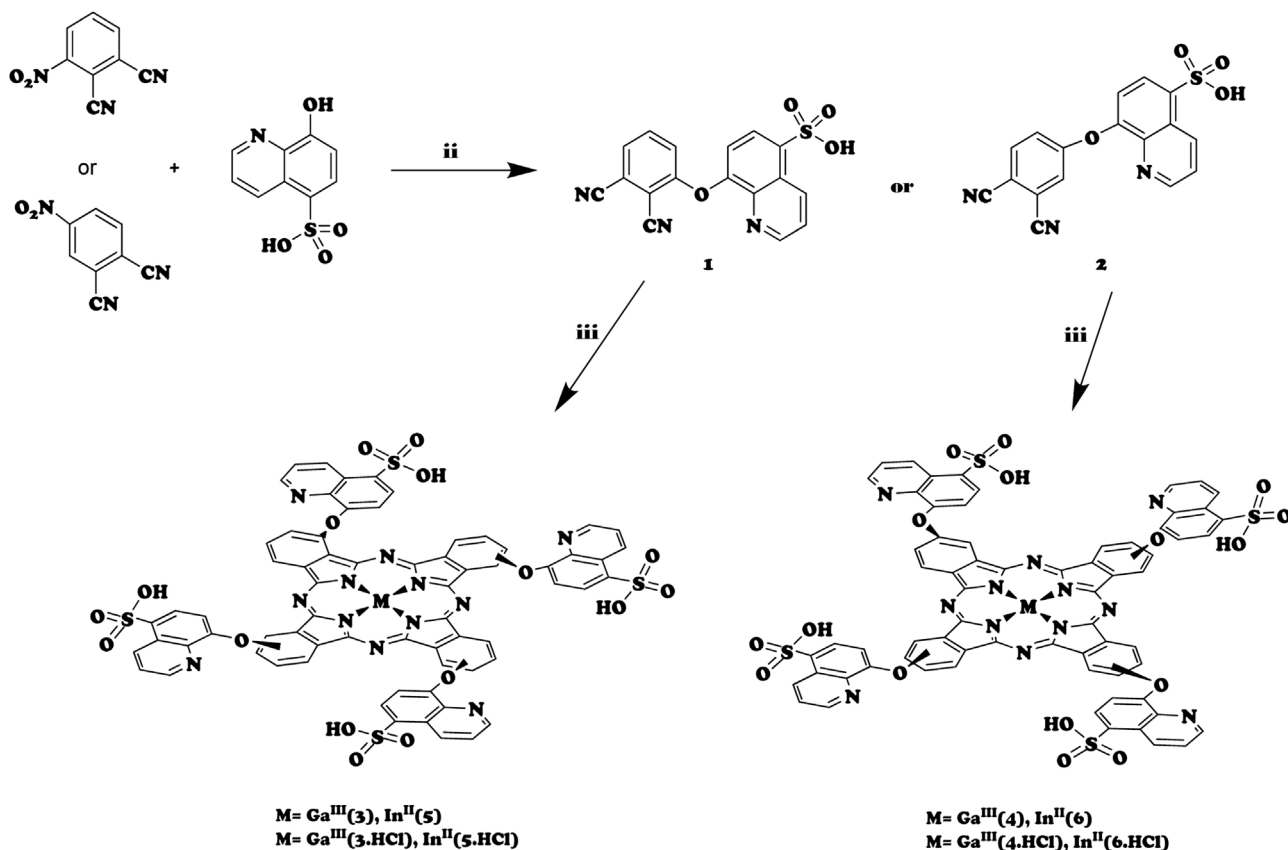
### 2.1. Materials

3-Nitrophthalonitrile and 4-nitrophthalonitrile used all solvents, 8-hydroxyquinoline-5-sulfonic acid, GaCl<sub>3</sub>, InCl<sub>3</sub>, and anhydrous K<sub>2</sub>CO<sub>3</sub> were obtained from commercial suppliers and used as received. 8-(3,4-Dicyanophenoxy) quinoline-5-sulfonic acid (2) was synthesized according to literature procedure [15]. All reactions were carried out under dry N<sub>2</sub> atmosphere. *n*-Hexanol and tetrahydrofuran (THF) were distilled from anhydrous CaCl<sub>2</sub> and acetophenon. An Agilent Model 8453 diode array

spectrophotometer were used to measure UV–vis spectra of complexes. FTIR (KBr) was monitored on Shimadzu IR-prestige-2 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker 300 MHz spectrometer instruments. Multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet). Elemental analysis (C, H and N) was carried out at the Instrumental Analysis Laboratory of Marmara University. Fluorescence excitation and emission spectra were recorded on a HITACHI F-7000 fluorescence spectrophotometer using 1 cm pathlength cuvettes at room temperatures in Marmara University. Complexes were purified by using chromatography with silica gel (Merck grade 60) which is obtained from Aldrich. Matrix-assisted laser desorption/ionisation time of flight (MALDI-TOF) mass spectra (MS) were recorded by using a Bruker Autoflex III mass spectrometer equipped with a nitrogen UV-laser operating at 337 nm. The compound, dihydroxy benzoic acid (DHBA) was chosen as the best MALDI matrix. Finally 1  $\mu$ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

### 2.2. Electrochemical measurements

The cyclic (CV) and differential pulse voltammetry (DPV) measurements were achieved with PARSTAT 2273 potentiostat/galvanostat (Ametek, USA) driven by the PowerSuite data processing software (version 1.07). DPV parameters were applied as pulse size 100 mV, pulse time 50 ms, step size 5 mV and sample period 100 ms. A conventional three-electrodes electrochemical cell was used at 25 °C. A platinum wire was served as the counter electrode (PAR-K0266). The working electrode (PAR-G0228) was a platinum (Pt) disc with surface area of 0.03 cm<sup>2</sup>. The surface of the platinum electrode was polished with a diamond suspension



**Scheme 1.** Synthetic route of 1 or (4), 8 or (11), 15 or (18), 22 or (25)-tetrakis 8-hydroxyquinoline-5-sulfonic acid (HQSA) phthalocyanine [(MPc- $\alpha$ -HQSA and MPc- $\beta$ -HQSA); (M = Ga(III) and In(III))].

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