



# Synthesis, characterization and dielectric properties of novel phthalocyanines bearing an octa-peripherally substituted mercaptoquinoline moiety



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## ABSTRACT

The synthesis, characterization, spectral and dielectric properties of peripherally ( $\alpha$ ) octa-mercaptoquinoline substituted Zn(II), Lu(III), Fe(III) and In(III) phthalocyanines are described for the first time. These complexes (**2–5**) and their precursor are characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR, electronic spectroscopy as well as mass spectroscopy. Complexes **2–5** have good solubility in organic solvents such as CHCl<sub>3</sub>, DCM, DMSO, DMF, THF and toluene and are not aggregated in any of the solvents over a wide concentration range. The dielectric properties and the dc conduction properties of **2–5** were investigated as a function of frequency and temperature. The dielectric properties were studied in the frequency range 400–1 × 10<sup>6</sup> Hz. and in the temperature range 300–500 K. It has been observed that both the dielectric constant ( $\epsilon'(\omega)$ ) and dielectric loss ( $\epsilon''(\omega)$ ) decrease with the rise in frequency, but increase with the rise in temperature. From the analysis of the dc conductivity ( $\sigma_{dc}$ ) dependence on temperature, a weak temperature dependence in the low temperature region and a strong temperature dependence in the higher temperature region was observed for films of **2–5**, which indicates the involvement of two conduction mechanisms.

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## 1. Introduction

Phthalocyanine (Pc) compounds have been used for many applications, such as photosensitizers for photodynamic therapy (PDT), imaging, non-linear optics, photocatalysis, as electrochemical sensors and in solar cells [1], light emitting diodes [2], optical limiting devices [3–5], molecular electronics [6], liquid crystals [7,8], gas sensors [9], semiconductor materials [10] and in photovoltaic cells [11,12], due to their unique physicochemical properties that arise from their aromatic structure [13–15]. Our previous studies have described the synthesis, characterization and photophysicochemical properties of metallophthalocyanines (Zn(II), TiO(IV), In(III), Co(II), Mn(III) and Fe(III)) bearing different substituents for PDT and electrochemical applications [16–21].

Materials based on phthalocyanines have been of particular significance in many fields concerning energy conversion [22,23], gas sensors [24–26], rectifying devices [27], optical data storage [28], non-linear optics and optical limiting [29,30]. The application of Pc compounds for the above devices is related to the electrical conductivity and dielectric relaxation process in

the phthalocyanine compounds and these are often the deciding factors about the suitability of the material for a particular device application. Therefore, the extraction of the true intrinsic nature of the electrical conduction and relaxation mechanism is essential for a material. The basic electrical properties of many metal phthalocyanines (MPcs) have been studied in some details by various workers in the form of both single crystals and thin film [31–33]. However, little previous work has been performed on dielectric spectra, most of this being confined to commercially available metal phthalocyanines, such as zinc phthalocyanine (ZnPc) [34], nickel phthalocyanine (NiPc) [35] and cobalt phthalocyanine (CoPc) [36]. Unlike some other mono phthalocyanines, the electronic properties and the dependence of the conductivity on the temperature of [mercaptoquinoline]phthalocyanines have not been widely studied.

This work reports the synthesis, characterization and electrical properties of a new phthalonitrile and its corresponding metallophthalocyanine derivatives, which are symmetrically octa-substituted at a peripheral position with the mercaptoquinoline substituent and are successfully reported here for the first time. The structures of the new compounds were characterized by elemental analysis, IR, <sup>1</sup>H NMR, UV–Vis and mass spectroscopies. The aggregation behavior of the metallophthalocyanine

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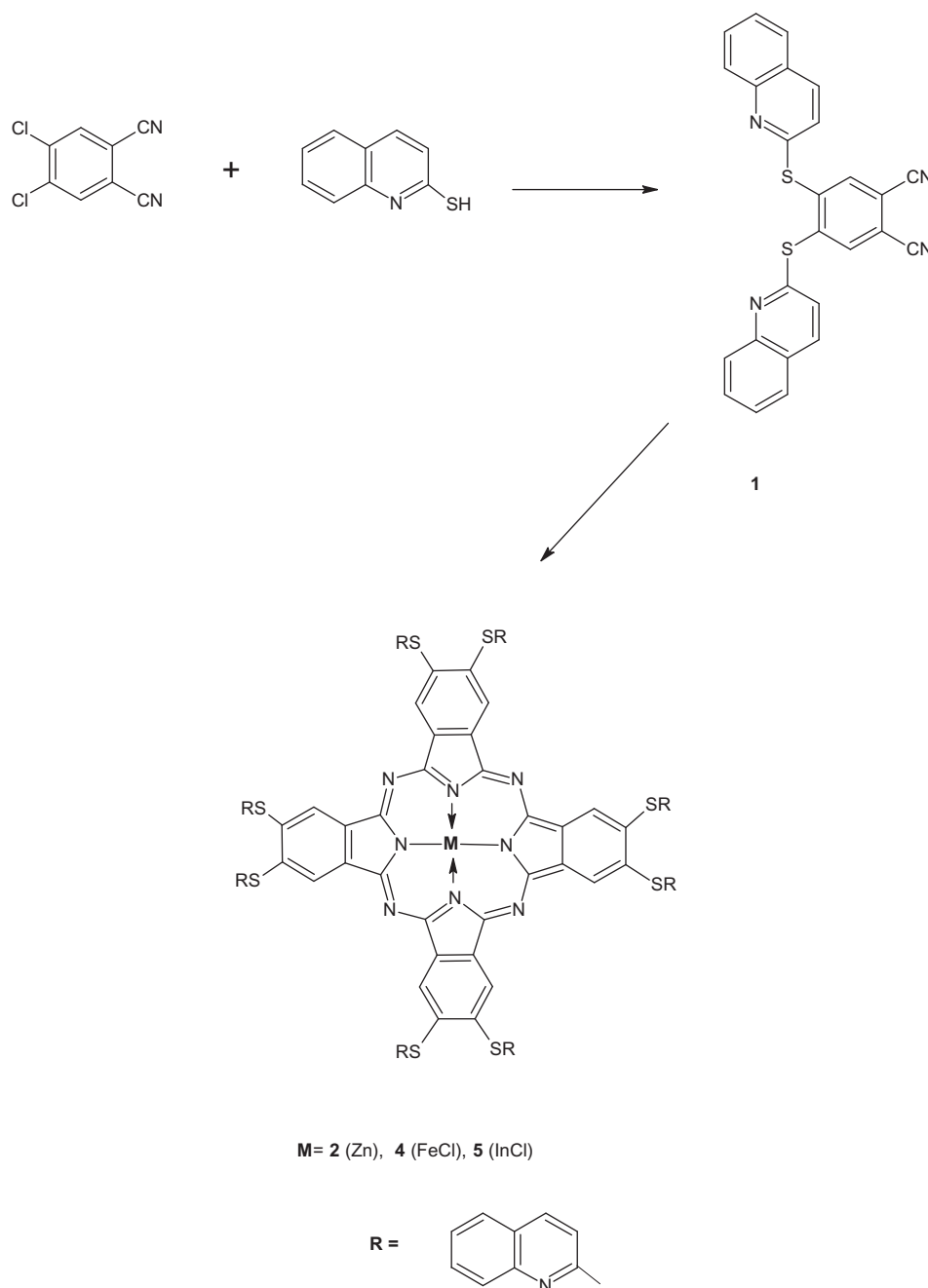
complexes were investigated in  $\text{CHCl}_3$ . The dc conduction and dielectric properties of these complexes were also investigated. [37,38].

## 2. Experimental

### 2.1. Materials and equipment

Dimethyl sulfoxide (DMSO), *N,N'*-dimethylformamide (DMF), chloroform ( $\text{CHCl}_3$ ), tetrahydrofuran (THF), methanol (MeOH), dichloromethane (DCM), 1-pentanol, *n*-hexane, acetone and toluene were purchased from SAARCHM; 4,5-dichlorophthalonitrile, 2-quinolinethiol, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), potassium carbonate, dimethylsulphate (DMS), zinc phthalocyanine,

lutetium(III) acetate, iron(II) acetate, indium(III) chloride and zinc(II) acetate were purchased from Aldrich. The IR spectra were obtained with a Perkin Elmer Spectrum One spectrometer using a KBr disc in the range  $400\text{--}4000\text{ cm}^{-1}$ . UV-Vis spectra were measured on a Shimadzu 2001 UV spectrophotometer. Mass spectra were acquired on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm. 2,5-Dihydroxybenzoic acid was used as a MALDI matrix for the mono- and bis-lutetium(III) phthalocyanines.  $^1\text{H}$  NMR spectra were recorded using a 104 Varian 500 MHz spectrometer in deuterated  $\text{CHCl}_3$ . Elemental analyses were carried out using a Thermo Flash EA 105 1112 Series. GC-MS spectra were acquired on an Agilent Technologies including 6890N network GC system and a 5973 inert mass selective detector.



**Scheme 1a.** Synthetic route to phthalonitrile **1** and its metallophthalocyanines (M =  $\text{Zn(OAc)}_2$ ,  $\text{InCl}_3$ ,  $\text{Fe(OAc)}_2$  and 1-pentanol, 12 h, argon atm.

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