

# Synthesis and characterization of new metal-free and metallophthalocyanines containing macrocyclic moieties

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## Abstract

The synthesis and characterization of new metal-free **7** and metallophthalocyanines **8**, **9** carrying macrocyclic N<sub>2</sub>S<sub>2</sub>O<sub>4</sub> donor groups on peripheral positions have been investigated. Phthalonitrile derivative **6** was synthesized according to Rosenmund von Braun procedure from compound **5**. The novel compounds were characterized by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR, UV–Vis and MS spectra data.

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## 1. Introduction

Phthalocyanines and structurally related compounds exhibit properties which are interesting for applications in various fields of material sciences [1]. For example, phthalocyanines are used in laser-beam printers and photocopiers [2], in nonlinear optics [3], as liquid crystals [4], as photosensitizers [5], in optical data storage [6], as gas sensors [7], as electrochromic substances [8] and as carrier generations materials in near infrared (NIR) [9]. Tetra- and symmetrically octasubstituted derivatives are useful compounds in nonlinear optics [10,11] as Langmuir–Blodgett (LB) films [12–16] as well as organic semiconductors. Specificity in the applications of phthalocyanines can be introduced by modification of the phthalocyanine ring or changes in the central metal. Remarkable progress has been made in recent years in the use of phthalocyanine derivatives as sensitizers for photodynamic therapy (PDT) of cancer [17,18]. As the second generation photosensitizers for photodynamic therapy (PDT) in the treatment of cancer, phthalocyanines, particularly the aluminum and zinc derivatives, are the most recently studied [19]. By controlling the kinds of central

metal ions or introducing appropriate substituents on the phthalocyanine ring, soluble complexes have been prepared, and some studies such as redox, photocatalytic, and oxidative catalytic reactions have been reported [20–24]. Macrocyclic ligands containing both nitrogen and sulfur donor atoms are of interest because of their potential for providing molecules capable of mimicking various aspects of macromolecular biological systems. As might be anticipated, the macrocyclic polyamino polythioether ligands exhibit an interesting range of properties intermediate between those of macrocyclic polythioethers and macrocyclic polyamines [25,26].

We have previously described the synthesis of novel metal-free phthalocyanines and metallophthalocyanines bearing four 27-membered dioxadiazapentathia macrocyclic moieties on peripheral positions [27]. In the present paper, we have discussed the synthesis, characterization and structural investigation of these novel symmetrical phthalocyanine and its nickel(II) and cobalt(II) derivative.

## 2. Results and discussion

The amine groups of 2,2'-(propane-1,3-diylbis(sulfanediy))diethanamine (**1**) were then tosylated in pyridine

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at  $-10\text{ }^{\circ}\text{C}$  with *p*-toluenesulfonylchloride (**2**) to protect amino groups and to make use of the high reactivity of tosylamides in cyclization reactions. In the IR spectra of **1** the intense absorption bands at  $3365\text{--}3291\text{ cm}^{-1}$  for **1** corresponding to the  $\text{--NH}_2$  groups, disappear after the conversion to the tosylamido compounds. In the IR spectrum of **3**, the intense absorption band at  $3272\text{ cm}^{-1}$  corresponds to the N–H stretching vibration. Mass spectrum and elemental analysis also confirm the formation of **3**  $m/z = 541\text{ [M+K]}^+$ .

As in the case of most other phthalocyanines containing macrocyclic moieties, a convenient method for similar compounds is to start with the dibromo or dicyano derivatives of the corresponding macrocyclic units. For this aim, **3** was reacted with 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**4**) [29] in dry acetonitrile containing finely ground anhydrous  $\text{Cs}_2\text{CO}_3$  as a template agent at reflux temperature in a Schlenk system under a nitrogen atmosphere to give the **5** in 62% yield. The relatively high yield of this macrocyclization reaction between two bifunctional reactants is clear indication of the template effect of the caesium ion. On the other hand, tosylation of aza groups, which are used as protective groups of aza functions in the cyclotetramerization, is also effective in the cyclization. Analytical and spectroscopic data of **5** clearly confirm the success of the cyclization reaction. In the  $^1\text{H}$  NMR spectrum of **5** the chemical shifts of NH protons in precursor compound **3** disappear after the macrocyclization reaction. The other resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, concerning methyl, methylene and aromatic protons and carbons, are very similar to those of the precursor compounds **3**. The  $^1\text{H}$  NMR spectrum of a  $\text{CDCl}_3$  solution of **5** was well resolved and showed that the formation of this macrocycle was accomplished. The chemical shifts belonging to the deuterium exchangeable NH groups at  $\delta = 5.36\text{ ppm}$  disappear after the condensation reaction between **3** and **4**. The differences between the infrared spectra of the precursor compounds and the macrocycle is clear from the presence of characteristic vibrations such as Ar–O–C ( $1089\text{ cm}^{-1}$ ), and the absence of N–H ( $3272\text{ cm}^{-1}$ ) stretching vibrations. The new macrocyclic **5** exhibited a molecular ion peak at  $m/z = 823\text{ ([M+1]}^+)$ , which supports the structure. The elemental analysis was confirm desired compound **5**.

19,20-Dicyano substituted macrocycle which synthesized by treating the dibromo compound **5** with three equivalents of  $\text{CuCN}$  according to Rosenmund von Braun reaction [30] in a moderately high-boiling solvent such as DMF at  $150\text{ }^{\circ}\text{C}$  under nitrogen atmosphere. After this reaction, the desired compound **6** was purified by column chromatography on silica gel using chloroform as eluent, was completed in 76% yield. In the IR spectrum of **6**, the intense absorption band at  $2229\text{ cm}^{-1}$  corresponds to the  $\text{C}\equiv\text{N}$  stretching vibrations. The  $^1\text{H}$  NMR spectrum of **6** closely resembles that of the precursor compound **5** as expected. The  $^{13}\text{C}$  NMR spectrum of **6** shows the presence of nitrile carbon atoms at  $\delta = 115.85\text{ ppm}$  which indicates the completion of conversion of **5**–**6**. FAB mass spectrum

and elemental analysis also confirm the formation of compound **6**.

Starting from the dicyano derivatives, many chemical routes may be used to form the corresponding metal-free phthalocyanine. The self-condensation of the dicyano compound **6** in the presence of a few drops of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as a strong base at  $198\text{ }^{\circ}\text{C}$  under nitrogen atmosphere afforded the metal-free phthalocyanine **7** in 25% yield as a green solid after purification by column chromatography on silica gel [ethanol:chloroform (3:7)]. A diagnostic feature of the formation of **7** from **6** is the disappearance of the sharp  $\text{C}\equiv\text{N}$  vibration at  $2229\text{ cm}^{-1}$  of the reactant. The stretching vibrations at  $3335\text{ cm}^{-1}$  for **7** can be attributed to the N–H band of the inner core of the metal-free phthalocyanine. The  $^1\text{H}$  NMR spectra of this compound the inner core protons of Pc-2H could not be observed due to strong aggregation of molecules [31]. The mass spectrum of this compound at  $m/z = 2862\text{ [M+1]}^+$  support to the proposed formula for this structure. The elemental analysis were confirm desired compound **7**.

The synthesis of NiPc **8** was accomplished by reacting **6** and the anhydrous  $\text{NiCl}_2$  salt in the presence of a few drops of DBU as a strong base at  $198\text{ }^{\circ}\text{C}$  temperature under nitrogen. Column chromatography with [ethanol:chloroform (3:7)] as eluents removed the nickel phthalocyanine formed by self-condensation of **8** in 37% yield. The NMR characteristics of this compound were similar to those of the precursor dicyano compound **6** and the metal-free phthalocyanine **7**. The IR spectrum of **8** clearly indicates the disappearance of the  $\text{C}\equiv\text{N}$  groups stretching vibration at  $2229\text{ cm}^{-1}$  of the precursor dicyano derivative after the conversion of **6** to nickel phthalocyanine **8**. The mass spectrum of **8** at  $m/z = 2918\text{ [M]}^+$ . The elemental analysis were confirm desired compound **8**.

The synthesis of CoPc **9** was accomplished by reacting **6** and the anhydrous  $\text{CoCl}_2$  salt in 2-(dimethylamino)ethanol at  $175\text{ }^{\circ}\text{C}$  temperature under microwaves (350 W power) for 10 min. Column chromatography with [ethanol:chloroform (3:7)] as eluents removed the cobalt phthalocyanine formed by self-condensation of **6** in 31% yield. The NMR characteristics of this compound were similar to those of the precursor dicyano compound **6** and the metal-free phthalocyanine **7**. The IR spectrum of **9** clearly indicates the disappearance of the  $\text{C}\equiv\text{N}$  groups stretching vibration at  $2229\text{ cm}^{-1}$  of the precursor dicyano derivative after the conversion of **6** to cobalt phthalocyanine **9**. The mass spectrum of **9** at  $m/z = 2955\text{ [M+2H}_2\text{O+1]}^+$ .

Phthalocyanines (**7**–**9**) show typical electronic spectra with two different strong absorption regions. The first, in the UV region at around 340 nm and called the Soret (or B) band [32], arising from the deeper  $\pi$  levels  $\rightarrow$  LUMO transition between an  $a_{2u}$  and the same eg orbitals and extending to the blue of the visible spectrum, is generally much less intense. The second, in the visible region at 600–700 nm and called the Q band, is attributed to the  $\pi \rightarrow \pi^*$  transition from the HOMO to the LUMO of the

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