

Synthesis and characterization of new organosoluble metal-free and metallophthalocyanines substituted by four macrocycles containing piperazine moiety

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ABSTRACT

The syntheses of metal-free phthalocyanine **3** and metallophthalocyanines **4** and **5** with four 12-membered dithiadiazia macrocycles containing piperazine moiety on peripheral position have been accomplished by cyclotetramerization of 1,4-bis(2-(4,5-dicyano-1,2-phenylene)sulfanediy)l)piperazine-2,5-dione **2**. The formation of macrocycle containing piperazine subunit **2** did not require a high dilution technique or template effect and was performed by the reaction of **1** containing N-substituted 2-chloroamide moiety and sodium hydroxide in DMF. Metal-free phthalocyanine and metallophthalocyanines showed the enhanced solubility in organic solvents. These new compounds were characterized by a combination of elemental analysis and ^1H NMR, ^{13}C NMR, IR, UV–vis and MS spectral data.

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Since Linstead reported the synthesis of phthalocyanine in the early 1930s [1], there has been increasing interest in these compounds as blue and green pigments for the industrial manufacture [2,3]. Nowadays, they are an important class of compounds with many applications such as photodynamic reagent for cancer therapy [4], optical read–write disks [5], gas sensor [6], corrosion inhibitors [7] and electrochromic displays [8].

The major encountered problem in the application of phthalocyanines is their low solubility in common organic solvents. For this purpose, many different modifications of the phthalocyanines, such as attachment of solubility-enhancing groups, changing the substituents and introducing bulky groups [9,10], long alkyl chains [11] and macrocycles [12], have been made to enhance the solubilities of phthalocyanines in various solvents.

Since the first introduction of macrocycle into a phthalocyanine was reported in 1986 [13], phthalocyanines containing macrocycles [14], macrobicycles [15] or macrotricycles [16] have been extensively synthesized with the aim of solving the solubility problem of this class of compounds in various solvents. In addition to that, introduction of macrocycles containing sulfur and nitrogen atoms as substituents on the phthalocyanine ring provides donor sites for binding transition metal ions and they might be interesting for usage in different applications such as cation extraction and cation-induced aggregation studies.

Many of biologically active compounds contain piperazine moiety in its structure which are important for therapeutic area such as antifungal [17], antibacterial [18] and anti-psychotic agents [19]. Due to the

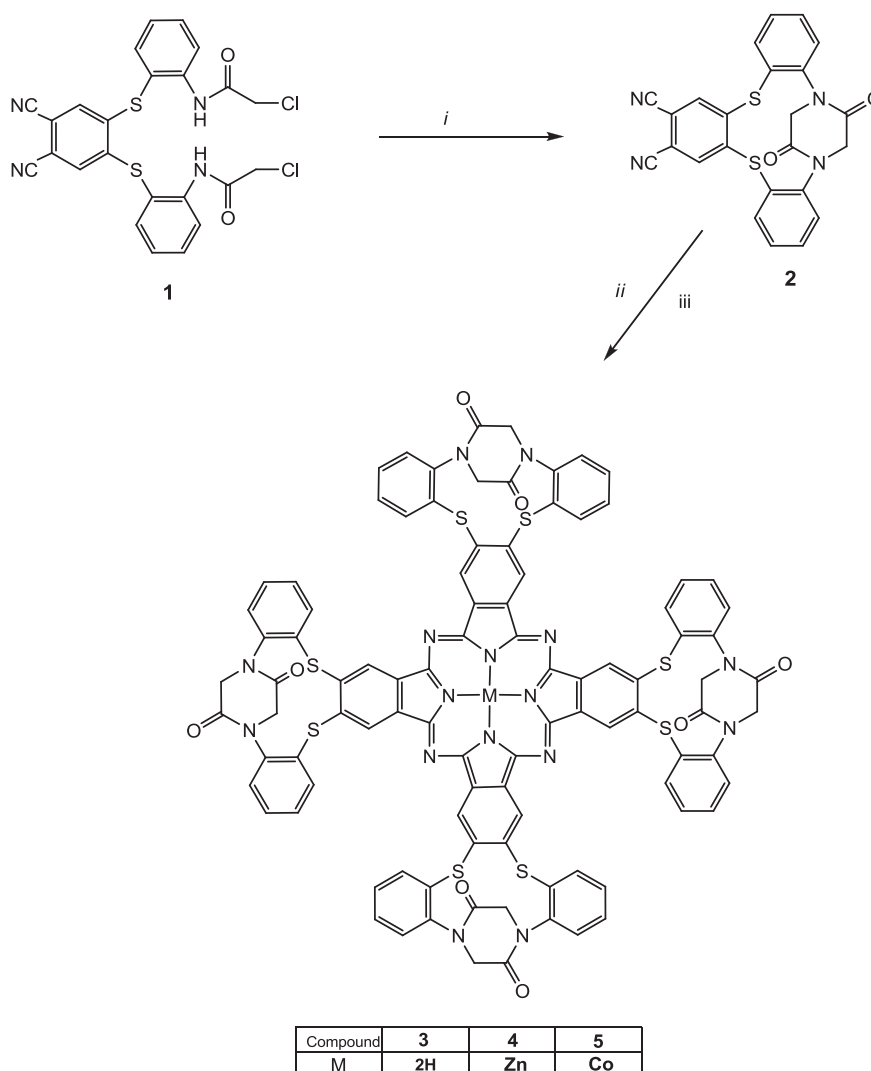
biological effects of piperazine derivatives, compounds such as macrocycle [20], vic-dioxime [18] and phthalocyanine [21] containing piperazine and its derivatives were synthesized and reported in literature in order to find new properties and better biological activities. Moreover, incorporation of piperazine unit in macrocycle reinforces the macrocyclic ring and affects the metal ion binding properties. It was reported that macrocycles containing piperazine unit circumscribed metal ion rigidly [22].

The present paper reports, for the first time the synthesis and characterization of metal-free and metallophthalocyanines substituted by four macrocycles containing piperazine moiety on peripheral positions. Herein, we also report, a convenient, one-pot procedure for the synthesis of the macrocycle containing piperazine moiety based on the mild condensation between two N-substituted 2-chloroamides of **1** in the presence of strong base such as NaOH.

The syntheses of metal-free phthalocyanine **3** and metallophthalocyanines **4** and **5** are described and summarized in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^1H NMR, ^{13}C NMR, IR, UV–vis and MS spectral data. All reagents and solvents were reagent grade and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [23]. Using the known procedure [24], N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediy)l)bis(2,1-phenylene))bis(2-chloroacetamide) **1** [25] was readily prepared in high yield by addition of the 2-chloroacetyl chloride to appropriate amine in CH_2Cl_2 .

Generally, the synthesis of a macrocycle requires high dilution techniques or template effect. The synthesis of N_2S_2 mixed donor macrocyclic

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Scheme 1. Synthesis of metal-free phthalocyanine **3** and metallophthalocyanines **4** and **5**; (i) NaOH, DMF, 65 °C.; (ii) DBU, dry *n*-pentanol, N₂, 145 °C for **3**. (iii) anhyd. Zn(CH₃CO₂)₂ for **4** and Co(CH₃CO₂)₂ for **5**, dry quinoline, N₂, 190 °C.

compound containing piperazine subunit **2** [26] was performed by self condensation reaction between two *N*-substituted 2-chloroamides of **1** at 65 °C in *N,N*-dimethylformamide. This efficient synthesis of the macrocycle **2** did not require high dilution techniques or a template effect and provided the expected macrocycle in high yield (70%) after purification by column chromatography. In the IR spectrum of **2**, very

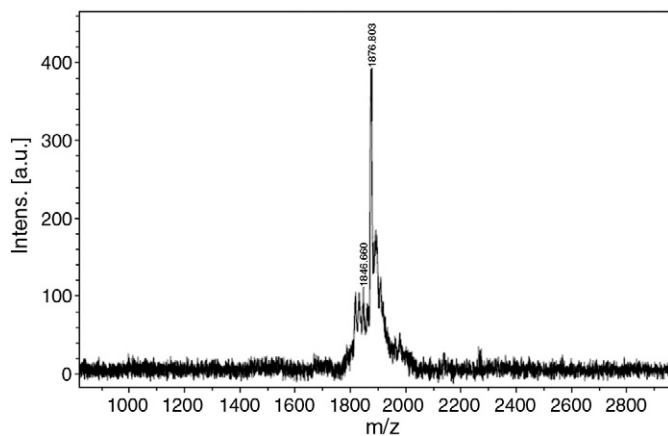


Fig. 1. MALDI-TOF mass spectrum of cobalt(II) phthalocyanine **5**.

specific stretching vibrations of –NH groups at 3336 cm⁻¹ disappeared after cyclization of **1** to **2**. The presence of an intense C≡N stretching band at 2235 cm⁻¹ and the sharp C=O vibration at 1692 cm⁻¹ confirmed the formation of compound **2**. The ¹H NMR spectrum of **2** was collected in CDCl₃. In the ¹H NMR spectrum of **2**, the chemical shifts of amide protons at δ = 9.27 ppm in starting compound **1** disappeared after self condensation reaction. The singlet for methylene protons in the piperazine moiety was observed at δ = 4.31 ppm as expected. The ¹³C NMR spectrum of **2** is in good agreement with the proposed structure. The characteristic signal for C=O, C≡N and CH₂ groups at 164.84, 114.21 and 31.28 ppm, respectively, clearly suggests that the self condensation occurred. The molecular ion peaks at *m/z* = 455.26 [M + H]⁺ and 477.29 [M + Na]⁺ in the LC-MS/MS mass spectra of **2** also confirmed the proposed structure.

Metal-free phthalocyanines are usually prepared from *o*-dinitriles in a hydrogen donor solvent with high boiling point such as *n*-pentanol, 2-(dimethylamino)ethanol. Organic bases such as DBU or anhydrous ammonia are added to the reaction mixture in the template synthesis of phthalocyanine in order to improve the yield [27,28]. Condensation of four molecules of N₂S₂ mixed donor macrocyclic compound containing piperazine subunit **2** into the metal-free phthalocyanine **3** [29] was carried out in dry pentanol in the presence of the non-nucleophilic base (DBU) as the ring-forming catalyst [30,31]. The metal-free phthalocyanine was obtained in 25% yield after purification by column

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