



Non-ionic peripherally substituted soluble phthalocyanines: Synthesis characterization and investigation of their solution properties



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ABSTRACT

Novel tetra aminopropylamid substituted phthalocyanines were synthesized as zinc(II), cobalt(II), copper(II) and manganese(II) metallophthalocyanines. The synthesis of the phthalocyanines **3–6** was achieved by the tetramerization of 4-substituted phthalonitrile, 2-(3,4-dicyanophenoxy)ethyl-N-(3-dimethylaminopropyl) carbamate (**2**), prepared via the nucleophilic aromatic substitution of 4-nitro phthalonitrile and 2-hydroxyethyl-N-(3-dimethylaminopropyl) carbamate (**1**). Solution properties of the prepared phthalocyanines were investigated by the examination of their UV–vis spectra. The zinc Pc showed surprisingly high solubility in water. The aggregation properties of the Pcs were examined in different organic solvents and water. The substituents on the periphery position of the phthalocyanine molecules acted as non-ionic surfactant and increased the solubility in hydrophilic solvents and water. Quaternization of these groups improved the solubility, as well.

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1. Introduction

Synthesis of novel metallophthalocyanine derivatives (MPc) has become very important for the molecular architecture in recent years [1–5]. Because, they have generated a great deal of interest due to their potential applications such as liquid crystals, semiconductor materials, photosensitizer for photodynamic therapy, oxidation or reduction catalysts, optical non-linearity, nanotechnology, intrinsic conductivity, electrochromic materials, medicine, electrochemistry, photo-catalysis and gas sensors [6–19]. The majority of these applications exploit the unique optical properties of Pc's, and thus a variety of spectroscopic techniques such as UV–vis spectroscopy, magnetic circular dichroism (MCD), and fluorescent as well as time-resolved fluorescent spectroscopy were used in the characterization of the excited states of Pc's and their analogs [20].

Phthalocyanines have two major absorption bands in their electronic spectrum, which are called the B (or Soret) band and the Q band. In recent years, on the photo-chemical and photo-physical behavior of phthalocyanines have been studied very extensively by the irradiation with violet or ultraviolet light (resonance with the B band) or visible light in the region 600–700 nm (resonance with the Q band) [21,22].

The applications of the phthalocyanines are restricted, since they are not soluble in common organic solvents and especially in water. It has been found that, the substitution with different substituents either at peripheral β or non-peripheral α position enhances the solubility of the complexes. Numbers of methods are reported to make the Pc molecules water soluble, i.e. by sulfonation at peripheral positions,

quaternizing substituted tertiary amine moieties [23,24], combining polyhydroxy compound such as polysaccharides [25–27] and attaching phosphate moieties [28].

Among these compounds, water-soluble tetra substituted or octa substituted phthalocyanines are the most promising materials as effective catalysts in environmental applications and photo sensors as well as photosensitizers in PDT [29,30]. One of the key factors for determining their photosensitizing efficacy is the intrinsic aggregation tendency of these macrocyclic oligomers which is usually significant in polar media such as water [31].

A compound soluble in molecular dimension in a solvent instead of making aggregates or micelles can be designated as molecular soluble. Designing of molecularly soluble phthalocyanine patterns is also important in terms of the abovementioned applications. The main purpose of the present work is to prepare soluble peripherally amide substituted phthalocyanines as the preliminary step to synthesize water soluble zwitterionic substituted phthalocyanine species. Surprisingly, the ZnPc (**3**) showed higher solubility in water than expected. So, the collected data by this time have been decided to be published at this stage to emphasize that the bearing alkylamide groups as substituents on the periphery positions of the phthalocyanine molecules might increase the solubility in polar solvents and water.

2. Experimental

2.1. Materials and characterization techniques

All reagents and solvents obtained from commercial suppliers were of reagent grade quality. Solvents were dried via A3 molecular sieve and stored in the presence of it. 4-Nitro phthalonitrile was prepared

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according to literature procedure [32]. All reactions were carried out under argon atmosphere, using standard Schlenk technique. Thin-layer chromatography (TLC) was performed using silica gel 60 HF₂₅₄ as an adsorbent. Electronic spectra were recorded on a Shimadzu UV-2401 Pc-spectrophotometer using a 1 cm quartz cell. Infrared spectra were recorded on a Shimadzu FTIR IRPrestige-21 spectrophotometer equipped with PIKE MIRacle™ diamond ATR and corrected by applying IR solution software's ATR-correction function. ¹H and ¹³C NMR spectra were recorded as CDCl₃ and DMSO-d₆ solutions on a Varian Mercury Plus 300 MHz spectrometer. Mass analyses were measured on an AB Sciex LC-MS/MS spectrometer. For MALDI-TOF spectra, the experiments were carried out using a Bruker micrOTOF (Germany) mass spectrometer and samples were run in positive ion mode (ESI⁺). pH measurements were recorded on PHM210 Standard pH meter calibrated up with three standards for 4, 7 and 10 values. The elemental analyses were performed on a Costech ECS 4010 and LECO CHNS-932 instruments at Karadeniz Technical University and Middle East Technical University Central Laboratory. The metal content of the metallophthalocyanines was determined by a flame atomic absorption spectrometer (Shimadzu AA-6701F).

2.2. Synthesis

2.2.1. 2-Hydroxyethyl-N-(3-dimethylaminopropyl) carbamate (1)

N,N-dimethyl-1,3-propanediamine (1.18 g, 11.6 mmol) was added drop-wise to ethylene carbonate (0.92 g, 10.5 mmol) at 45 °C. While continuing the adding process of N,N-dimethyl-1,3-propanediamine, the reaction temperature raised up till 75 °C at the end. The reaction mixture was stirred at room temperature for future 15 h. The residue was dissolved in dichloromethane (50 mL) and the organic phase was washed with brine solution (2 × 25 mL). The solvent was evaporated to dryness and the residue was dried up under vacuum at 40 °C on a sonication bath for 6 h. The pure product was obtained as colorless viscose liquid. Yield: 1.82 g, (91%), anal. calc. for C₈H₁₈N₂O₃: C, 50.51; H, 9.54; and N, 14.73%. Found: C, 51.19; H, 9.76; and N, 15.05. FT-IR (PIKE MIRacle™ ATR) ν_{\max} , cm⁻¹: 3316 (O–H), 3200 (N–H), 2943–2778 (C–H), 1793 (C=O), 1533 (N–H) 1462–1375 (C–C), 1245 (COO), 1141, 1042, 1074, and 1040. ¹H NMR (CDCl₃), (δ : ppm): 6.16 (s, 1H, NH), 4.52 (s, 1H, OH), 3.91 (t, 2H, CH₂), 3.51 (t, 2H, CH₂), 2.97 (q, 2H, CH₂), 2.11 (t, 2H, CH₂), 1.99 (s, 6H, CH₃), and 1.49 (t, 2H, CH₂). ¹³C NMR (CDCl₃), (δ : ppm): 157.2, 66.4, 60.7, 57.3, 45.3, 39.6, and 27.3. MS (ESI⁺), (m/z): 235 [M + 2Na – 1]⁺, 207 [M + H₂O + Na – 1]⁺, and 191 [M + 1]⁺.

2.2.2. 2-(3,4-Dicyanophenoxy)ethyl-N-(3-dimethylaminopropyl) carbamate (2)

The mixture of **1** (1.00 g, 5.26 mmol), 4-nitroptalonitrile (0.625 g, 3.6 mmol) and K₂CO₃ (1.1 g, 8.12 mmol) in dry dimethylsulfoxide (DMSO, 9.5 mL) was stirred at room temperature. Further K₂CO₃ (1.1 g, 8.12 mmol) were added in portion wise after 3 h and after 24 hour intervals. The suspension was stirred at 25 °C for 3 days. The reaction was monitored by TLC using THF/methanol/ NH₃ (90/8/2) mobile phase on SiO₂ plates. After completion of the reaction, 50 mL water was added to the reaction mixture and it was extracted by ethyl acetate (3 × 30 mL). The collected organic phases were combined, washed with brine solution (2 × 20 mL), dried over magnesium sulfate and evaporated to dryness. The oily crude product was purified by column chromatography using methanol/TEA (98/2) mixture as mobile phase. The organic phases were combined, evaporated to dryness and dried over P₂O₅ in vacuum to yield the pure product as reddish brown sticky solid. Yield: 0.8 g (69.57%), anal. calc. for C₁₆H₂₀N₄O₃: C, 60.75; H, 6.37; and N, 17.71%. Found: C, 60.93; H, 5.95; and N, 17.87. FT-IR (PIKE MIRacle™ ATR) ν_{\max} /cm⁻¹: 3267 (N–H), 3078–3027 (Ar–CH), 2945–2778 (C–H), 2230 (C≡N), 1711 (C=O), 1597–1562 (C=C), 1462–1435 (C–C), 1241 (COO), 1142, 1099, and 1041. ¹H NMR (CDCl₃), (δ : ppm): 7.66 (d, 1H, Ar=H), 7.26 (s, 1H, Ar–H), 7.20 (d, 1H, Ar–H), 5.95 (s, 1H,

N–H), 4.36 (t, 2H, O–CH₂), 4.21 (t, 2H, O–CH₂), 3.16 (t, 2H, N–CH₂), 2.56 (s, 6H, N–CH₃), 2.26 (t, 2H, NH–CH₂), and 1.60 (m, 2H, –CH₂–). ¹³C NMR (CDCl₃), (δ : ppm): 161.9, 156.3, 135.5, 120.1, 119.6, 117.5, 115.9, 115.5, 107.6, 67.8, 62.3, 58.1, 45.6, 41.1, and 27.0. MS (MALDI-TOF), m/z: 585 [M + 2Na + 2H₂O + matrix]⁺, 516 [M – 2(CH₃) + Na + H₂O + matrix]⁺, 459, and 410.

2.2.3. 2(3),9(10),16(17),23(24)-Tetrakis-[2-ethoxy-N-(3-dimethylaminopropyl) carbamate]phthalocyaninato zinc(II) (3)

The mixture of **2** (0.4 g, 1.27 mmol) and anhydrous zinc(II) chloride (0.06 g, 0.45 mmol) in dry dimethylaminoethanol (DMAE, 6 mL) was heated at 145 °C for 5 h under argon atmosphere. Progress of the reaction was monitored by TLC using THF/hexane (3/4) mobile phase system on SiO₂ plates. After cooling to ambient temperature, the green reaction mixture was poured into distilled water (15 mL) and the pH was adjusted to 9–10 using concentrated NH₃ solution. The green precipitate was collected by centrifuging. The crude-phthalocyanines mixture was solved in 1/1 diluted HCl and the un-dissolved precipitate was centrifuged off. The acidic solutions were combined and the pure amino amide substituted ZnPc (**3**) was recovered by re-adjusting pH to 9–10 using concentrated NH₃ solution. The green precipitate was separated by centrifuging and washed with diluted NH₃ solution and acetone, respectively. Then, the obtained phthalocyanine product was dried over P₂O₅ in vacuum. Yield: 0.153 g (36.4%), UV/vis (DMSO): λ_{\max} (log ϵ) 354.0 (4.61), 614.5 (4.23), and 681.5 (4.84). Elemental analysis: calcd. (%) for C₆₄H₈₀N₁₆O₁₂Zn: C, 57.76; H, 6.06; N, 16.84; and Zn, 4.91; found: C, 56.97; H, 6.46; N, 16.15; and Zn, 5.19; FT-IR (PIKE MIRacle™ ATR) ν_{\max} /cm⁻¹: 3310 (N–H), 3065 (Ar–CH), 2930–2872 (C–H), 1697 (C=O), 1607 (C=C), 1487–1335 (C–C), 1225 (COO), 1121, 1090, and 1043. ¹H NMR (DMSO-d₆), (δ : ppm): 9.35–7.75 (m, 12H, Ar–H), 7.54 (m, 4H, CON–H), 4.76 (m, 8H, O–CH₂), 4.62 (m, 8H, O–CH₂), 3.12 (m, 8H, N–CH₂), 2.64 (m, 8H, NH–CH₂), 2.48 (m, 24H, N–CH₃), and 1.72 (m, 8H, –CH₂–). MS (MALDI-TOF), m/z: 1331 [M]⁺, 1203 [M–(C₆H₁₃N₂O)]⁺, 1143, 1074, 1014, 946, 886, 817, and 759.

2.2.4. 2(3),9(10),16(17),23(24)-Tetrakis-[2-ethoxy-N-(3-dimethylaminopropyl) carbamate]phthalocyaninato cobalt(II) (4)

The mixture of **2** (0.093 g, 0.294 mmol) and anhydrous cobalt(II) acetate (0.013 g, 0.073 mmol) in dry dimethylaminoethanol (DMAE, 2.5 mL) was heated at 150 °C for 15 h under argon atmosphere. The reaction was monitored by TLC using the same system applied for **3**. After cooled to room temperature, the blue reaction mixture was poured into distilled water (10 mL) and the pH was adjusted to 9–10 using NH₃ solution. The blue precipitate was separated by centrifuging and the crude product was purified same as for compound **3**. Yield: 0.0687 g (70.8%), UV/vis (DMSO): λ_{\max} (log ϵ) 333 (4.64), 606.0 (4.23), 661.5 (4.76). Elemental analysis: calcd. (%) for C₆₄H₈₀N₁₆O₁₂Co: C, 58.04; H, 6.09; N, 16.92; and Co, 4.45; found: C, 57.41; H, 5.72; N, 15.96; and Co, 5.37; FT-IR (PIKE MIRacle™ ATR) ν_{\max} /cm⁻¹: 3325 (N–H), 3062 (Ar–CH), 2943, 2872 (C–H), 1699 (C=O), 1608 (C=C), 1521–1338 (C–C), 1230 (COO), 1126, 1093, 1056, and 960. MS (ESI⁺), (m/z): 1324 [M]⁺.

2.2.5. 2(3),9(10),16(17),23(24)-Tetrakis-[2-ethoxy-N-(3-dimethylaminopropyl) carbamate]phthalocyaninato copper(II) (5)

The mixture of **2** (0.093 g, 0.294 mmol) and anhydrous copper(II) chloride (0.010 g, 0.075 mmol) in dry dimethylaminoethanol (DMAE, 2 mL) was heated at 130 °C for 15 h under argon atmosphere. After completion of the reaction, the green reaction mixture was cooled to ambient temperature and poured into distilled water (10 mL). The precipitated greenish crude product was collected by centrifuge, and it was purified by milling in acetone (10 mL). The purified product was re-collected by centrifuge and washed again with acetone. The purity of the final product was controlled by TLC using THF/hexane (3/4) mobile phase system on SiO₂ plates. Yield: 0.0523 g (53.42%). UV/vis (DMSO): λ_{\max} (log ϵ) 333.0 (4.42), 612.0 (3.92), and 679.0 (4.46).

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