Synthesis and Characterization of New Zinc-phthalocyanine with Four Dodecenyl-benzoic Pendant Groups

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Abstract
Substituted zinc phthalocyanine was synthesized in this study. The reaction of 4-nitro Phthalonitrile with ZnCl₂ in the presence of dimethyl amino ethanol (DMEA) afforded 4,4',4'',4'''-tetranitro zinc phthalocyanine. This was reacted with 5-amino salicylic acid to yield tetra-(5-amino salicylic acid)zinc phthalocyanine. After that, dodecenyl succinic anhydride was added on amine group of benzoic rings afforded tetra-(E)-5-(3-(dodec-1-enyl)-2,5-dioxopyrrolidin-1-yl)-2-hydroxybenzoic acid)zinc phthalocyanine. The phthalocyanine was separated and washed using different solvents. The newly synthesized compounds have been characterized by elemental analysis, FT-IR, ¹H NMR and UV-Visible spectroscopy techniques.

Keywords: zinc phthalocyanine, 5-amino salicylic acid, dodecenyl succinic anhydride.

Introduction
Structural relationship between phthalocyanines (Pcs) and porphyrins, Phthalocyanines are tetrabenzoporphyrins with substituting four meso-carbons in position α-γ and β-δ axis of the porphyrin by four nitrogen atoms. In other words, Phthalocyanines are tetraazaporphyrins (porphyrazines) with four addition benzene groups (Scheme 1) (Leonardo et al. 2008)
Scheme 1: Schematic description for the difference between phthalocyanines and porphyrin structures.

Phthalocyanines can be synthesized by different routes according to the kind of phthalocyanines to be created; metal-free, symmetrical or asymmetrical Phthalocyanine. Synthetic phthalocyanines based on many factors: solvent (high boiling point solvents), precursor metal salt (metals, sulphates, halides, metal salts and oxides), temperature (to facilitate melting of the precursor and rapid cyclotetramerization), catalyst and base. Pcs is formed through cyclotetramerization of phthalimide, phthalic acids, phthalonitrile precursors, phthalic anhydrides in the presence of a metal salt and in the absence of a metal salt for unmetallated Pcs (Scheme 2) (Rodriguez-Morgade, de la Torre et al. 2003; Louati et al. 1985).
Scheme 2: Schematic description for the synthetic routes of metallophthalocyanines from different precursors.

Pcs has extensive range of applications in the field of material science because the properties of their electrical, optical and their thermal stability (Kadish et al., 2003; Leznoff et al., 1995; Boyle et al., 1996; Eberhardt et al., 1997). These compounds have been prepared by reaction between urea, metal salts and phthalimide or phthalic anhydride or phthalonitrile. Typically, reaction times of several hours are needed for such reactions and temperatures around 200 °C. (Czech, 1994; Kempa et al., 1988; Tse et al., 1991; Hanack et al., 1992).

The use of phthalocyanine has newly extended to many technological processes. Appropriate substitution in the peripheral position of the phthalocyanine. It produces many of the uses of the phthalocyanine, such as in optical limiters, optical recording materials, Langmuir-Blodgett films, field-effect transistors (Gerdes et al., 1997), gas sensors, (Liu et al., 1998), liquid crystals (Cosimelli et al., 2003) and thin films (solar cells) (Snow et al., 2000). In addition, they are used as oxidative degradation of pollutants or catalysts for photo and as photosensitizers (Hirth et al., 1999).

Phthalocyanine are the second most important class of colorant. Phthalocyanine derivatives and substitutes in the past years were studied intensively as a second-generation therapy for cancer photosynthesis (Moser, 1998; Leznoff et al., 1989). The presence of hydrophilic and hydrophobic ring in the Pc are beneficial to selective tumor (Pascalati et al., 2001) amino groups or imido substitutes in the ring. Pc seem useful because of hydrophobic property and possible interaction of the protein or covalent bonds with antibodies monoclonal. (Oda et al., 2000)
Experimental part

Synthesis of 4,4′,4″,4‴-tetranitro zinc phthalocyanine (A)

A mixture of 4-nitro phthalonitrile (1.00 g, 5.77 mmol) and ZnCl₂ (0.98 g, 7.21 mmol) in 2 mL of DMAE (dimethylaminoethanol) was stirred under nitrogen atmosphere and stirred at 185 °C for 1 hr. The dark green mixture was cooled to room temperature and washed with water and ethanol. The precipitate was purified by column chromatography over silica gel using a mixture of (DMF: n-hexane) (50:1) as an eluent which afforded (2.47 g, 57%) of compound A, TLC 0.45 cm (dichloromethane: hexane) (2:1), m.p >300°C, Elemental analyses for C₃₂H₁₂N₁₂O₈Zn: C, 50.71; H, 1.60; N, 22.18; Found: C, 51.70; H, 1.91; N, 22.55.

Synthesis of tetra-(5-amino salicylic acid)zinc phthalocyanine (B)

A mixture of compound A (0.50 g, 0.66 mmol), 5-Amino-2-hydroxybenzoic Acid (0.80 g, 5.22 mmol) and K₂CO₃ (0.36 g, 2.63 mmol), in DMF (10 mL) was heated at 70°C and stirred for 9 hr under nitrogen atmosphere. After that, the precipitate was filtered. The mixture was cooled to room temperature, and 1N HCl was added and filtered. After that, the precipitate was purified by column chromatography over silica gel using a mixture of (DMF: n-hexane) (50:1) as an eluent which afforded (0.47 g, 60%) of the title compound, TLC 0.8 cm (dichloromethane: hexane) (2:1), m.p. >300°C, Elemental analyses for C₆₀H₃₆N₁₂O₁₂Zn: C, 60.95; H, 3.07; N, 14.22; Found: C, 59.62; H, 3.14; N, 14.58.

Synthesis of tetra-(E)-5-(3-(dodec-1-enyl)-2,5-dioxopyrrolidin-1-yl)-2-hydroxybenzoic acid)zinc phthalocyanine (C)

Dodecenylnsuccinic anhydride (0.04 g, 0.165 mmol) and (B) (0.05 g, 0.04 mmol) were dissolved separately in DMF (10 mL) to yield solutions A and B, respectively. Solution A was added dropwise into solution B to give solution C. which was heated at 30 °C and was stirred for 2 hr. P₂O₅ (0.013g, 0.092 mmol) was dissolved in H₂SO₄ (5 mL) and DMF (10 mL) and added dropwise into solution C and the mixture was stirred at 70 °C and stirred for 2 hr. The mixture was cooled in the ice bath and was added cold water to affording green precipitate. A precipitate formed was filtered and washed with distilled water. (0.065 g, 75%) of compound (C) is afforded, TLC 0.6 cm (dichloromethane: hexane) (3:1), m.p. >300°C, Elemental analyses for C₁₂₃H₁₃₀N₁₂O₂₀Zn: C, 68.34; H, 6.06; N, 7.77; Found: C, 69.84; H, 5.02; N, 6.14.

Results and Discussion

Synthesis of 4,4′,4″,4‴-tetranitro zinc phthalocyanine (A)

Compound (A) 4,4′,4″,4‴-tetranitro zinc phthalocyanine was prepared by mixing of 4-nitro phthalonitrile (5.77 mmol) and ZnCl₂ (7.211 mmol) in DMAE (Scheme 3).
Scheme 3: Synthesis of compound (A).

FT-IR spectrum of compound (A) shows peaks at 1340 cm$^{-1}$ and 1475 cm$^{-1}$ for NO$_2$, C–H of aromatic at 3090 cm$^{-1}$, –C=C– of aromatic at 1658 cm$^{-1}$. Disappearance of nitrile group band at 2241 cm$^{-1}$ confirms successful conversion of 4-nitro phthalonitrile into 4,4’,4”,4””- tetranitro zinc Phthalocyanine (A) Figure (1).

Figure 1: FT-IR spectrum of compound (A).

$^1$H NMR spectrum of 4,4’,4”,4””- tetranitro zinc phthalocyanine (A) shows appearance of a broad singlet at range 7.4- 8.5 ppm (12H, Pc-CH) Figure (2).
Figure 2: $^1$H NMR spectrum of compound (A).

The UV – Visible spectra of compound (A) show appearance of two absorption bands, the first at (355) nm which is called B or soret – band and the second at the (660) nm which is called Q – band which is a near of IR region and it corresponds to an optically determined band gap energy (1.78 eV) Figure (3).

Figure 3: UV – Visible spectrum of compound 4-nitro phthalonitrile and compound (A).
Synthesis of tetra-(5-amino salicylic acid) zinc phthalocyanine (B)

Tetra-(5-amino salicylic acid) zinc phthalocyanine (B) was prepared by mixing zinc(II) tetranitro phthalocyanines (0.66 mmol), 5-Amino-2-hydroxybenzoic acid (5.22 mmol), (Scheme 3).

Scheme 4: Synthesis of compound (B).

FT-IR spectrum of compound (B) shows appearance peaks at 3349.57 cm\(^{-1}\) and 3421.42 cm\(^{-1}\) for NH\(_2\), C–H of aromatic at 3100 cm\(^{-1}\), –C=C– stretch of aromatic at 1658.9 cm\(^{-1}\), C–O at 1123.8 cm\(^{-1}\), O–H of carboxylic acids at 3200 cm\(^{-1}\). Disappearance of NO\(_2\) band at 1475 cm\(^{-1}\), 1540 cm\(^{-1}\) confirmed linking of 4,4’,4’’,4’’’-tetranitro zinc phthalocyanine with 5-amino salicylic acid Figure (4).

Figure 4: FT-IR spectrum of compound (B).

\(^1\)H NMR of tetra-(5-amino salicylic acid) zinc phthalocyanine protons shows OH proton of carboxylic acid as a broad singlet at 10.78 ppm, 7.25-7.6 ppm (12H, Pc-CH), 7.942 ppm (12H, benzoic rings) and a broad singlet peak at 1.221 ppm of NH\(_2\) proton Figure (5).
Figure 5: $^1$H NMR spectrum of compound (B).

The UV – Visible spectrum of compound (B) shows two absorption bands, the first one at (362.8) nm which is called B or soret band and the second at (670.2) nm which is called Q – band which shows shifting about 9.51 nm into IR region and corresponds to an optically determined band gap energy (1.72 eV) Figure 6.

![Figure 6: UV – Visible spectrum of compound (A) and compound (B).](image)

**Synthesis of tetra-((E)-5-(3-(dodec-1-enyl)-2,5-dioxopyrrolidin-1-yl)-2-hydroxybenzoic acid)zinc phthalocyanines (C)**

Tetra-((E)-5-(3-(dodec-1-enyl)-2,5-dioxopyrrolidin-1-yl)-2-hydroxybenzoic acid)zinc phthalocyanines was prepared by mixing (0.17 mmol) dodecenyl succinic anhydride, (0.04 mmol) tetra-(5-amino salicylic acid)zinc phthalocyanine (Scheme 4).
Scheme 5: Synthesis of compound (C).

FT-IR spectra show disappearance of NH$_2$ peaks at 3399 cm$^{-1}$ and 3421 cm$^{-1}$, C–H stretch aromatic at 3100 cm$^{-1}$, C=C– stretch aromatic at 1652 cm$^{-1}$, C–O stretch at 1311 cm$^{-1}$, O–H of carboxylic acids at 2957 cm$^{-1}$ which confirms linking dodecenyl succinic anhydride with tetra-(5-amino salicylic acid)zinc phthalocyanine.

Figure 7: FT-IR spectrum of compound (C).

The tetra-( (E)-5-(3-(dodec-1-enyl)-2,5-dioxopyrrolidin-1-yl)-2-hydroxybenzoic acid) zinc phthalocyanine protons in the $^1$H NMR spectrum shows appearance of OH protons for carboxylic acid broad singlet at 10.65 ppm, and at 5.954 ppm of alkene, (7.453,7.785) ppm of (12H, Pc-CH), 8.1 ppm (12H, benzoic rings), a broad singlet peak at 0.842 ppm of CH$_3$ proton and a broad singlet peak at 1.252 ppm of CH$_2$ proton.

Figure 8:
Figure 8: $^1$H NMR spectrum of compound (C).

The UV –Vis spectrum shows the appearance of two absorption bands, the first at the range (371.8) nm which is called B-band or soret band and the second at the range (690.3) nm which is called Q-band which shows shifting about 20.1 nm into IR region, corresponds to an optically determined band gap energy (1.67 eV) Figure (9).

Figure 9: UV – Visible spectrum of compound (C) and compound (B).
References
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