

The determination of photophysical and photochemical parameters of novel metal-free, zinc(II) and lead(II) phthalocyanines bearing 1,2,4-triazole groups



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ABSTRACT

In this study the synthesis and characterization of novel phthalonitrile compound (**3**) and its metal-free (**4**), zinc(II) (**5**), and lead(II) (**6**) phthalocyanines bearing four 4-(4-methoxyphenylethyl)-5-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one groups at peripheral positions were synthesized for the first time. These novel compounds were fully characterized by FT-FT-IR, ¹H NMR, UV-vis and MALDI-TOF mass spectroscopic techniques. Their photochemical and photophysical properties were also investigated in *N,N*-dimethylformamide solutions. In addition, the effect of 4-(4-methoxyphenylethyl)-5-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one groups as substituents and central metal ions (without metal, zinc(II) or lead(II)) in the phthalocyanine cavity on these properties were also compared. The studied zinc(II) or lead(II) phthalocyanines can be potential Type II photosensitizers for photodynamic therapy in cancer applications because these phthalocyanines showed good singlet oxygen generation and appropriate photodegradation.

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1. Introduction

Phthalocyanines have many potential applications in different areas such as chemical sensors [1–3], electrochromic displaying systems [4], non-linear optics [5], solar cells [6], photo-voltaic optics, molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10], laser dyes [11], catalyst [12] and photodynamic therapeutic agents (PDT) [13]. These properties thanks to their strong delocalized 18 π -electronic structure, good thermal stability and strong absorption in the visible area of the electronic spectrum,

Thanks to their pharmacological and biological properties [14] of [1,2,4]-triazole derivatives used as anti-inflammatory [15], antiviral/anti-HIV and anti-tuberculosis [16], antibacterial agents [17] in medicine. In addition, triazole derivatives are used as photosensitizer in some application and their photophysical and

photochemical properties have been discussed in the literature [18,19].

There are only a few studies about the synthesis of [1,2,4]-triazole substituted phthalocyanines. Although photophysical and photochemical properties of phthalocyanine ring has widely known, the investigation of these properties have been made for only a few of [1,2,4]-triazole bearing phthalocyanines [20].

In this study, we designed and prepared metal-free phthalocyanine and its Zn(II), Pb(II) metallo complexes bearing [1,2,4]-triazole containing four 4-(4-methoxyphenylethyl)-5-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one groups at peripheral positions to obtained novel soluble, no aggregated and bifunctional phthalocyanines. Their photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen production and photodegradation under light irradiation) properties were also investigated to determine possible usage of these phthalocyanines in various technologies such as photosensitizers for PDT. The photochemical and photophysical measurements were determined in *N,N*-dimethylformamide (DMF) and compared with each other to explore the effects of ring substitution and central metals in the cavity. As a result of these measurements, the

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4-(4-methoxyphenylethyl)-5-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one substituted metallo Pcs (**5** and **6**) showed good singlet oxygen quantum yields (Φ_D), especially the ZnPc (**5**) results in the highest Φ_Δ value in DMF.

2. Experimental

The used equipments, materials, photochemical and photo-physical formulas and parameters were given as supplementary materials.

2.1. Synthesis

2.1.1 4-(4-(4-methoxyphenylethyl)-5-oxo-3-propyl-4,5-dihydro-1H-1,2,4-triazol-1-yl)phthalonitrile (**3**)

4-(4-Methoxyphenylethyl)-5-propyl-2,4-dihydro-3H-1,2,4-triazol-3-one (**1**) (2.00 g, 7.65 mmol) and 4-nitrophthalonitrile (**2**) (1.33 g, 7.65 mmol) was dissolved in dry DMF (10 mL) under inert N₂ atmosphere. Anhydrous K₂CO₃ (3.17 g, 22.95 mmol) was added portion wise within 2 h to reaction mixture. The mixture was stirred at 50 °C for 3 days. Then the mixture was poured into 200 mL ice-water, stirred for 1 h at room temperature and then was filtered off. The solid product was crystallized from ethanol. Yield 2.05 g (69%), mp 136–138 °C, C₂₂H₂₁N₅O₂. IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3114, 3099, 2963, 2934, 2232 (C≡N), 1719, 1591, 1362, 1248, 1029, 849, 822, 796. ¹H NMR (DMSO-*d*₆), (δ : ppm): 8.49 (s, 1H/ArH), 8.34–8.35 (d, 1H/ArH), 8.21–8.19 (d, 1H/ArH), 7.13–6.85 (dd, 4H/ArH), 3.84–3.82 (t, 2H/NCH₂), 3.71 (s, 3H/OCH₃), 2.88–2.86 (t, 2H/Ar-CH₂), 2.25–2.21 (t, 2H/=C-CH₂), 1.57–1.55 (t, 2H/CH₂), 0.87 (s, 3H/CH₃). ¹³C NMR (DMSO-*d*₆), (δ : ppm): 158.64 (C=O), 152.14 (C=N), 150.52, 141.62, 135.92, 130.44, 130.10, 121.59, 121.46, 116.41, 116.35 (C≡N), 116.08 (C≡N), 114.47, 109.80, 55.52 (OCH₃), 43.46 (NCH₂), 33.29 (CH₂), 26.77 (CH₂), 18.41 (CH₂), 13.88 (CH₃). MS (ESI),

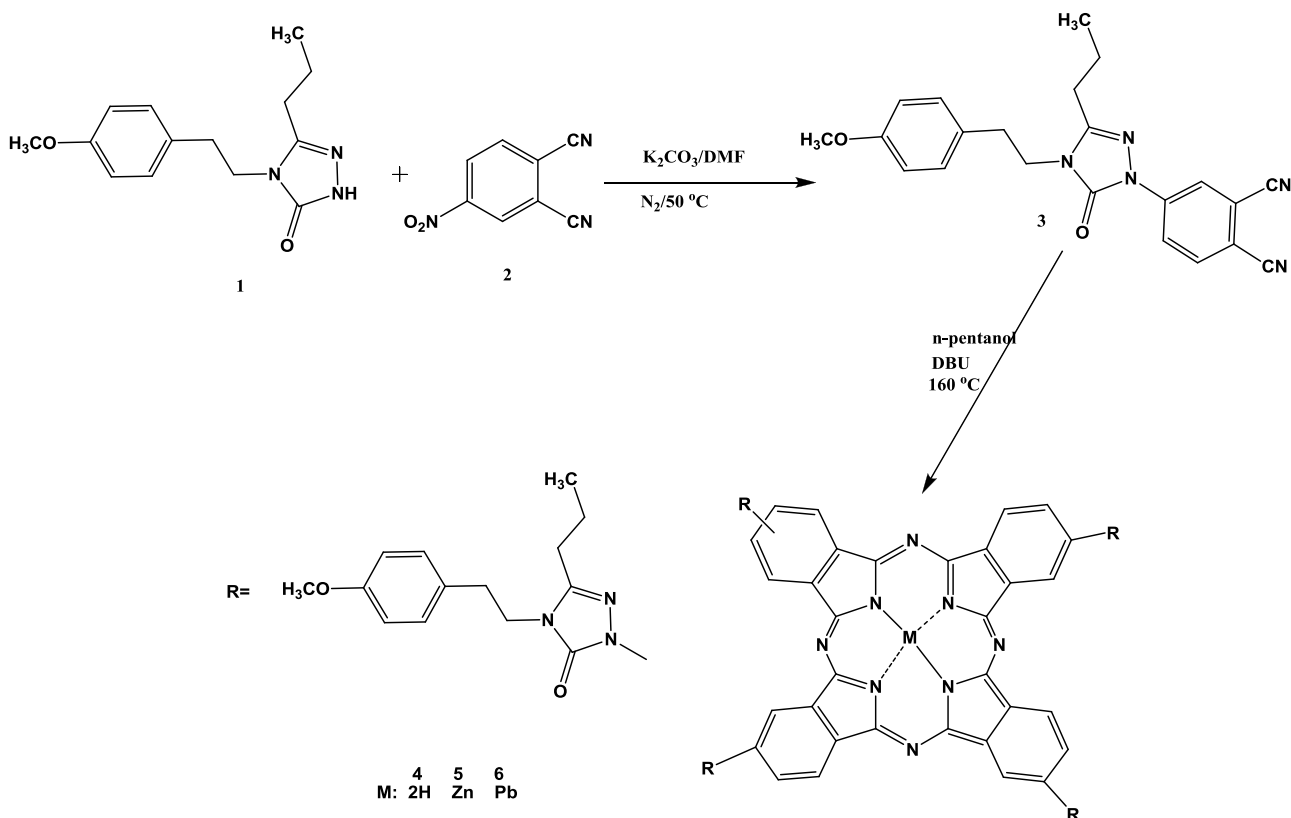
(*m/z*): Calculated: 387.17; Found: 387.46 [M]⁺ (%100), 388.20 [M+H]⁺ (%25).

2.1.1. General procedure for synthesis of phthalocyanines (**4–6**)

The mixture of compound (**3**) (0.2 g, 0.58 mmol), dry *n*-pentanol, 1,8-diazabicyclo [4.5.0] undec-7-ene (DBU) (5 drops), and no metal salts for compound **4** or equivalent amounts of related anhydrous metal salts (for compound **5** Zn(CH₃COO)₂, for compound **6** Pb(CH₃COO)₂) was heated to 160 °C and stirred 24 h. After cooling to room temperature, the mixture was precipitated by hexane and filtered off. After washing with hot ethanol, acetone and ethyl acetate the green solid product was chromatographed on silica gel column with chloroform-methanol solvent system.

2.1.1.1. Metal-free phthalocyanine (**4**). Chloroform:methanol (100:1.5) solvent system was used for purification of this phthalocyanine by column chromatography. Yield: 68 mg (34%), M.p. > 300 °C. C₈₈H₈₆N₂₀O₈. IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3291 (NH), 3046, 3012, 2963, 2930, 1701, 1583, 1359, 1244, 1011, 823, 738. ¹H NMR (DMSO-*d*₆), (δ : ppm): 7.96–7.44 (bs, 12H/ArH), 7.22–7.18 (bs, 10H/ArH), 6.94–6.91 (bs, 6H/ArH), 3.76 (bs, 20H/NCH₂+OCH₃), 2.63–2.58 (bs, 8H/Ar-CH₂), 2.22–2.20 (bs, 8H/=C-CH₂), 1.58–1.53 (bs, 8H/CH₂), 0.96 (bs, 12H/CH₃). UV-vis (DMF, 1 × 10⁻⁵ M): λ_{\max}/nm (log ϵ): 344 (4.74), 414 (4.44), 627 (4.53), 652 (4.62), 684 (4.77), 711 (4.68). MS (ESI), (*m/z*): Calculated: 1550.69, Found: 1551.84 [M+H]⁺.

2.1.1.2. Synthesis of zinc (II) phthalocyanine (**5**). Chloroform:methanol (100:2.5) solvent system was used for purification of this phthalocyanine by column chromatography. Yield: 92 mg (44%), M.p. > 300 °C. C₈₈H₈₄N₂₀O₈Zn. IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3034, 3008, 2958, 2932, 1701, 1611, 1492, 1244, 1091, 813, 744. ¹H NMR (DMSO-*d*₆), (δ : ppm): 8.63–8.44 (m, 12H/ArH), 7.32–7.00 (d,



Scheme 1. Synthetic route of novel metal-free (**4**), zinc(II) (**5**) and lead(II) (**6**) phthalocyanines.

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