



Unmetallated and metallated phthalocyanines bearing oxadiazole groups: Synthesis, photophysical and photochemical studies



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ABSTRACT

Unmetallated (**4**) and metallated (zinc(II), cobalt(II), lead(II)) phthalocyanines (**5–7**) carrying four 4-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenoxy) groups on the peripheral positions were synthesized by cyclotetramerization of 4-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenoxy)phthalonitrile (**3**) in the presence of corresponding metal salts (zinc(II) acetate, cobalt(II) chloride, lead(II) oxide) for metallated and without any metal for unmetallated phthalocyanines. The obtained organo-soluble phthalocyanines were characterized by infrared, electronic absorption, nuclear magnetic resonance and mass spectral techniques and elemental analysis as well. The photophysical and photochemical properties of newly synthesized tetra-substituted unmetallated (**4**), zinc(II) (**5**) and lead(II) (**7**) phthalocyanines were reported in N,N-dimethylformamide (DMF). The synthesized phthalocyanine compound **6** was not evaluated for photophysical and photochemical studies due to open shell and paramagnetic behavior of cobalt(II) metal ions in the phthalocyanine cavity.

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1. Introduction

Prior to 1960, there existed only one well-established category of synthetic cyclic ligands which were the highly conjugated phthalocyanines. Phthalocyanines (Pcs) and their derivatives bear a strong structural resemblance to the natural porphyrin systems [1]. Their useful chemical and physical features such as bright colors and conductivity [2] as well as chemical and thermal stability [3], have made them comparatively desirable for many applications. Phthalocyanine complexes have been used in some technological applications such as solar cells [4,5], catalysts [6,7], semiconductors [8,9] and liquid crystals [10,11]. In the last few decades, the phthalocyanine derivatives have also been used as photosensitizers in photodynamic therapy (PDT) [12–14]. PDT is a new and developing technique for the treatment of cancer tissues using photosensitizers and this technique does not harm the normal surrounding tissues seriously when compared with traditional treatments such as surgery or radiotherapy [15,16].

The low solubility of unsubstituted phthalocyanine derivatives in organic solvents or water is an important disadvantage, because it limits their practical applications. However, substitution of different groups to the periphery of the phthalocyanines increases their solubility drastically [17]. In this case, their solubility can be enhanced

by addition of bulky or long chain groups (e.g. alkyl, alkoxy, alkylthio, ...) into the peripheral positions of the phthalocyanine framework [18,19]. Furthermore, anionic or cationic substituents (e.g. sulfo-groups, carboxylic acids, quaternized ammonium groups) increase the solubility of phthalocyanines in aqueous media [20,21].

Oxadiazoles, which are a class of heterocyclic aromatic compounds, contain two nitrogen, one oxygen and two carbon atoms. Depending on the placement of the nitrogen atoms in the aromatic ring, four different regioisomeric forms exist, namely 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,4-oxadiazole and 1,2,3-axadiazole. However, 1,3,4-oxadiazoles and their derivatives have attracted a wide attention of chemist in searching for new therapeutic molecules, such as antitumor, antioxidant, antimicrobial, anti HIV, antifungal, and antitubercular agents [22–24]. In contrast to this wide range of applications, there are very few studies on PDT properties of oxadiazole substituted phthalocyanines in literature [25,26]. In this study, it is thought that oxadiazole substituted unmetallated and metallated phthalocyanines, especially zinc(II) phthalocyanine, are a good candidate for PDT applications.

In this paper we report the synthesis and characterization of unmetallated (**4**), zinc(II) (**5**), cobalt(II) (**6**) and lead(II) (**7**) phthalocyanines containing 4-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenoxy) groups. The characterization of novel compounds was achieved by using several spectral methods and elemental analysis results. The synthesized unmetallated and metallated phthalocyanines showed good solubility in most organic solvents. In this study, the fluorescence, singlet oxygen, photodegradation quantum yields and fluorescence

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lifetime values of these phthalocyanines were determined in DMF and these values were also compared depending on the nature of the metal ions in the phthalocyanine cavity.

2. Experimental

2.1. Materials

All solvents and chemicals were of reagent-grade quality and obtained from commercial suppliers. All reagents and solvents were dried and purified as described by Perrin and Armarego [27] before use. 4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenol (**1**) [28] and 4-nitrophthalonitrile (**2**) [29] were prepared according to the literature procedures.

Details of the used equipment as well as photophysical and photochemical parameters are provided as Supplementary information.

2.2. Synthesis

2.2.1. 4-(4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenoxy)phthalonitrile (**3**)

4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenol (**1**) (1.30 g, 5.46 mmol) and 4-nitrophthalonitrile (**2**) (0.95 g, 5.46 mmol) were dissolved in 15 mL of dry DMF at 50 °C under a nitrogen atmosphere. Then finely ground anhydrous K₂CO₃ (3.00 g, 21.84 mmol) was added portionwise to this mixture over 2 h with efficient stirring. The reaction mixture was stirred under a nitrogen atmosphere at 50 °C for 120 h. After the progress of reaction was checked by thin layer chromatography (TLC), the obtained mixture was poured into 150 mL ice-water. The aqueous phase was extracted with 3 × 50 mL portions of chloroform and the extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. Finally, the residue was dried in vacuum and recrystallized from ethanol to give white precipitate. Yield: 1.43 g (72%), m.p.: 203–207 °C. Calc. for C₂₂H₁₂N₄O₂: C 72.52%, H 3.32%, N 15.38%. Found: C 72.45%, H 3.27%, N 15.43%. FT-IR ν_{\max} (cm⁻¹): 3076 (Ar-H), 2230 (C≡N), 1588 (C=N), 1480, 1279, 1247 (Ar-O-C), 1063, 951, 842, 704, 686. ¹H NMR (CDCl₃) (δ : ppm): 8.26 (d, ArH, 2H), 8.16 (d, ArH, 2H), 7.80 (d, ArH, 1H), 7.58 (m, ArH, 3H), 7.36 (t, ArH, 4H). ¹³C NMR (CDCl₃) (δ : ppm): 165.09, 160.83, 156.75, 135.88, 132.24, 129.76, 129.42, 127.23, 123.92, 122.60, 122.35, 122.03, 121.51, 118.24, 115.37, 114.94, 110.24. MALDI-TOF, *m/z*: Calc.: 364.36; Found: 364.49 [M]⁺.

2.2.2. Unmetallated phthalocyanine (**4**)

4-(4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenoxy)phthalonitrile (**3**) (0.3 g, 0.82 mmol), three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 3 mL of dry *n*-pentanol were placed in a standard sealed glass tube under a nitrogen atmosphere and the mixture was refluxed for 24 h at 160 °C. After cooling to room temperature, the reaction mixture was precipitated by the addition of ethanol and this green product was filtered off. After the refluxing with ethanol for 4 h, the obtained green product was filtered off again and it was successively washed plenty of times with ethanol, distilled water and diethyl ether in order to remove unreacted organic materials. After drying in vacuum, the crude product was further purified by chromatography over a silica gel column using chloroform/methanol (91:9) as elution. Yield: 129 mg (43%), m.p.: > 300 °C (decomposition). Calc. for C₈₈H₅₀N₁₆O₈: C 72.42%, H 3.45%, N 15.36%. Found: C 72.37%, H 3.40%, N 15.39%. FT-IR ν_{\max} (cm⁻¹): 3291 (N-H), 3057 (Ar-H), 1605 (NH, bend.), 1548 (C=N), 1492, 1237 (Ar-O-C), 1092, 743. ¹H NMR (CDCl₃) (δ : ppm): 7.85 (m, ArH, 16H), 7.33 (m, ArH, 32H). UV/vis (CHCl₃): λ (nm) (log ϵ): 704 (5.24), 668 (5.24), 641 (5.04), 611 (4.89), 290 (5.19). MALDI-TOF, *m/z*: Calc.: 1459.47; Found: 1459.63 [M]⁺.

2.2.3. General procedure for metallated phthalocyanine derivatives (**5–7**)

4-(4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenoxy)phthalonitrile (**3**) (0.3 g, 0.82 mmol), anhydrous metal salt [Zn(CH₃COO)₂ (38 mg, 0.21 mmol), CoCl₂ (27 mg, 0.21 mmol) or PbO (47 mg, 0.21 mmol)], three drops of DBU and 3 mL of dry *n*-pentanol were placed in a standard sealed glass tube under a nitrogen atmosphere and the mixture was refluxed for 24 h at 160 °C. After cooling to room temperature, the reaction mixture was precipitated by the addition of ethanol and this crude product was filtered off. After refluxing with ethanol for 4 h, the obtained product was filtered off again and it was successively washed plenty of times with hot ethanol, distilled water and diethyl ether in order to remove unreacted organic materials and then dried in vacuum over P₂O₅. Then it was further purified by preparative thin layer chromatography using chloroform:methanol solvent system [(80:20) for compound **5**, (93:7) for compound **6**, and (80:20) for compound **7**] as eluent.

2.2.3.1. Zinc(II) phthalocyanine (**5**). Yield: 120 mg (38%), m.p.: > 300 °C (decomposition). Calc. for C₈₈H₄₈N₁₆O₈Zn: % C 69.41%, % H 3.18%, % N 14.72%. Found: C 69.38%, H 3.22%, N 14.76%. FT-IR ν_{\max} (cm⁻¹): 3063 (Ar-H), 1604 (C=N), 1486, 1235 (Ar-O-C), 1086, 943, 837, 709, 689. ¹H NMR (DMSO-d₆) (δ : ppm): 8.48 (m, ArH, 16H), 7.79 (m, ArH, 32H). UV/vis (CHCl₃): λ (nm) (log ϵ): 682 (5.28), 618 (4.71), 354 (4.77), 293 (5.05). MALDI-TOF, *m/z*: Calc.: 1522.84; Found: 1522.46 [M]⁺.

2.2.3.2. Cobalt(II) phthalocyanine (**6**). Yield: 165 mg (53%), m.p.: > 300 °C (decomposition). Calc. for C₈₈H₄₈CoN₁₆O₈: C 69.70%, H 3.19%, N 14.78%. Found: C 69.68%, H 3.25%, N 14.83%. FT-IR ν_{\max} (cm⁻¹): 3061 (Ar-H), 1603 (C=N), 1467, 1407, 1232 (Ar-O-C), 1164, 1058, 957, 836, 709, 687. UV/vis (CHCl₃): λ (nm) (log ϵ): 677 (5.22), 614 (4.81), 296 (5.15). MALDI-TOF, *m/z*: Calc.: 1516.38; Found: 1517.38 [M+H]⁺.

2.2.3.3. Lead(II) phthalocyanine (**7**). Yield: 94 mg (27%), m.p.: > 300 °C (decomposition). Calc. for C₈₈H₄₈N₁₆O₈Pb: C 63.49%, H 2.91%, N 13.46%. Found: C 63.51%, H 2.96%, N 13.41%. FT-IR ν_{\max} (cm⁻¹): 3061 (Ar-H), 1602 (C=N), 1469, 1387, 1227 (Ar-O-C), 1074, 939, 833, 708, 686. ¹H NMR (CDCl₃) (δ : ppm): 7.79 (m, ArH, 12H), 7.18 (m, ArH, 36H). UV/vis (CHCl₃): λ (nm) (log ϵ): 716 (5.29), 651 (4.76), 365 (5.03). MALDI-TOF, *m/z*: Calc.: 1664.65; Found: 1664.26 [M]⁺.

3. Results and discussion

3.1. Synthesis and characterization

4-(4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenoxy)phthalonitrile (**3**) was used as precursor material for the synthesis of tetra substituted phthalocyanine complexes (**4–7**). The general synthetic routes for the synthesis of new phthalocyanines are given in Schemes 1 and 2. The synthesis of the compound **3** was achieved by the reaction of 4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol (**1**) with 4-nitrophthalonitrile (**2**) at 50 °C for 120 h in dry DMF in the presence of anhydrous K₂CO₃ as a base [30]. Unmetallated phthalocyanine (**4**) was synthesized by cyclotetramerization of the compound **3** in *n*-pentanol which is a high boiling solvent and DBU which is a N-donor base at 160 °C for 24 h under a nitrogen atmosphere with the yield of 43% after purification by column chromatography method utilizing chloroform/methanol (91:9) as eluent. The syntheses of metallated phthalocyanines (**5–7**) (Zn, Co and Pb phthalocyanines) were achieved by reacting compound **3** with anhydrous metal salts (Zn(CH₃COO)₂, CoCl₂, PbO) in

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