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Research paper

Synthesis, characterisation, photophysical and photochemical properties of free-base tetra-(5-chloro-2-(2,4-dichlorophenoxy) phenoxy)phthalocyanine and respective zinc(II) and lead(II) complexes

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ABSTRACT

In this study, novel peripherally tetra-(5-chloro-2-(2,4-dichlorophenoxy)phenol) substituted metal-free **(4)**, zinc(II) **(5)** and lead(II) **(6)** phthalocyanine derivatives were synthesised. The novel phthalocyanines **(4–6)** were characterised by general spectroscopic methods such as IR, ^{1}H NMR, UV–vis, mass spectrometry and elemental analysis. Once the solubilities of the compounds were investigated, it was noticed that they have excellent solubility and did not tend to aggregation behaviour in common solvents. The photophysical and photochemical properties of novel phthalocyanines **(4–6)** were investigated in dimethysulfoxide. The effects of substituted 5-chloro-2-(2,4-dichlorophenoxy)phenoxy group and central metal ion [zinc(II)/lead(II)] on photophysical and photochemical properties of the novel phthalocyanines have also been examined, and the results were compared with unsubstituted zinc (II) phthalocyanine. According to photophysical and photochemical investigation results, it was observed that the novel phthalocyanines **(4–6)** have a potential for PDT application.

1. Introduction

Phthalocyanines (Pcs) are planar macrocyclic compounds containing nitrogen in the core cycle, and the diversity of heteroatoms can be increased preparing their peripheral and non-peripheral derivatives. Very different metal complexes of these compounds can be synthesised by using metal salts during the steps for phthalocyanine preparation or after that. Both metal ion and substituents have significant effects on physical and chemical characteristics of phthalocyanines. These tunable options and their 18 π-electronic structure, high thermal and optical properties make phthalocyanines functional compounds in important scientific areas such as sensors [1–3], electrochromic systems [4], non-linear optical materials [5], dye based solar cells and molecular electronics [6,7], semiconductors [8], liquid crystals [9], data storage materials [10], laser dyes [11], catalysts [12] and photodynamic therapeutic agents (PDT) [13].

5-Chloro-2-(2,4-dichlorophenoxy)phenol is an important antimicrobial and protective agent known as triclosan and is used in personal hygiene, disinfection products such as antiseptic soaps, toothpastes, fabrics, and plastics. In addition, it is known that triclosan derivatives can be used against M. Tuberculosis InhA [14,15]. In this study we aimed to use this biologically and pharmacologically important compound in the preparation of novel phthalocyanines. Although there are different studies in the literature about the pharmacological and biological properties of 5-chloro-2-(2,4-dichlorophenoxy)phenol, an investigation of photophysical and photochemical properties of tetra-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy) substituted phthalocyanines was performed for the first time.

2. Experimental

The experimental setup, used materials, and formulations are given in the Supplementary material.

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2.1. Synthesis

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

The mixture of the compound **(3)** (0.2 g, 0.48 mmol), dry *n*-pentanol (5 mL), 1,8-Diazabicyclo [4.5.0] undec-7-ene (DBU) (5 drops) and stoichiometric amounts of anhydrous $Zn(CH_3COO)_2$ for compound (**5**) and $Pb(CH_3COO)_2$) for compound (**6**) was heated to 160 °C and stirred for 24 h. After the reaction, the mixture was poured on hexane and filtered off. The solid product was washed with hot ethanol, acetone and ethyl acetate and chromatographed on a silica gel column with a chloroform-methanol solvent system.

2.1.2. Metal-free phthalocyanine (4)

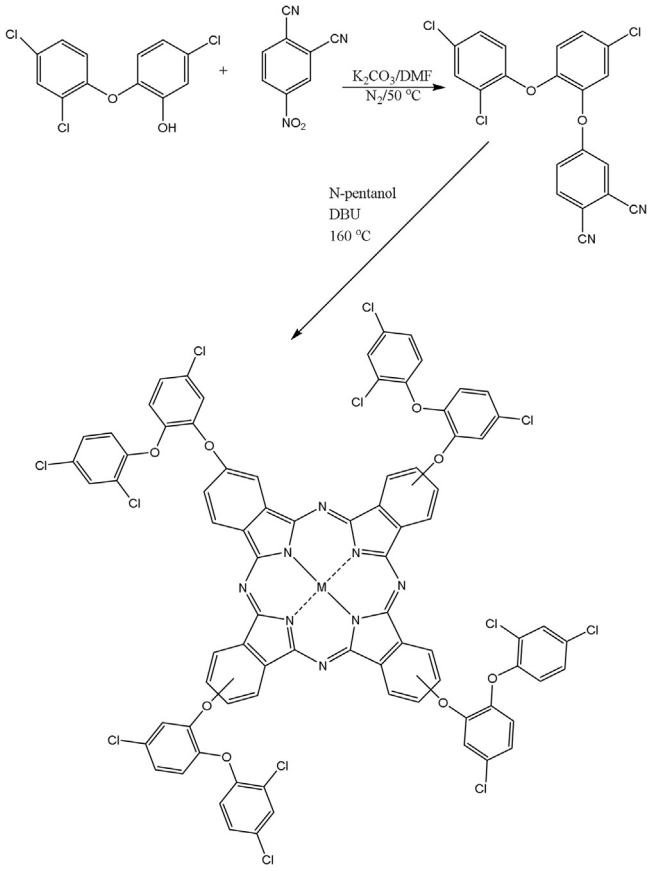
The solvent system for column chromatography of a green solid product was chloroform/methanol (100:1.5). Yield: 84 mg (42%), mp > 300 °C, Anal. calc. for $C_{80}H_{38}Cl_{12}N_8O_8$: C, 57.72; H, 2.30; N, 6.73; Found: C, 57.52; H, 2.42; N, 6.82. IR (KBr tablet) υ_{max}/cm^{-1}: 3286, 3095, 3068, 1586, 1469, 1401, 1223, 1090, 936, 797. ^1H NMR (DMSO d_6), (δ: ppm): 7.87–7.78 (bm, 4H); 7.72–7.55 (bm, 6H); 7.51–7.46 (bs, 12H), 7.42–7.19 (bs, 6H); 7.13–7.05 (bs, 8H) UV–vis (DMSO, 1×10^{-5} M): λ_{max}/nm (log ε): 339 (4.70), 612 (4.45), 640 (4.57), 672 (4.76), 702 (4.73). MS (ESI), (*m*/*z*): Calculated: 1663.90, Found: 1664.84 $[M+H]^+$.

2.1.3. Zinc (II) phthalocyanine (5)

The solvent system for the column chromatography of the green solid product was chloroform/methanol (100:2.5). Yield: 127 mg (61%), mp > 300 °C, Anal. calc. for $C_{80}H_{36}Cl_{12}N_8O_8Zn$: C, 55.60; H, 2.10; N, 6.48; Found: C, 55.83; H, 2.01; N, 6.63. IR (KBr tablet) υ_{max}/cm^{-1}: 3090, 3063, 1586, 1469,1400, 1223, 1096, 946, 744. ^1H NMR (DMSO d_6), (δ: ppm): 8.66–8.34 (bd, 4H); 8.06–7.67 (bm, 12H), 7.64 (s, 2H); 7.61–7.56 (d, 2H); 7.52–7.47 (t, 4H); 7.44–7.35 (d, 2H); 7.32–7.25 (d, 4H), 7.22–6.97 (bs, 6H). UV–*vis* (DMSO, 1×10^{-5} M): λ_{max}/nm (log ε): 358 (4.68), 613 (4.27), 682 (5.00). MS (ESI), (*m*/*z*): Calculated: 1725.81, Found: 1726.78 $[M+H]^+$.

2.1.4. Lead (II) phthalocyanine (6)

The solvent system for column chromatography of the green solid product was chloroform/methanol (100:2). Yield: 121 mg (54%), mp > 300 °C, Anal. calc. for $C_{80}H_{36}Cl_{12}N_8O_8Pb$: C, 51.39; H, 1.94; N, 5.99; Found: C, 51.19; H, 2.11; N, 6.13. IR (KBr tablet) υ_{max}/cm^{-1}: 3090, 3066, 1585, 1469, 1387, 1222, 1076, 944, 798. ^1H NMR (DMSO d_6), (δ: ppm): 8.75 (s, 2H); 8.62 (s, 2H); 7.86–7.78 (q, 5H), 7.74–7.67 (bm, 5H), 7.67 (d, 2H), 7.63 (d, 4H), 7.58–7.32 (m, 10H), 7.29–7.27 (d, 4H), 7.22–7.20 (d, 2H). UV–vis (DMSO, 1×10^{-5} M): λ_{max}/nm (log ε): 358 (4.63), 676 (4.37), 712 (5.08). MS (ESI), (*m*/*z*): Calculated: 1869.86, Found: 1870.84 $[M+H]^+$.



Scheme 1. Synthetic route of phthalonitrile compound (**3**) and its metal-free **(4)**, zinc(II) **(5)** and lead(II) **(6)** phthalocyanine derivatives **M** = metal-free (**4**), zinc(II) (**5**), lead (II) (**6**).

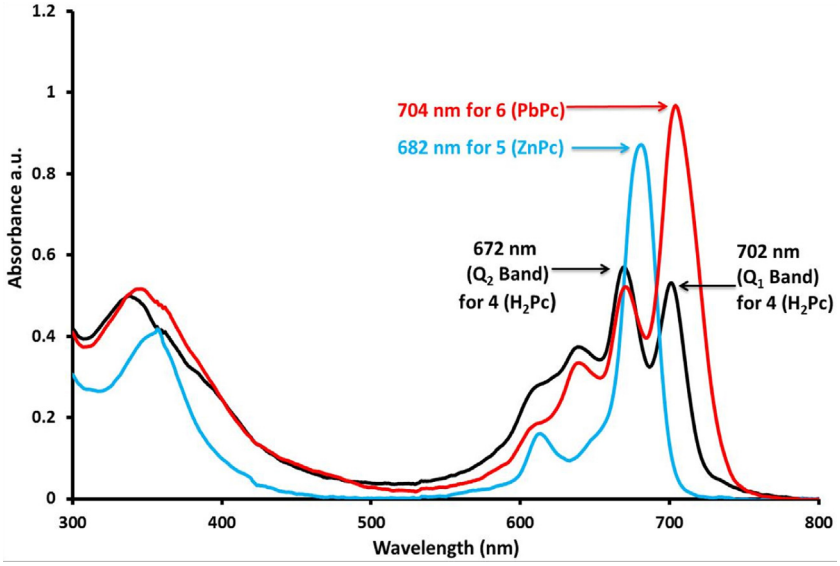


Fig. 1. Absorption spectra of tetra-5-chloro-2-(2,4-dichlorophenoxy)phenoxy substituted phthalocyanines (**4–6**) in DMSO at 1.0×10^{-5} M.