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The synthesis of novel unmetallated and metallated phthalocyanines including (*E*)-4-(3-cinnamoylphenoxy) groups at the peripheral positions and photophysicochemical properties of their zinc phthalocyanine derivatives

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ABSTRACT

This paper reports on the synthesis and characterization of new peripherally tetra-substituted metal-free (**4**), nickel(II) (**5**), zinc(II) (**6**), cobalt(II) (**7**), copper(II) (**8**), lead(II) (**9**) and octa-substituted zinc(II) (**12**) phthalocyanines containing (*E*)-4-(3-cinnamoylphenoxy) groups for the first time. Synthesized compounds have been characterized by electronic absorption, FT-IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, mass spectra and thermogravimetric analysis. The photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of zinc phthalocyanine derivatives (**6** and **12**) were investigated in dimethylsulfoxide. The fluorescence quenching behavior of zinc phthalocyanine derivatives (**6** and **12**) by 1,4-benzoquinone was also examined in same solution.

1. Introduction

Phthalocyanines were incidentally discovered in London by Braun and Tcherniac in 1907 and were first used by Professor Linstead at the Imperial College of Science and Technology in 1933 [1].

Since their first synthesis early in the last century, phthalocyanines, both a class of organic compounds and also called as blue–green products later, have been of great interest to chemists, physicists and industrial scientists. Because of this great and increasing interest, phthalocyanines are continuously produced with incremental quantity, variety and functionality year after year. These productions have brought about outstanding achievement and spectacular changes in the way we think and work for scientific innovation. In literature, well-oriented and documented phthalocyanine researches have continuously increased, broadened and cited to serve several purposes by researchers. These innovative works ensure the producing brand new knowledge, the efficient use of sources and thus they contribute to current economic development.

The phthalocyanine macrocycle was assumed to exhibit aromatic behavior like porphyrin macrocycle, because of its planar conjugated array of 18-π electrons, as predicted by Huckel's theory of aromaticity, published only a few years previously [2].

The large number of appreciable applications of phthalocyanines arises from their aforementioned unique 18-π electron conjugated system, which makes them present high thermal and chemical stability and noteworthy photoelectric properties [3,4]. Other applications of these blue-green compounds have been intensively investigated, such as solar cells [5–7], Langmuir–Blodgett films [8,9], liquid crystals [10–12], optical applications [13,14], semiconductor materials [15,16] in addition to particularly treatment of cancer by photodynamic therapy (PDT) [17–20].

Photodynamic therapy (PDT) is a sophisticated innovative treatment that uses special form of light-activated drugs, called as *photosensitizing/photosensitizer agents*, accompanied by light to detect and destroy cancer cells [21]. Metallophthalocyanines have also been introduced as photosensitizers for PDT of cancer in recent years since diamagnetic central metals, such as Zn or Mg enhance phototoxicity of phthalocyanines [22,23]. Compared with conventional treatments, the extraordinary advantage of PDT is that it can

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destroy cancer cells and treat symptomatic tissues selectively and does not harm the normal surrounding tissues severely [24].

A significant characteristic disadvantage of phthalocyanines is their nominal solubility in most known solvents or aqueous media. Introduction of peripheral substituents on the ring increases the solubility dramatically. The presence of bulky or long chain alkyl substituents into the peripheral or non-peripheral positions of the phthalocyanines increases solubility in non-polar solvents [25,26].

The main purpose of this study is to synthesize and characterize symmetrical tetra-substituted metal-free (**4**) and metallophthalocyanines [Ni(II) (**5**), Zn(II) (**6**), Co(II) (**7**), Cu(II) (**8**), Pb(II) (**9**) and octa-substituted Zn(II) (**12**)]. Furthermore, we examined the thermal stability of novel phthalocyanines using by thermogravimetric analysis (TGA). The synthesized compounds have very good solubility in common organic solvents such as chloroform, dichloromethane, THF, DMSO, DMF and pyridine. The photophysical and photochemical properties of the zinc phthalocyanine derivatives (**6** and **12**) were investigated in this study. The designations of these properties are very useful for the determination of the PDT activity of photosensitizer compounds. Only zinc phthalocyanine derivatives (**6** and **12**) were studied for this purpose in this study because the phthalocyanines containing zinc atoms in their cavity are most suitable among the phthalocyanine derivatives due to the d^{10} electronic configuration of zinc atoms.

2. Experimental

2.1. Materials

All reagents and solvents were dried and purified as described by Perrin and Armarego prior to use [27]. (*E*)-1-(3-hydroxyphenyl)-3-phenylprop-2-en-1-one (**1**) [28], *4*-nitro phthalonitrile (**2**) [29] and 4,5-dichlorophthalonitrile (**10**) [30] were prepared and purified according to the literatures. All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers.

The photophysical and photochemical parameters were supplied as supplementary information.

2.2. Synthesis

2.2.1. (E)-4-(3-cinnamoylphenoxy)phthalonitrile (*3*)

Compound **1** ((*E*)-1-(3-hydroxyphenyl)-3-phenylprop-2-en-1-one) (2.40 g, 10.7 mmol) and compound **2** (*4*-nitro phthalonitrile) (1.85 g, 10.7 mmol) were dissolved in dry DMF (30 mL) under a nitrogen atmosphere at 50 °C. After 15 min of stirring, finely ground anhydrous K_2CO_3 (5.9 g, 42.8 mmol) was added portionwise over a period of 2 h. Thereafter, the reaction mixture left to stir under N_2 atmosphere at this temperature for 5 days. The mixture was cooled to the room temperature and poured into ice-water (100 mL) and stirred for 30 min. The yellow product was filtered off and recrystallized from ethanol. Yield: 1.5 g (40%), m.p.: 115–118 °C. Calcd. for $C_{23}H_{14}N_2O_2$: C 78.84%, H 4.03%, N 8.00%. Found: C 78.80%, H 4.12, N 8.04%. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3068 (Ar–H), 2967–2912 (Aliph. C–H), 2231 (C≡N), 1664 (C=O), 1596, 1578, 1483, 1308, 1281, 1249, 1087, 955, 765, 688. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.98–6.86 (ArH, 14H, m). ^{13}C NMR ($CDCl_3$) (δ: ppm): 189.19, 161.54, 154.31, 146.25, 135.89, 135.74, 134.67, 131.29, 130.94, 128.89, 128.25, 126.42, 125.55, 125.19, 122.07, 120.66, 119.75, 117.71, 115.66, 115.22, 109.48. MS (ES^+), *m*/*z*: Calc.: 350.37; Found: 351.19 $[M+H]^+$.

2.2.2. Metal-free phthalocyanine (*4*)

The mixture of (*E*)-4-(3-cinnamoylphenoxy)phthalonitrile (**3**) (0.2 g, 0.5708 mmol), and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 3 mL of dry *n*-pentanol was heated at 160 °C in a sealed tube and stirred for 24 h under a nitrogen atmosphere. The crude product was precipitated by the addition of 20 mL of ethanol and refluxed with ethanol, and then treated with several times hot ethanol, distilled water, methanol and diethyl ether. After drying under vacuum, this compound was purified by preparative thin layer chromatography (TLC) using chloroform-methanol (92:8) solvent system as eluent. Yield: 48 mg (24%), m.p.: 365–434 °C (decomposition). Calcd. for $C_{92}H_{58}N_8O_8.H_2O$: C 77.73%, H 4.25%, N 7.88%. Found: C 77.27%, H 4.88%, N 7.55%. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3054 (Ar–H), 2924–2851 (Aliph. C–H), 1728 (C=O), 1604, 1577, 1476, 1358, 1241, 1033, 942, 821, 761. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.70–6.97 (ArH, 56H, m). ^{13}C NMR ($CDCl_3$) (δ: ppm): 188.16, 167.45, 160.27, 154.15, 140.41, 136.12, 134.92, 133.33, 131.19, 129.25, 128.82, 127.16, 125.05, 125.67, 122.88, 121.68, 119.21, 118.97, 113.07, 108.73, 106.05. UV–Vis ($CHCl_3$): λ, nm (log ε): 707 (5.20), 674 (5.20), 644 (5.07), 617 (4.94), 389 (5.20). MS (ES^+), *m*/*z*: Calc.: 1403.52; Found: 1427.44 $[M+Na+H]^+$.

2.2.3. General procedures for metallophthalocyanine derivatives (*5*–*9*)

Compound **3** ((*E*)-4-(3-cinnamoylphenoxy)phthalonitrile) (0.2 g, 0.5708 mmol) was irradiated with anhydrous metal salt ($NiCl_2$ (18.6 mg, 0.1427 mmol), $Zn(CH_3COO)_2$ (26 mg, 0.1427 mmol), $CoCl_2$ (18.6 mg, 0.1427 mmol), $CuCl_2$ (19.2 mg, 0.1427 mmol), PbO (32 mg, 0.1427 mmol)) in the presence of two drops of DBU in 2 mL of *2*-(dimethylamino)ethanol in a microwave oven at 175 °C, 350 W, for a few minutes. After cooling, 20 mL of ethanol was added to this mixture and stirred overnight. This mixture was filtered off, refluxed with ethanol. Then it was washed several times with hot ethanol, distilled water and diethyl ether. After drying under vacuum over P_2O_5, it was purified by preparative thin layer chromatography (TLC) using chloroform: methanol solvent system (97:3 for compound **5**, 95:5 for compound **6**, 96:4 for compound **7**, 95:5 for compound **8** and 97:3 for compound **9**) as eluent.

*2.2.3.1. Nickel(II) phthalocyanine (**5**).* Yield: 37 mg (18%), m.p.: 335–415 °C (decomposition). Calcd. for $C_{92}H_{56}N_8NiO_8$: C 75.68%, H 3.87%, N 7.67%. Found: C 75.26%, H 3.20%, N 7.93%. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3060 (Ar–H), 2917–2846 (Aliph. C–H), 1663 (C=O), 1578, 1472, 1434, 1307, 1240, 1088, 1059, 952, 877, 761, 699. ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.03–6.87 (ArH, 56H, m). ^{13}C NMR ($CDCl_3$) (δ: ppm): 189.17, 161.29, 159.45, 154.33, 147.95, 133.80, 134.29, 131.36, 130.79, 128.93, 124.43, 123.92, 121.80, 120.73, 119.46, 117.79, 106.16. UV–Vis ($CHCl_3$): λ, nm (log ε): 676 (5.24), 632 (5.10), 395 (5.20). MS (ES^+), *m*/*z*: Calc.: 1460.20; Found: 1499.12 $[M+K]^+$.

*2.2.3.2. Zinc(II) phthalocyanine (**6**).* Yield: 56 mg (27%), m.p.: 331–406 °C (decomposition). Calcd. for $C_{92}H_{56}N_8O_8Zn$: C 75.33%, H 3.85%, N 7.64%. Found: C 74.44%, H 3.96%, N 6.97%. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3054 (Ar–H), 2921–2846 (Aliph. C–H), 1662 (C=O), 1575, 1479, 1392, 1241, 1087, 1043, 947, 759, 686. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.78–6.92 (ArH, 56H, m). ^{13}C NMR ($CDCl_3$) (δ: ppm): 187.65, 160.13, 159.76, 155.27, 148.36, 134.83, 132.74, 130.85, 129.09, 128.82, 124.05, 122.54, 120.86, 118.64, 114.26, 110.42, 105.00. UV–Vis ($CHCl_3$): λ, nm (log ε): 683 (5.22), 616 (4.67), 325 (5.18). MS (ES^+), *m*/*z*: Calc.: 1466.90; Found: 1466.03 $[M]^+$.

*2.2.3.3. Cobalt(II) phthalocyanine (**7**).* Yield: 33 mg (16%), m.p.: 295–400 °C (decomposition). Calcd. for $C_{92}H_{56}CoN_8O_8$: C 75.66%, H 3.86%, N 7.67%. Found: C 74.91%, H 4.12%, N 7.47%. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3061 (Ar–H), 2923–2851 (Aliph. C–H), 1663 (C=O), 1597, 1577, 1474, 1331, 1242, 1092, 956, 761, 688. UV–Vis ($CHCl_3$): λ, nm (log ε): 675 (5.25), 615 (4.94), 402 (5.13). MS (ES^+), *m*/*z*: Calc.: 1460.44; Found: 1483.72 $[M+Na]^+$.