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The novel mesityloxy substituted metallo-phthalocyanine dyes with long fluorescence lifetimes and high singlet oxygen quantum yields

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ABSTRACT

The synthesis of novel peripheral or non-peripheral tetra-mesityloxy substituted metal-free, zinc and indium phthalocyanines, which are highly soluble in organic solvents, has been achieved. The phthalocyanines have been characterized by UV–vis, IR, MALDI-TOF Mass, ¹H NMR, ¹³C NMR spectroscopies and elemental analysis. On their spectroscopic, photochemical and photophysical properties, the effects of the substituent position and the variety of central metal ions in phthalocyanine cavity are also investigated. Photodegradation, singlet oxygen and fluorescence quantum yields, and fluorescence lifetimes in dimethylformamide for the phthalocyanines are described. These properties of the compounds are very useful for photodynamic therapy applications and their high singlet oxygen quantum yields are very important for Type II mechanisms. The phthalocyanines can be appropriate candidates as Type II photosensitizers.

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1. Introduction

Synthetic porphyrin analogues called phthalocyanines (Pcs) are widely used as dyes and pigments [1–3]. Pc compounds show a two-dimensional aromatic system due to delocalized 18 π electronic system in the Pc core and this system is structurally similar to the aza-[18]-annulene series. The particular electronic delocalization of 18 π system gives rise to outstanding electronic, unconventional physical and chemical properties, which make them valuable in different applications and technology [4]. There are a number of scientific documents about Pcs and their applications that discuss the developments in these interesting fields [5–7]. Pcs are used in a wide variety of applications. More recently, Pcs have been found to be useful in a number of areas outside their traditional uses as dyes; they have been also used technological applications as sensing elements in gas and chemical sensors [8–10], electrocatalysts [11], electrochromic display devices [12], information storage systems [13], optical switching and limiting devices [14], molecular solar cells [15,16], nonlinear optical materials [17], light-emitting devices [18,19], organic field effect transistors [20], a colour ink [21] and marker [22], and the photosensitizers for photodynamic therapy [23,24]. To increase the

utility of Pcs in applications, Pc compounds can be derived by multiple modifications in the macrocyclic core, through the introduction of different metal atoms, as well as the functionalization with a variety of groups in the peripheral and non-peripheral position on the Pc skeleton [25,26].

The unsubstituted Pcs can present solubility problems and aggregation behaviour for some applications [27,28]. Hence many research activities focused on synthesizing of soluble Pcs by adding different functional groups to the molecule [29–31]. In addition to the solubility, chemical and physical properties of the Pcs in organic solvents also depend on the substituents on the Pc ring. Methylphenoxy or methoxyphenoxy groups on Pc skeleton increase Pc solubility in common solvents and it is known that phenolic compounds have potential related health benefits as antioxidants and they have also become apparent potential in therapeutic in the treatment of the diseases such as liver cirrhosis, cancer, diabetes, aging etc. in recent times [32–35]. In previous study [36], methylphenoxy group as both a bioactive compound and antioxidant and Pc as photosensitizers for photodynamic therapy (PDT) were combined to produce soluble, nonaggregated and bifunctional new Pc complexes. The study revealed that the novel Pcs can be potential Type II photosensitizers for PDT. We wondered how substitution position of methyl group on phenoxy skeleton affect photophysical and photochemical properties as compared with 2,4,6-trimethylphenoxy (mesityloxy) substituted Pcs derivatives. Hence, in this study, 3- and 4-mesityloxyphthalonitrile derivatives (**1** and **2**),

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which are starting materials for target Pcs, have been obtained by the reaction of 2,4,6-trimethylphenol with 3- or 4-nitrophthalonitrile and novel soluble and non-aggregated metal-free (**7** and **8**), zinc (**5** and **6**) and indium Pc (**3** and **4**) compounds have been synthesized by using **1** and **2**.

It is worth noting that each Pc product was obtained as a mixture of four regioisomers of C_{4h} , D_{2h} , C_{2v} and C_s symmetry with similar physical and chemical properties. While it is theoretically possible to separate these isomers due to their different geometries, it has been accomplished only for very specific Pcs by use of specially designed HPLC columns [37]. Thus, singlet oxygen generation by the Pcs and their usability as photosensitizer dyes for PDT in cancer treatment have been investigated (Scheme 1). The effects of different isomer substituent position and the nature of the central metal ions in the Pc on photophysical and photochemical properties were also studied and compared with the counterparts in our previous study [36].

2. Experimental

The used materials, equipments, photophysical and photochemical formulas and parameters were supplied as supplementary information.

2.1. Synthesis

2.1.1. General procedure for the phthalonitrile syntheses

3-/or 4-Nitrophthalonitrile (3.50 g, 20 mmol), 2,4,6-trimethylphenol (2.78 g, 21.40 mmol) and anhydrous K_2CO_3 (14 g, 100 mmol) were added in 35 mL dimethylsulfoxide (DMSO). The mixture was stirred at 45 °C for 36 h under inert atmosphere. Then the reaction mixture was poured into cold water. The light yellow solid was filtered off and washed using cold water and dried in room temperature. The crude products were purified by column chromatography using silica gel eluting with $CHCl_3$.

3-(Mesityloxy) phthalonitrile (1): Solubility: Dichloromethane (DCM), $CHCl_3$, tetrahydrofuran (THF), DMSO and dimethylformamide (DMF). Mp: 160 °C. Yield: 4.45 g (84.30%). Anal. calculated for $C_{17}H_{14}N_2O$ C, 77.84%; H, 5.38%; N, 10.68%; found C, 77.65%; H, 5.54%; N, 10.83%. IR (ATR) ν_{max}/cm^{-1} : 728, 774, 795, 802, 854, 908, 986(C—C str.), 1035(C—C str.), 1125, 1138, 1173, 1196, 1269(C—O str.), 1312(C—O str.), 1453(C—H bend.), 1480(C—H bend.), 1575(C=C str.), 1596(C=C str.), 2226(C≡N str.), 2853(> CH_2 str.), 2920(> CH_2 str.), 3032(=C—H str.), 3084(=C—H str.). H-NMR ($CDCl_3$): d, ppm 2.08 (s, 6H), 2.32 (s, 3H), 6.95 (s, 2H), 6.76 (dd, $J=8.67$ Hz, $J=2.36$ Hz, 1H), 7.4 (dd, $J=7.56$ Hz, $J=2.05$ Hz, 1H), 7.5 (t, $J=8.50$ Hz, $J=7.85$ Hz, 1H) [22].

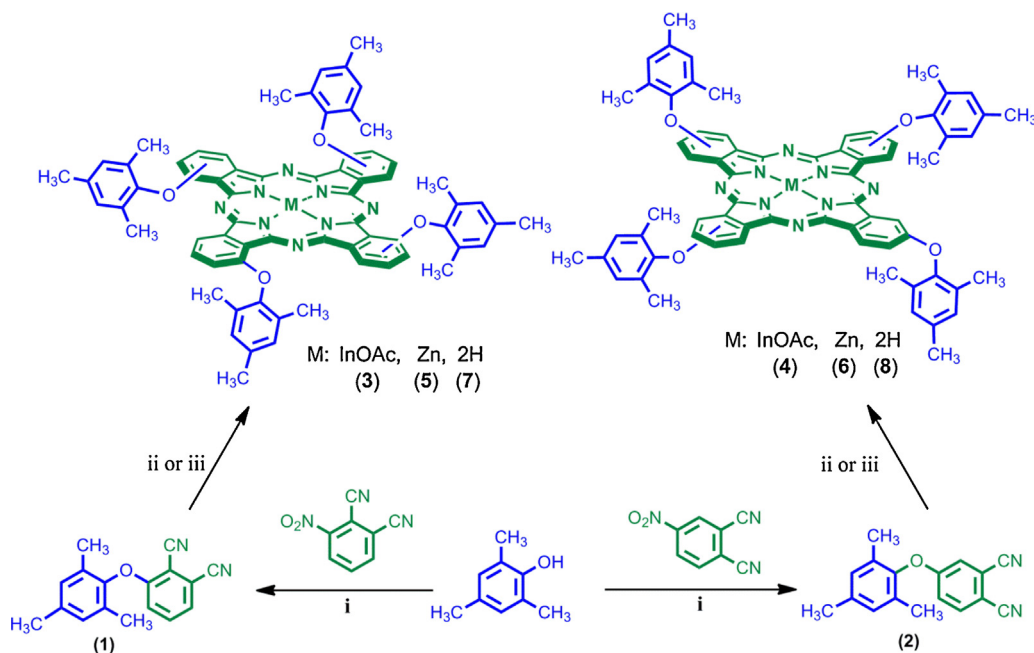
4-(Mesityloxy) phthalonitrile (2): Solubility: DCM, $CHCl_3$, THF, DMSO and DMF. Mp: 155 °C. Yield: 4.24 g (80.12%). Anal. calculated for $C_{17}H_{14}N_2O$ C, 77.84%; H, 5.38%; N, 10.68%; found C, 78.02%; H, 5.43%; N, 10.52%. IR (ATR) ν_{max}/cm^{-1} : 756, 772, 807, 842, 856, 870, 947, 958, 1037(C—C str.), 1086(C—C str.), 1136, 1163, 1196, 1244(C—O str.), 1277(C—O str.), 1317(C—O str.), 1379, 1478(C—H bend.), 1575(C=C str.), 1591(C=C str.), 2228(C≡N str.), 2855(> CH_2 str.), 2917(> CH_2 str.), 3083(=C—H str.). 1H NMR ($CHCl_3$ -d): d, ppm 2.04 (s, 6H), 2.32 (s, 3H), 6.95 (s, 2H), 7.12 (d, $J=2.15$ Hz, 1H), 7.11 (dd, $J=7.25$ Hz, $J=2.52$ Hz, 1H), 7.70 (d, $J=9.15$ Hz, 1H).

4-(Mesityloxy) phthalonitrile (2): Solubility: DCM, $CHCl_3$, THF, DMSO and DMF. Mp: 155 °C. Yield: 4.24 g (80.12%). Anal. calculated for $C_{17}H_{14}N_2O$ C, 77.84%; H, 5.38%; N, 10.68%; found C, 78.02%; H, 5.43%; N, 10.52%. IR (ATR) ν_{max}/cm^{-1} : 756, 772, 807, 842, 856, 870, 947, 958, 1037(C—C str.), 1086(C—C str.), 1136, 1163, 1196, 1244(C—O str.), 1277(C—O str.), 1317(C—O str.), 1379, 1478(C—H bend.), 1575(C=C str.), 1591(C=C str.), 2228(C≡N str.), 2855(> CH_2 str.), 2917(> CH_2 str.), 3083(=C—H str.). 1H NMR ($CHCl_3$ -d): d, ppm 2.04 (s, 6H), 2.32 (s, 3H), 6.95 (s, 2H), 7.12 (d, $J=2.15$ Hz, 1H), 7.11 (dd, $J=7.25$ Hz, $J=2.52$ Hz, 1H), 7.70 (d, $J=9.15$ Hz, 1H).

2.1.2. Synthesis of metallo-phthalocyanines (general procedure)

Compounds **1** or **2** (0.20 g, 0.76 mmol), 0.45 mmol zinc acetate dihydrate or indium acetate and 0.30 mL of DMF mixture was heated at 360 °C in a reaction tube for 20 min under inert atmosphere. The new green mixture was precipitated by adding MeOH solution. The precipitate was filtered and washed with acetic acid, water and methanol (except InPcs **3** and **4**, they were washed only by methanol) for 12 h in the Soxhlet apparatus. The new products were purified by silica gel column chromatography with $CHCl_3$.

1(4), 8(11), 15(18), 22(25)-Tetrakis-(2,4,6-trimethylphenoxy) phthalocyaninato indium (III) acetate (3): Solubility: $CHCl_3$, DCM, toluene, THF, DMSO and DMF. Mp > 300 °C. Yield: 30 mg (15.00%). Calculated for $C_{70}H_{59}InN_8O_6$: C, 68.74%; H, 4.86%; N, 9.16%; found C, 68.45%; H, 5.14%; N, 9.35%. IR (ATR) ν_{max}/cm^{-1} : 741, 773, 851, 877, 1005(C—C str.), 1075(C—C str.), 1119(C—N str.), 1196(C—N str.), 1245(C—O str.), 1326(C—O str.), 1410(C—H bend.), 1473(C—H bend.), 1584(C=C str.), 1603(C=C str.), 1670(C=N str.), 1731(axial C=O), 2847(> CH_2 str.), 2917(> CH_2 str.), 2953(> CH_2 str.), 3046(=C—H str.), 3073(=C—H str.). UV-vis (DMF, 1.0×10^{-5} M): λ_{max}



Scheme 1. Synthesis of 2,4,6-trimethylphenoxy substituted phthalonitriles (**1** and **2**) and their phthalocyanine derivatives (**3-8**). Reagents and conditions: (i) N_2 , K_2CO_3 , DMSO, 50 °C, 36 h. (ii) N_2 , DMF, DBU, 360 °C, 20 min; (iii) N_2 , $Zn(CH_3COO)_2 \cdot 2H_2O$ or $In(CH_3COO)_3$, DMF, 360 °C, 20 min.

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