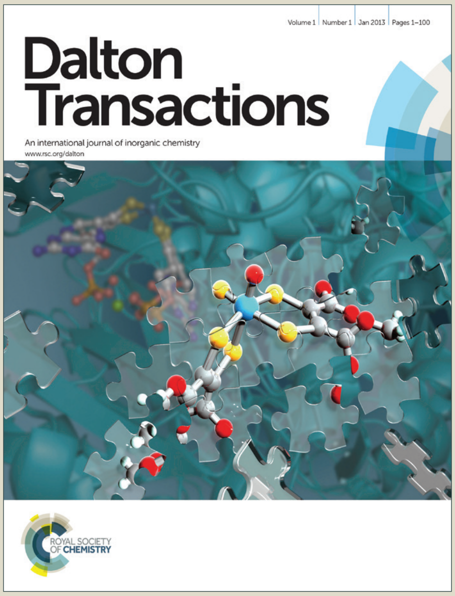
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis, characterization and investigation of photophysical and photochemical properties of highly soluble novel metal-free, zinc(II), and indium(III) phthalocyanines substituted with 2,3,6-trimethylphenoxy moieties

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

This work presents the synthesis and characterization of metal-free, zinc(II), and indium(III)acetate phthalocyanines substituted with 2,3,6-trimethylphenoxy groups at peripheral and non-peripheral positions. The photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of these novel phthalocyanines and unsubstituted zinc(II) and indium(III) acetate phthalocyanines were investigated in dimethylformamide solution. The effects of the types substituent and their positions and the variety of central metal ions on the phthalocyanine core on their spectroscopic, photophysical and photochemical properties were also determined. The studied 2,3,6-trimethylphenoxy substituted metal-free, zinc(II) and indium(III)acetate phthalocyanines especially indium(III)acetate derivative exhibited appropriate photophysical and photochemical properties such as highly singlet oxygen generation and these phthalocyanines can be potential Type II photosensitizers for the photodynamic therapy of cancer applications.

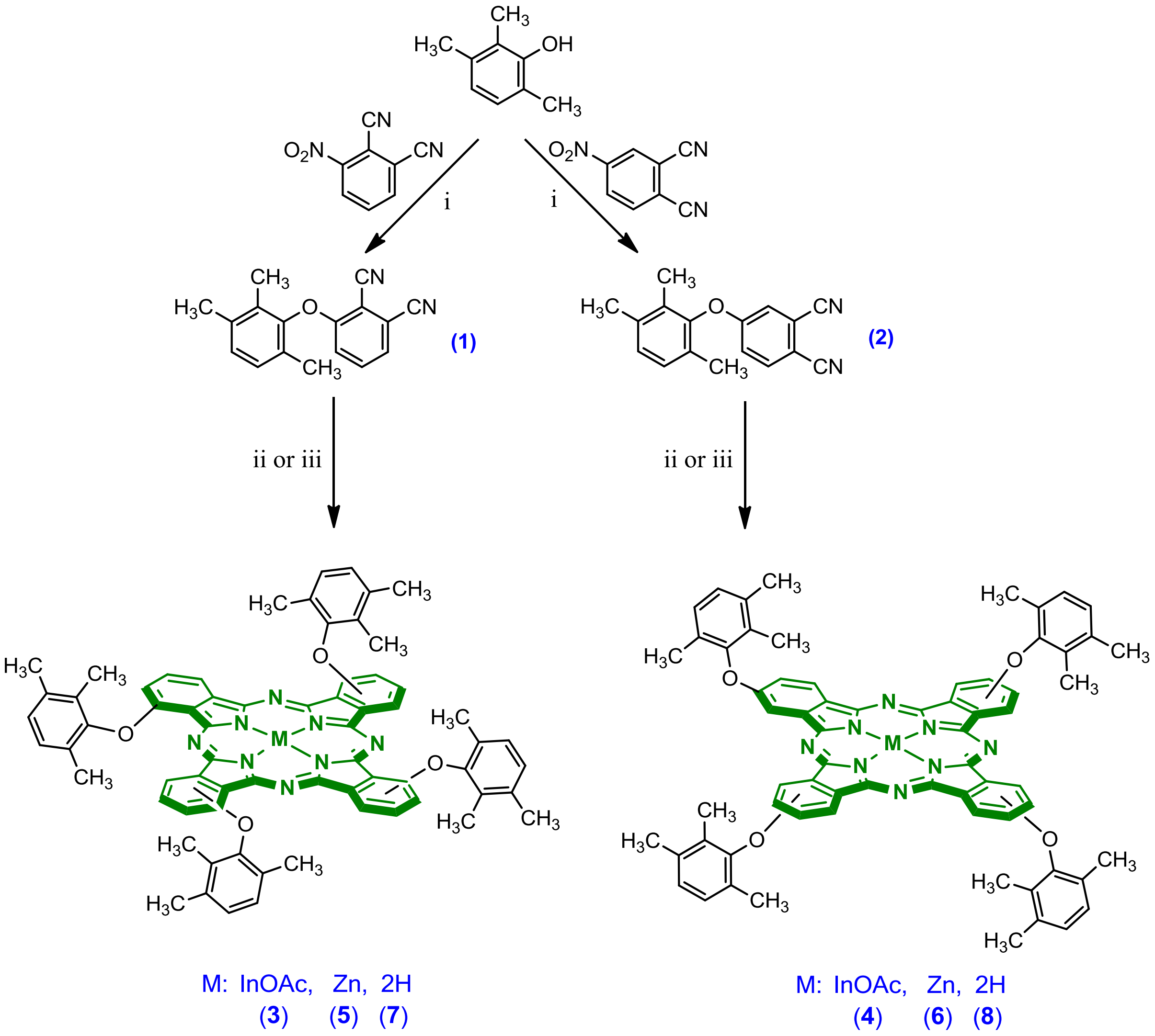
1. Introduction

Phthalocyanines (Pcs) are a tetra pyrrolic macrocycles that have a number of unusual physical and chemical properties arise from their characteristic 18 π-electron delocalization, such as high chemical and thermal stability which makes them valuable in different fields of science and technology.[1] In the last few decades, Pcs have been extensively used in a number of technological applications in fields such as optical switching and limiting devices,[2] organic field effect transistors,[3] sensors,[4,5] light-emitting devices,[6,7] molecular solar cells,[8,9] optical information recording media,[10] photosensitizers for photodynamic therapy,[11-13] and nonlinear optical materials.[14]

To increase the utility of Pcs in materials science, chemical modification of the Pc ring has been extensively investigated. The technologically important properties of Pc derivatives can be tuned by varying of the central metal atom, changing the size of the π-conjugated system, or alternating the type, number, and positions of the substituents on the macrocycle.[1] For some applications, the lower solubility and aggregation behaviour of unsubstituted metallo Pcs can present problems, but low solubility in common organic solvents can be overcome by the introduction of appropriate substituents such as alkyl or alkoxy groups in the peripheral or non-peripheral positions of Pc framework.[15,16] Central metals play a major role in tuning the properties of MPcs, some central metal ions such as indium (III) and manganese (III) can allow axial linking, which increases solubility and reduces molecular aggregation.[17]

In this study, the metal-free, zinc(II) and indium(III)acetate Pcs containing four 2,3,6-trimethylphenoxy groups at peripheral and non-peripheral positions on the Pc core were synthesized and characterized by elemental analysis, IR, UV-*Vis*, ^{1}H-NMR, ^{13}C-NMR (for phthalonitrile compounds) and MALDI-TOF mass spectroscopies. The unsubstituted ZnPc and In(OAc)Pc were also used for comparison purposes. The photophysical and photochemical properties of newly synthesized tetrakis(2,3,6-trimethylphenoxy) substituted In(OAc)Pcs (**3** and **4**), ZnPcs (**5** and **6**) and H_2Pcs (**7** and **8**) and their unsubstituted counterparts (In(OAc)Pc and ZnPc) were investigated in dimethylformamide (DMF) solution. The photophysical and photochemical properties of the unsubstituted metal-free derivative were not studied due to its solubility problem in DMF. The effects of the substituents and their positions on the Pc core and the variety of central metal ions in the Pc cavity on the spectroscopic, photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of novel phthalocyanines were also investigated and compared with each other. The investigation of photophysical and photochemical properties of these compounds is warranted due to their photocatalytic applications such as photodynamic therapy (PDT) of cancer.

2. Experimental Section



Scheme 1. Synthesis of 2,3,6-trimethylphenoxy substituted phthalonitriles (**1** and **2**) and their phthalocyanine (**3**- **8**) derivatives. Reagents and conditions: (i) N_2, K_2CO_3, DMSO, 50° C, 60 hrs. (ii) N_2, DMF, DBU, 360° C, 20 min.; (iii) N_2, $Zn(CH_3COO)_2.2H_2O$ or $In(CH_3COO)_3$, DMF, DBU, 360° C, 20 min.

2.1. Materials and methods

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

2.2. Synthesis

The unsubstituted In(OAc)Pc compound was synthesized according to the literature.[18]

2.2.1. General procedure for the synthesis of the phthalonitriles (1 and 2)

3-nitrophthalonitrile or 4-nitrophthalonitrile (3.50 g, 20 mmol) and 2,3,6-trimethylphenol (2.93 g, 21.50 mmol) were dissolved in 40 mL anhydrous dimethylsulfoxide (DMSO). After stirring for 10 minutes; finely ground anhydrous K_2CO_3 (14 g, 100 mmol) was added to this solution. The reaction mixture was stirred at 50° C for 60 hours under nitrogen atmosphere. Then the mixture was poured into ice-water. The white product precipitated and the solid product was filtered off, washed by using water and dried in vacuum at 50° C. The crude product was purified by column chromatography using silica gel eluting with chloroform ($CHCl_3$).

*2.2.1.1. 3-(2,3,6-trimethylphenoxy)phthalonitrile (**1**)*

Compound **1** is soluble in dichloromethane (DCM), $CHCl_3$, tetrahydrofuran (THF), DMF, DMSO. Mp: 152° C. Yield: 5.00 g (95.00%). Anal calculated for $C_{17}H_{14}N_2O$ C, 77.84%; H, 5.38%; N, 10.68%; found C, 77.66%; H, 5.51%; N, 10.86%. IR (ATR) λ_{max} /cm^{-1}: 551, 605, 732, 802, 865, 905, 985, 1004(C–C str.), 1078(C–C str.), 1125, 1162, 1179, 1197, 1273(C–O std.), 1325(C–O std.), 1383, 1409, 1451(C–H bend.), 1494(C–H bend.), 1572(C=C str.), 1585(C=C str.), 2231(C≡N str.), 2861(>CH_2 str.), 2925(>CH_2 str.), 2946(>CH_2 str.), 3031(=C–H str.), 3088(=C–H str.). ^{1}H-NMR ($CDCl_3$): δ, ppm 2.03 (s, 3H), 2.08 (s, 3H), 2.29 (s, 3H), 6.71 (d, J = 8.67, 1H), 7.03 (s, 2H), 7.40 (d, J = 7.72 Hz, 1H), 7.49 (t, J = 8.36 Hz, 1H). ^{13}C-NMR ($CDCl_3$) (δ: ppm): 160.55, 149.42, 136.88, 134.54, 129.11, 128.62, 127.97, 127.71, 126.12, 117.95, 117.31, 115.27, 112.27, 104.34, 19.86, 16.11, 12.47.

*2.2.1.2. 4-(2,3,6-trimethylphenoxy)phthalonitrile (**2**)*

Compound **2** is soluble in DCM, $CHCl_3$, THF, DMF and DMSO. Mp: 159^o C Yield: 4.95 g (88.85%). 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) λ_{max}/cm^{-1}: 706, 711, 816, 843, 882, 953,1038(C–C str.), 1068(C–C str.), 1090, 1162, 1124, 1176, 1184, 1244, 1279(C–O std.), 1321(C–O std.), 1462(C–H bend.), 1483(C–H bend.), 1563(C=C str.), 1596(C=C str.), 2229(C≡N str.), 2861(>CH_2 str.), 2925(>CH_2 str.), 3078(=C–H str.). ^{1}H-NMR ($CDCl_3$): δ, ppm 1.94 (s, 3H), 1.98 (s, 3H), 2.24 (s, 3H), 7.08 (d, *J* = 7.72 Hz, 1H), 7.09 (d, *J* = 7.72 Hz, 1H), 7.12 (dd, *J* = 8.83 Hz, *J* = 2.05 Hz, 1H), 7.54 (d, *J* = 2.05 Hz, 1H), 8.02 (d, *J* = 8.99 Hz, 1H). ^{13}C-NMR ($CDCl_3$) (δ: ppm): 161.32, 149.25, 137.04, 135.60, 128.99, 128.75, 127.98, 127.58, 119.79, 119.70, 117.80, 115.55, 115.14, 108.16, 19.88, 16.13, 12.47.

2.2.2. General procedure for the synthesis of metallophthalocyanines (3-6)

Compound **1** or **2** (0.76 mmol) and 0.45 mmol metal salts [0.10 g $Zn(OAc)_2.2H_2O$ or 0.13 g $In(OAc)_3$] were powdered in a quartz crucible and transferred in a reaction tube. 0.25 mL of DMF was added to this reaction mixture, and then the mixture was heated at 360^o C in a sealed glass tube for 20 minutes under dry nitrogen atmosphere. The reaction mixture was precipitated by adding methanol. The green products were filtered and washed with acetic acid, water, methanol and acetonitrile (except for compounds **3** and **4**, they were washed with only methanol and acetonitrile) for 12 hours in the soxhlet apparatus. The crude products were purified by column chromatography with silica gel eluting with $CHCl_3$.

*2.2.2.1. 1(4),8(11),15(18),22(25)-Tetrakis-(2,3,6-trimethylphenoxy)phthalocyaninatoindium(III)acetate (**3**):*

The In(OAc)Pc (**3**) is soluble in toluene, $CHCl_3$, DCM, THF, DMF and DMSO. Mp>300^o C. Yield: 15 mg (7.60 %). 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) λ_{max}/cm^{-1}: 558, 698, 740, 804, 882, 965, 1002(C–C str.), 1075(C–C str.), 1119(C–N str.), 1161(C–N str.), 1200, 1248(C–O std.), 1267, 1327(C–O std.), 1381, 1410(C–H bend.), 1462, 1480(C–H bend.), 1575, 1585(C=C str.), 1603(C=C str.), 1672,(C=N str.), 1731(C=O str.), 2856(>CH_2 str.), 2920(>CH_2 str.), 3023(=C–H str.), 3068(=C–H str.). UV–*Vis* (DMF, 1x10^{-5} M): λ_{max}(nm), (log ε): 323 (4.559), 642 (4.410), 719 (5.155). MALDI-TOF-MS: 1199.14 [M–OAc+2H_2O]$^+$, 1318.11 [M–OAc+DHB]$^+$. DHB (2,6-dihydroxybenzoicacid) was used a MALDI matrix.

*2.2.2.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2,3,6-trimethylphenoxy)phthalocyaninatoindium(III)acetate (**4**):*

The In(OAc)Pc (**4**) is soluble in toluene, $CHCl_3$, DCM, THF, DMF and DMSO. Mp>300^o C. Yield: 42.10 mg (21.04%). Calculated for $C_{70}H_{59}InN_8O_6$: C, 68.74%; H, 4.86%; N, 9.16%; found C, 68.70%; H, 5.17%; N, 9.29 %. IR (ATR) λ_{max}/cm^{-1}: 698, 744, 807, 824, 871, 948, 1042(C–C str.), 1086(C–C str.), 1116(C–N str.), 1183(C–N str.), 1219, 1267(C–O std.), 1335(C–O std.), 1394, 1462(C–H bend.), 1477(C–H bend.), 1573(C=C str.), 1609(C=C str.), 1649,(C=N str.), 1676,(C=N str.), 1734(C=O str.), 2856(>CH_2 str.), 2922(>CH_2 str.), 3013(=C–H str.), 3058(=C–H str.). UV–*Vis* (DMF, 1x10^{-5} M): λ_{max}(nm), (log ε): 360 (4.780), 622 (4.398), 694 (5.078). MALDI-TOF-MS: 1162.07 [M–OAc]$^+$.

*2.2.2.3. 1(4),8(11),15(18),22(25)-Tetrakis-(2,3,6-trimethylphenoxy)phthalocyaninatozinc(II) (**5**)*

The ZnPc (**5**) is soluble in toluene, $CHCl_3$, DCM, THF, DMF and DMSO. Mp>300^o C. Yield: 12 mg (6.30 %). Calculated for $C_{68}H_{56}ZnN_8O_4$: C, 73.28%; H, 5.06%; N, 10.05%; found C, 73.10%; H, 5.19%; N, 10.18 %. IR (ATR) λ_{max}/cm^{-1}: 562, 673, 688, 744, 761, 803, 883, 966, 1001(C–C str.), 1078(C–C str.), 1118(C–N str.), 1168(C–N str.), 1201, 1233, 1267(C–O std.), 1333(C–O std.), 1381, 1408, 1456(C–H bend.), 1481(C–H bend.), 1570(C=C str.), 1589(C=C str.), 1657,(C=N str.), 2856(>CH_2 str.), 2922(>CH_2 str.), 3023(=C–H str.), 3058(=C–H str.). ^{1}H-NMR ($CDCl_3$): δ, ppm : 8.65–6.90 (m, 20H, arom.), 2.50–2.00 (bs, 36H, –CH_3). UV–*Vis* (DMF, 1x10^{-5} M): λ_{max}(nm), (log ε): 317 (4.699), 628 (4.685), 700 (5.436). MALDI-TOF-MS: 1113.09 [M]$^+$.

*2.2.2.4. 2(3),9(10),16(17),23(24)-Tetrakis-(2,3,6-trimethylphenoxy)phthalocyaninatozinc(II) (**6**)*:

The ZnPc (**6**) is soluble in toluene, $CHCl_3$, DCM, THF, DMF and DMSO. Mp>300^o C. Yield: 37.80 mg (18.57%). Calculated for $C_{68}H_{56}ZnN_8O_4$: C, 73.28%; H, 5.06%; N, 10.05%; found C, 73.42%; H, 5.16%; N, 10.21%. IR (ATR) λ_{max}/cm^{-1}: 725, 744, 805, 820, 870, 947, 996(C–C str.), 1041, 1090(C–C str.), 1117(C–N str.), 1166(C–N str.), 1216, 1267(C–O std.), 1336(C–O std.), 1394, 1460(C–H bend.), 1484(C–H bend.), 1575(C=C str.), 1608(C=C str.), 1656,(C=N str.), 2856(>CH_2 str.), 2921(>CH_2 str.), 3018(=C–H str.), 3058(=C–H str.). ^{1}H-NMR ($CDCl_3$): δ, ppm : 8.80–7.00 (m, 20H, arom.), 2.45–2.05 (bs, 36H, –CH_3). UV–*Vis* (DMF, 1x10^{-5} M): λ_{max}(nm), (log ε): 354 (4.756), 609 (4.418), 6.80 (5.186). MALDI-TOF-MS: 1113.24 [M]$^+$.

2.2.3. General procedure for the synthesis of metal-free phthalocyanines (7 and 8)

The mixture of phthalonitrile compounds **1** or **2** (0.20 g, 0.76 mmol), 0.25 mL dry DMF and 0.25 mL 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a catalyst was heated for 20 minutes at 360^o C under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was treated with dilute HCl solution. The green products were precipitated, filtered off and washed with water until the filtrate became neutral. The crude products were taken in the Soxhlet apparatus then purified by washing with acetic acid, water, methanol and acetonitrile for 12 hours, respectively. The crude products were purified by column chromatography with silica gel eluting with $CHCl_3$.

*2.2.3.1. 1(4),8(11),15(18),22(25)-Tetrakis-(2,3,6-trimethylphenoxy)phthalocyanine (**7**)*

The H_2Pc (**7**) is soluble in toluene, $CHCl_3$, DCM, THF, DMF and DMSO (slightly). Mp>300^o C. Yield: 15.80 mg (7.90%). Calculated for $C_{68}H_{58}N_8O_4$: C, 77.69%; H, 5.56%; N, 10.66%; found C, 77.52%; H, 5.68%; N, 10.52%. IR (ATR) λ_{max}/cm^{-1}: 561, 613, 691, 743, 747, 801, 876, 950, 1019(C–C str.), 1077(C–C str.), 1110(C–N str.), 1155(C–N str.), 1201, 1222, 1248(C–O std.), 1264, 1310, 1333(C–O std.), 1381, 1410(C–H bend.), 1462, 1486(C–H bend.), 1575(C=C str.), 1595(C=C str.), 1683,(C=N str.), 2851(>CH_2 str.), 2921(>CH_2 str.), 3023(=C–H str.), 3058(=C–H str.), 3292(N–H str.). ^{1}H-NMR ($CDCl_3$): δ, ppm : 8.90–7.10 (m, 20H, aromatic), 2.45–2.00 (bs, 36H, –CH_3), -1.60 (bs, 2H). UV–*Vis* (DMF, 1x10^{-5} M): λ_{max}(nm), (log ε): 316 (4.751), 629 (4.515), 662 (4.620), 696 (5.118), 724 (5.147). MALDI-TOF-MS: m/z 1051.56 [M]$^+$.

*2.2.3.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2,3,6-trimethylphenoxy)phthalocyanine (**8**)*

The H_2Pc (**8**) is soluble in toluene, $CHCl_3$, DCM, THF, DMF and DMSO (slightly). Mp>300^o C. Yield: 61.00 mg (30.80%). Calculated for $C_{68}H_{58}N_8O_4$: C, 77.69%; H, 5.56%; N, 10.66%; found C, 77.80%; H, 5.64%; N, 10.81%. IR (ATR) λ_{max}/cm^{-1}: 804, 866, 926, 938, 1007(C–C str.), 1076(C–C str.), 1112(C–N str.), 1160(C–N str.), 1206, 1262(C–O std.), 1273, 1318(C–O std.), 1327, 1395, 1423(C–H bend.), 1462(C–H bend.), 1579(C=C str.), 1614(C=C str.), 1684,(C=N str.), 2854(>CH_2 str.), 2916(>CH_2 str.), 2983(>CH_2 str.), 3012(=C–H str.), 3290(N–H str.). ^{1}H-NMR ($CDCl_3$): δ, ppm : 9.00–6.90 (m, 20H, aromatic), 2.50–1.80 (bs, 36H, –CH_3), -1.55 (bs, 2H). UV–*Vis* (DMF, 1x10^{-5} M): λ_{max} (nm), (log ε): 342 (4.663), 607 (4.262), 640 (4.455), 670 (4.843), 704 (4.843). MALDI-TOF-MS: m/z 1051.51 [M]$^+$.

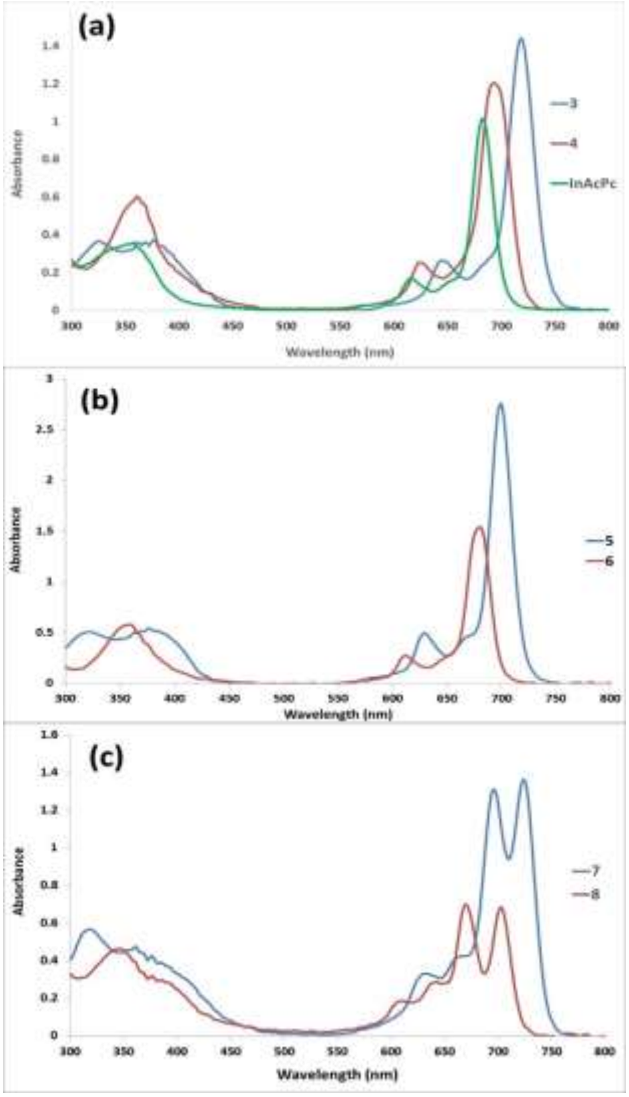


Fig. 1 Absorption spectra of (a) In(OAc)Pcs (**In(OAc)Pc**, **3** and **4**), (b) ZnPcs (**5** and **6**) and (c) H_2Pcs (**7** and **8**) in DMF at 1.0x10^{-5} M.

3. RESULTS AND DISCUSSION

3.1. Characterization

The IR spectra of starting materials indicated the formation of compounds **1** and **2** by the disappearance of the NO_2 band nearby at 1350 cm^{-1} and the appearance of new absorption band at 1270 and 1279 cm^{-1} belonging to Ar−O−Ar, respectively. While the strong −C≡N bands of **1** and **2** were appeared at 2231 and 2229 cm^{-1} in the IR spectrum, these bands were disappeared after conversion to the Pc (**3-8**) derivatives. The IR spectra of the Pcs were similar in most peaks with the exception of the compounds **7** and **8** showing a N−H stretching band peak at 3292 and 3290 cm^{-1} and N−H bending bands at 1462, 1022 and 1462, 1007 cm^{-1} due to N−H bounds in the inner core. The peaks [ca. 1600 cm^{-1} (–C=C– stretch), ca. 1400 cm^{-1} (C–H bend), ca. 1325 cm^{-1} (C–N stretch), ca. 1270 cm^{-1} (C–O–C stretch), ca.950 cm^{-1} (–C=C– bend)] of H_2Pcs and metallo-Pcs (MPcs) were almost at the same place, indicating that central metal has a small influence on the IR vibrations (Table S1 in supporting information).

The electronic spectra of the MPcs (**3-6**) and unsubstituted **In(OAc)Pc** showed monomeric behaviour as evidenced by a single (narrow) Q band and split two Q bands for metal-free phthalocyanines (H_2Pcs) **7** and **8** up to ~ 1 x 10^{-5} mol dm^{-3} in DMF as typical of metallo and metal-free Pcs.[19,20] The UV-*Vis* spectra of the unsubstituted **In(OAc)Pc** and 2,3,6-trimethylphenoxy substituted In(OAc)Pcs (**3** and **4**) showed characteristic absorption in the Q band region at 683, 719 and 694 nm in DMF, respectively (Table 1). The 2,3,6-trimethylphenoxy substituted ZnPcs (**5** and **6**) also exhibited characteristic absorption in the Q band region at 700 and 680 nm in DMF, respectively (Table 1). The splitting Q band was observed at 724 and 696 nm for **7,** 704 and 670 nm for **8** indicating the structure with non-degenerate D_{2h} symmetry of H_2Pcs.

The Q bands of the non-peripherally substituted Pcs **3**, **5** and **7** were red-shifted when compared to the corresponding peripherally substituted Pcs **4**, **6** and **8** in DMF (Fig. 1a-1c). The observed red-shifts, 25 nm between **3** and **4**; 20 nm between **5** and **6**; 20 nm between **7** and **8**. When strongly electron donating substituents, such as phenoxy groups in this study, are bound to non-peripheral positions on the phthalocyanine core, the Q bands highly shift to the red region of the spectra.[21].These effects can be readily explained by considering the size of the atomic orbital coefficients in molecular orbital calculations. The coefficients at the non-peripheral carbons in the $1a_{1u}$ HOMO are larger than those at the peripheral carbons, so the extent of destabilization of this orbital is larger when electron-donating groups are introduced at the non-peripheral positions. As a result, the HOMO-LUMO gap becomes smaller and the Q band, which arises primarily from the $1a_{1u} \longrightarrow 1e_g^*$ transition, shifts to longer wavelength as explained in the literature.[22-24]

The Q bands of the In(OAc)Pcs **3** and **4** were red-shifted compared to the corresponding ZnPcs **5** and **6** in DMF, indicated the non-planar effect of the indium(III) ion, because atomic radius of indium is fairly bigger than zinc radius (Fig. 1a-1b) as the central metal ion in the Pc cavity. The B bands were observed at around 320-360 nm for substituted Pcs (**3-8**) and unsubstituted **In(OAc)Pc**, and in DMF (Fig. 1a-1c).

The [M–OAc+DHB]$^+$ peak of the compound **3**, [M–OAc]$^+$ peak of the compound **4**, and the [M]$^+$ molecular ion peaks of compounds **5**, **6**, **7** and **8** were found at 1318.11, 1162.07, 1113.09, 1113.24, 1050.51 and 1049.62 Da in MALDI-TOF mass

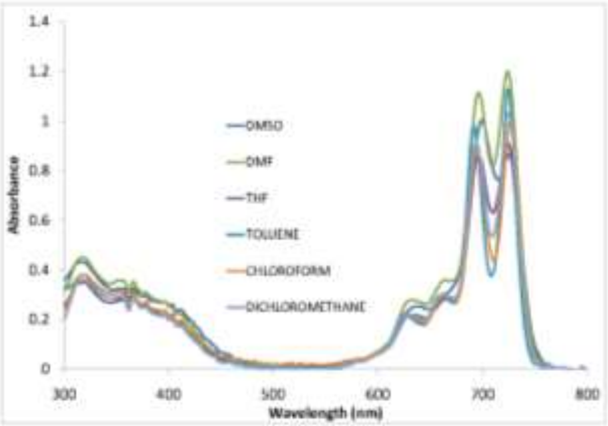


Fig. 2 Absorption spectra of metal-free Pc **7** in different solvents.

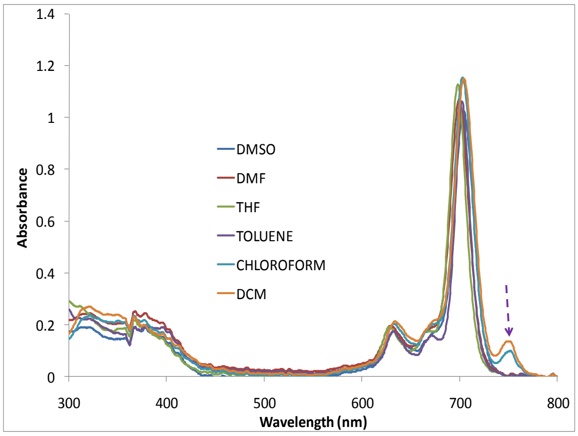


Fig. 3 Absorption spectra of compound **5** in different solvents.

spectra (Fig. S1-S6 in supporting information).

The ^{1}H-NMR spectra of Pcs (**5-8**) are also consistent with the proposed structures. The ^{1}H-NMR spectra of compounds **1** and **2** exhibited characteristic signals for methyl ($-CH_3$) protons at δ 2.03(3H), 2.08 (3H), 2.29 (3H) and 1.94(3H), 1.98(3H), 2.23(3H) ppm each a singlet, respectively. The aromatic CH protons of trimethylbenzene groups on the phthalonitrile compounds (**1** and **2**) were observed at around 6.68-6.90 and 7.07-7.10 ppm. The aromatic CH protons on the cyanobenzene group were observed at around 6.94-7.51 and 7.12-8.20 ppm for compounds **1** and **2**, respectively. Moreover, the ^{13}C-NMR spectra were also in good correlation with the structure of the synthesized phthalonitrile compounds (**1** and **2**) (Fig. S7A, S7B, S8A, S8B in supporting information).

3.2. Aggregation studies

In this study, the aggregation behaviour of the newly synthesized 2,3,6-trimethylphenoxy substituted Pcs were examined in different solvents (DMSO, DMF, THF, toluene, chloroform and DCM) to select a suitable solvent for investigation of their photophysical and photochemical properties. The non-peripherally substituted H_2Pc **7** did not show any aggregation in used solvents (Fig. 2 for Pc **7** and Fig. S9 for Pc **8**), but peripherally substituted H_2Pc **8** formed highly aggregated species in DMSO. Therefore DMF was preferred as the non-aggregated solvent for further studies about photophysical and photochemical properties of newly synthesized Pcs. Moreover, the small amount (0.1% is a non-toxic level) of DMF can be used for without any toxic effect in biological applications.[25-28]

The non-peripherally substituted ZnPc **5** showed an extra peak at 752 nm in chloroform and DCM solutions (Fig. 3). This peak could be due to formation of J-type aggregation among the Pc molecules or protonation of the inner nitrogen atoms on the Pc core. We suggest that this extra peak is due to lowering in symmetry of Pc molecules because of the protonation instead of J-type aggregation. DCM and chloroform contain small amounts of acid (generally HCl) and acidic impurities may protonate the inner nitrogen atoms so the symmetry of Pc core can turn into D_{4h} symmetry. The absorption intensity of this extra peak at 752 nm increased by adding trifluoroacetic acid and decreased by adding pyridine (Fig. S10 and S11 in supporting information).[29,30] This result verified the protonation of inner nitrogen atoms in the cavity of ZnPc **5** in DCM and chloroform solutions.

The aggregation behaviour of the substituted Pcs (**3-8**) and unsubstituted **In(OAc)Pc** was also studied at different concentration in DMF. When the concentration was increased, the intensity of absorption of the Q band also increased. Lambert–Beer law was obeyed for UV-*Vis* studies of all Pcs in the concentrations ranging from 1.2×10^{-5} to 2×10^{-6} M in DMF. Any new band formation was observed belong to H-type and J-type aggregation of Pcs depending on the concentration change (Fig. 4 for Pc **6** and Fig. S12 for unsubstituted In(OAc)Pc as an example).

3.3. Fluorescence spectra

The fluorescence emission, absorption and excitation spectra of 2,3,6-trimethylphenoxy substituted Pcs **4** (Fig. 5a), **6** (Fig. 5b), **8** (Fig. 5c) and unsubstituted **In(OAc)Pc** in DMF were showed in Fig. 5 and Fig. S13, respectively. Fluorescence emission peaks were listed in Table 1. The fluorescence emission of In(OAc)Pcs (**3**, **4** and unsubstituted **In(OAc)Pc**) were observed lower intense peaks than that of ZnPcs and H_2Pcs (**5-8**) in DMF due to heavy atom effect of indium metal. The Stokes shifts of the substituted In(OAc)Pcs (**3** and **4**) were higher than that of the other Pcs (**5**, **6, 7, 8** and unsubstituted **In(OAc)Pc**) in DMF. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for all ZnPcs in DMF. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the

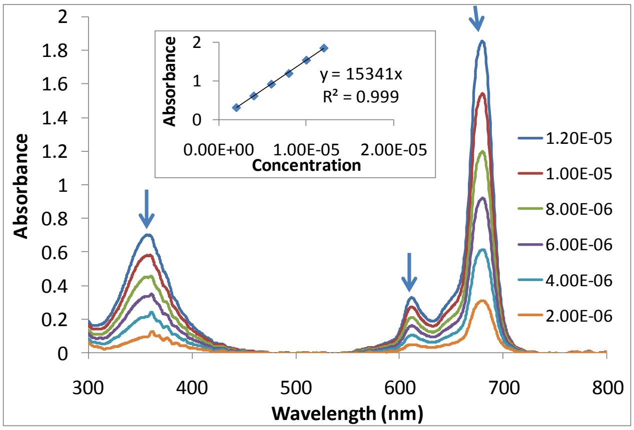


Fig. 4 Absorption spectra of compound **6** in DMF at different concentrations. (Inset: plot of absorbance vs. concentration.)

Table 1 Absorption, excitation and emission spectral data for unsubstituted indium(III) acetate (**In(OAc)Pc**), zinc (**ZnPc**) and substituted indium(III) acetate (**3** and **4**), zinc (**5** and **6**) and metal-free (**7** and **8**) phthalocyanines in DMF.

Sample	Q band λ_{max}, (nm)	(log ε)	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
In(OAc)Pc	683	4.93	690	693	10
3	719	5.15	726	729	10
4	694	5.08	684	708	14
ZnPc [a,b]	670	5.37	670	676	6
5	700	5.44	699	705	5
6	680	5.19	682	688	8
7	724 696	5.15 5.12	697 725	726	2
8	704 670	4.84 4.85	677 705	708	4

[a] Data from Ref.[31]

[b] Data from Ref.[32]

excitation spectra for Pcs (In(OAc)Pc, **3-8**) suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation (Fig. 5 for **4** (a), **6** (b), **8** (c) and Fig. S13 for unsubstituted In(OAc)Pc).

3.4. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of the 2,3,6-trimethylphenoxy substituted Pcs **3-8** as well as unsubstituted **In(OAc)Pc** and **ZnPc** in DMF were given in Table 2. The Φ_F values of the substituted In(OAc)Pcs (**3** and **4**) and H_2Pcs (**7** and **8**) were lower than those of the unsubstituted **In(OAc)Pc** and **ZnPc** in DMF because of the more quenching of fluorescence by the substituent. The Φ_F values for unsubstituted **In(OAc)Pc** and substituted In(OAc)Pcs (**3** and **4**) were much smaller than Φ_F values of substituted ZnPcs (**5** and **6**) and H_2Pcs (**7** and **8**) in DMF. This result can be attributed to the heavy atom effect of indium atom which increases the number of the triplet state species and causes quenching of the fluorescence. Furthermore, the In(OAc)Pc **3** and **4** have very high singlet oxygen quantum yields (Φ_Δ) values. The sum of Φ_F and Φ_Δ, two major deactivation pathways of excited state, is close to unity and therefore no quenching is expected.

The Φ_F values for the substituted ZnPcs **5** and **6** were higher than those of the unsubstituted **ZnPc** in DMF (Table 2). An increase in fluorescence intensity may be caused by the presence of substituents, which declines the fluorescence quenching.

The H_2Pcs **7** and **8** showed approximately two times lower Φ_F value than the ZnPc counterparts **5** and **6** in DMF. This result might be related to d^{10} configuration of zinc metal in **5** and **6**. On the other hand, the H_2Pcs **7** and **8** were more deactivated by non-radiative processes and another competitive relaxation channel of singlet excited state is present for **7** and **8**.

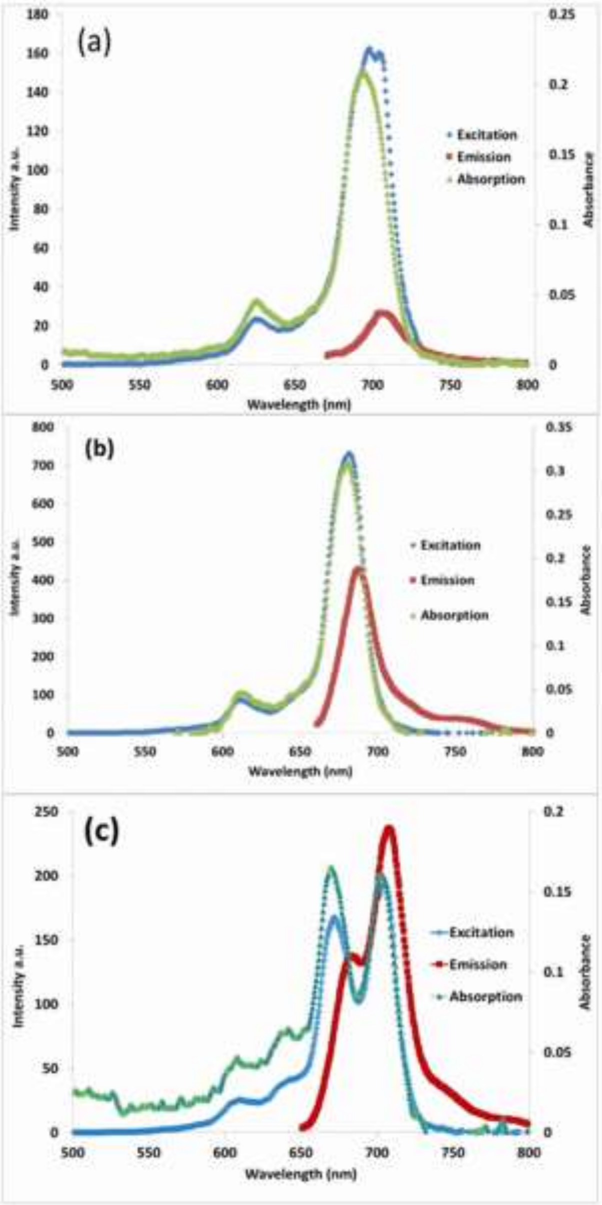


Fig. 5 Absorption, excitation and emission spectra of the compounds **4** (a), **6** (b) and **8** (c) in DMF. Excitation wavelength = 651 nm for **4** and **6** and 641 nm for **8**.

Φ_F values for the peripherally substituted Pcs **4**, **6** and **8** were higher than of the non-peripherally substituted counterparts **3**, **5** and **7** due to the effect of the substitutents' position on the Pc ring. This result implies that the peripherally substituted Pcs have less quenching of the excited states.

Fluorescence lifetime refers to the average time the molecule stays in its excited state before emitting a photon and it was determined for all studied Pcs by using time correlated single photon counting (TCSPC). The results were given in Table 2 and related graphic for ZnPc **6** and unsubstituted **In(OAc)Pc** were supplied in Fig. 6 and Fig. S.14, respectively. In general, the presence of two lifetimes for Pcs has been explained in terms of the presence of aggregates. The first of the lifetimes, long life-

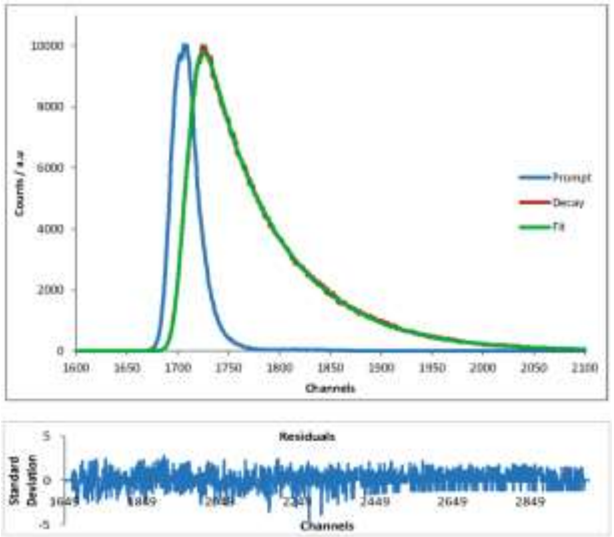


Fig.6 Time correlated single photon counting **(**TCSPC) trace for compound **6** in DMF with residuals. Excitation wavelength = 651 nm.

time, may be associated with monomeric non-interacting MPc molecules, while the second of them may be attributed to quenching as a result of the interaction between the MPc framework and the substituents. In our study, two lifetimes were observed in DMF for all the substituted Pcs. Average lifetimes were also given in Table 2. The fluorescence lifetimes of the Pcs in DMF were observed within the range expected for Pcs (Table 2).[33-35] The Pcs **7** and **8** showed shorter fluorescence lifetimes in DMF due to lack of metal in the cavity of Pc. On the other hand, the fluorescence lifetimes of the non-peripherally substituted Pcs **3**, **5** and **7** were shorter than those of peripherally substituted Pcs **4**, **6** and **8**, respectively. This result shows the position effect of Pc on fluorescence properties. The natural radiative life time (τ_0) and the rate constants for fluorescence (k_F) values of Pcs (**3-8** and **In(OAc)Pc**) were also determined in DMF. The τ_0 values of unsubstituted **In(OAc)Pc** and the substituted In(OAc)Pcs **3** and **4** were quite longer than ZnPcs (**5** and **6)** and H_2Pcs (**7** and **8)** in DMF. The τ_0 values of the ZnPcs **5** and **6** were also about 5 times longer than those of metal-free counterparts due to metal effect (zinc). The peripheral substituted Pcs **3**, **5** and **7** showed longer τ_0 values than non-peripheral counterparts **4**, **6** and **8** because of the the substituent's position on the Pc ring. The k_F value of the unsubstituted **In(OAc)Pc** and the substituted In(OAc)Pcs **3** and **4** were quite lower than those of other Pcs (**5-8**) due to the heavy metal atom effect of indium.

3.5 Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) of the substituted Pcs and unsubstituted In(OAc)Pc in DMF solution were determined by

Table 2. Photophysical and photochemical parameters for for unsubstituted indium(III) acetate (In(OAc)Pc), zinc (ZnPc) and substituted indium(III) acetate (**3** and **4**), zinc (**5** and **6**) and metal-free (**7** and **8**) phthalocyanines in DMF.

Sample	ΦF	$^a\tau_{F1}$ (ns) ± 0.01	$^a\tau_{F2}$ (ns) ± 0.03	$^a\tau_F$ (average) (ns)	^bk_F(s^{-1}) (x10^7)	τ0 (ns)	Φd (x10^{-3})	ΦΔ
In(OAc)Pc	0.019	0.56 (59.36)	3.27 (40.64)	1.66	1.15	87.37	0.54	0.75
3	0.010	3.06 (68.34)	0.24 (31.96)	2.16	0.46	216.00	2.25	0.88
4	0.013	3.87 (75.32)	0.28 (24.68)	2.98	0.43	229.34	1.91	0.85
ZnPc[c]	0.120	3.64 (100.00)	-	3.64	3.30	30.34	0.023	0.56
5	0.130	2.85 (86.74)	1.31 (13.26)	2.65	4.91	20.38	1.87	0.82
6	0.167	3.90 (89.07)	1.09 (10.93)	3.59	4.65	21.50	1.10	0.76
7	0.085	0.14 (89.24)	2.09 (10.76)	0.36	23.61	4.24	0. 68	0.29
8	0.100	0.53 (89.44)	0.20 (10.56)	0.49	20.41	4.90	0.64	0.22

[a] Abundances shown in brackets.

[b] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_{F\,(average)}$.

[c] Data from Ref.[36]

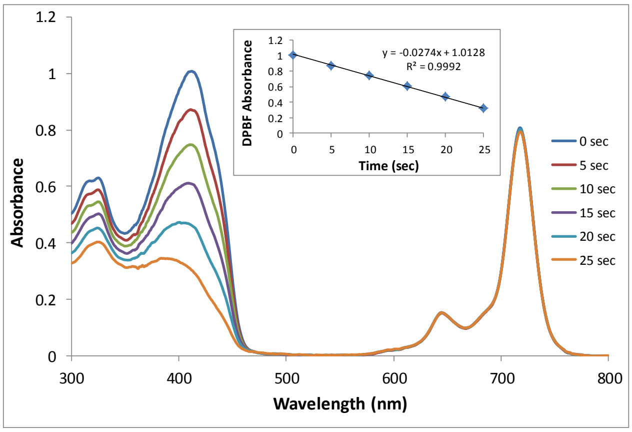


Fig. 7 A typical spectrum for the determination of singlet oxygen quantum yield of compound **3** in DMF at 1x10^{-5} M. (inset: plots of DPBF absorbance versus time)

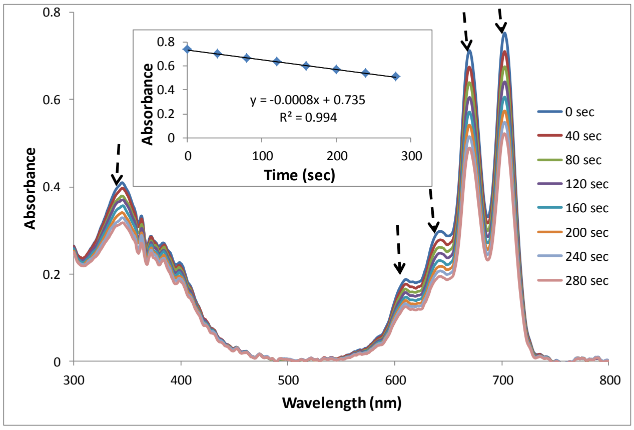


Fig. 8 A typical spectrum for the determination of photodegradation quantum yield of compound **8** in DMF (inset: plot of Q band absorbance versus)

using 1,3-diphenylisobenzofuran (DPBF) as a quencher. There was no change in the Q band intensity during the Φ_Δ determinations and the disappearance of DPBF absorbance at 417 nm, confirmed that complexes were not degraded during singlet oxygen studies (Fig.7 for Pc **3** and Fig. S15 for Pcs **5**, **8** and unsubstituted **In(OAc)Pc** are examples). The Φ_Δ values of In(OAc)Pcs (**3**, **4** and unsubstituted **In(OAc)Pc**) were higher than those of ZnPcs (**5**, **6** and unsubstituted **ZnPc**) and H_2Pcs (**7** and **8**) in DMF. It seems that the coordination of large metal atoms in the Pc cavity remarkably enhances the efficiency of singlet oxygen formation. The Φ_Δ values of the H_2Pcs (**7** and **8**) were lower than those of the other studied Pcs and all the metallo-Pcs gave good singlet oxygen quantum yields (Φ_Δ) which indicate the potential of the metallo-complexes as photosensitizers in applications of PDT (Table 2). On the other hand, the Φ_Δ values of the substituted In(OAc)Pcs (**3** and **4**) and ZnPcs (**5** and **6**) were higher than those of the unsubstituted counterparts (**In(OAc)Pc** and **ZnPc**). The substituent (2,3,6-trimethyl-phenoxy) on the Pc skeleton might increase the singlet oxygen generation and similar results were observed in the literature bearing similar substituents like phenoxy groups.[37-42] The Φ_Δ values of the non-peripherally substituted Pcs (**3**, **5** and **7**) were higher than those of the corresponding peripherally substituted Pcs (**4**, **6** and **8**) in DMF. This result can be explained with the substituent position effect.

3.6. Photodegradation studies

The determination of the degradation of the molecules under irradiation is especially important for those molecules intended for use as photo-catalysts. Generally, Pcs exhibit optimal stability against the decomposition caused by light irradiation. The band shapes of the spectra of the Pcs were not deteriorated under light irradiation and their intensities were observed to be decreasing in B and Q bands (Fig. 8 for **8** and Fig. S16 for **4**, **6** and unsubstituted **In(OAc)Pc**). This result confirmed that the only degradation (not photo-transformation) occurred during the were quite lower than those of other Pcs (**5-8**) due to the heavy metal unsubstituted **In(OAc)Pc** and the substituted In(OAc)Pcs **3** and **4** atom effect of indium.photodegradation studies under light-irradiation. The photo-degradation quantum yield (Φ_d) values of the Pcs were similar to the values of the Pcs in the literature.[43] Stable Pc compounds show Φ_d values as low as 10^{-6} and these values for unstable Pcs in the order of 10^{-3} have been reported.[43] It is believed that the formed singlet oxygen are a decisive species which is responsible for the photodegradation of Pcs.[44] The Φ_d values of the substituted Pcs (**3-8**), unsubstituted **In(AcO)Pc** and **ZnPc** derivatives in DMF were presented in Table 2 In this study, the Φ_d values of the substituted Pc compounds (**3–8**) were higher than those of the unsubstituted counterparts (**In(OAc)Pc** and **ZnPc**). The substituted In(AcO)Pcs (**3** and **4**) also showed lower stability against light irradiation compared to the ZnPcs (**5** and **6**) and H_2Pcs (**7** and **8**) counterparts. Furthermore, the non-peripherally substituted Pcs (**3, 5** and **7**) were less stable when compared to the corresponding peripherally substituted Pcs (**4, 6** and **8**). The higher photodegradation quantum yields of non-peripherally substitution can be explained the HOMO of the phthalocyanine π-system has large molecular orbital coefficients at non-peripherally positions and is destabilized by electron-donating substituents, resulting in a narrowing of the HOMO-LUMO gap and a decrease in the first oxidation potential.[24] While the non-peripherally substituted In(OAc)Pc **3** was the least stable compared to the other complexes, the peripherally substituted metal-free Pc **8** was the most stable compared to the other complexes.

4. Conclusion

In the present work, the syntheses of new non-peripherally and peripherally 2,3,6-trimethylphenoxy tetra-substituted In(III), Zn(II), metal-free phthalocyanines and unsubstituted indium(III)acetate were described and novel compounds were characterized by standard methods (elemental analysis, ^{1}H-NMR, ^{13}C-NMR, (for phthalonitrile compound) MALDI-TOF, IR and UV-*Vis* and fluorescence spectral data). All phthalocyanines (**3-8**) were quite soluble in general organic solvents such as chloroform, DCM, toluene, THF, DMF and DMSO. The photophysical and photochemical properties of the phthalocyanine compounds in DMF were also determined in DMF. The effects of substituent and its positions and the variety of metal on the Pc cavity on these properties were also compared. The excitation spectra of these complexes were similar to absorption spectra of them and both spectra were mirror images of the fluorescent spectra for zinc and metal-free phthalocyanines.

Their fluorescence properties are affected significantly by the change of the central metal. The increase of atom size of the metal remarkably enhances the efficiency of singlet oxygen formation whilst good fluorescence characteristics were retained. The 2,3,6-trimethylphenoxy substituted In(OAc)Pcs (**3** and **4**) and ZnPcs (**5** and **6**) have good singlet oxygen quantum yields (Φ_{Δ}), especially the non-peripherally In(OAc)Pc **3** results in the highest value in DMF. The values of singlet oxygen quantum yield ranging from 0.22 (for the peripherally substituted metal-free Pc **8**) to 0.88 (for the non-peripherally In(OAc)Pc **3**) in DMF indicate of the potential of these complexes as photosensitizers for the PDT of cancer where singlet oxygen is required (Type II mechanism). It was observed that the substitution of the Pc framework with 2,3,6-trimethylphenoxy group as a substituent decreases the photostability of metallo and metal free Pcs in DMF.

Acknowledgment

We are thankful to Marmara University, The Commission of Scientific Research Projects (BAPKO) (Project No: FEN-C-YLP-041213-0459 and FEN-A-130511-0159)

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

[1] K. M. Kadish, K. M. Smith, R. Guilard, (Eds.) *The Porphyrin Handbook, Phthalocyanines: Synthesis of phthalocyanine precursors*, Academic press, California, 2003, vol. 15, Chapter 97.

[2] C. B. Yao, Y. D. Zhang, D. T. Chen, H. T. Yin, C. Q. Yu, J. Li, P. Yuan, *Opt. Laser Technol.*, 2013, **47**, 228.

[3] Y. Shi, X. Y. Li, *Org. Electron.*, 2014, **15**, 286.

[4] O. Adegoke, T. Nyokong, *Synth. Met.*, 2014, **188**, 35.

[5] E. Kakı, A. R. Özkaya, A. Altındal, B. Salih, Ö. Bekaroğlu, *Sens. Actuators, B*, 2013, **188**, 1033.

[6] Z. B. Deng, Z. Y. Lu, Y. L. Chen, Y. H. Yin, Y. Zou, J. Xiao, Y. S. Wang, *Solid-State Electron.*, 2013, **89**, 22.

[7] S. Rao, G. M. Varma, M. M. Srinivas, T. Narayan, K. Varadharajaperumal, *Curr. Appl Phys.*, 2013, **13**,18.

[8] T. Ikeuchi, H. Nomoto, N. Masaki, M. J. Griffith, S. Mori, M. Kimura, *Chem. Commun.*, 2014, **50**, 1941.

[9] M. Kimura, H. Nomoto, H. Suzuki, T. Ikeuchi, H. Matsuzaki, T. N. Murakami, A. Furube, N. Masaki, M. J. Griffith, S. Mori, *Chem. Eur. J.*, 2013, **19**,7496.

[10] B. Lohse, R. Vestberg, M. T. Ivanov, S. Hvilsted, R. H. Berg, C. J. Hawker, P. S. Ramanujam, *Chem. Mater.*, 2008, **20**, 6715.

[11] M. Durmuş, V. Ahsen, *J. Inorg. Biochem.*, 2010, **104**, 297.

[12] D. Çakır, V. Çakır, Z. Bıyıklıoğlu, M. Durmuş, H. Kantekin, *J. Organomet. Chem.*, 2013, **745**, 423.

[13] E. Ranyuk, N. Cauchon, K. Klarskov, B. Guerin, J. E. van Lier, *J. Med. Chem.*, 2013, **56**, 1520.

[14] M. M. Ayhan, A. Singh, C. Hirel, A. G. Gurek, V. Ahsen, E. Jeanneau, I. Ledoux-Rak, J. Zyss, C. Andraud, Y. Bretonniere, *J. Am. Chem. Soc*., 2012, **134**, 3655.

[15] S. Vagin, M. Hanack, *Eur. J. Org. Chem.*, 2003, 2661.

[16] M. V. Martinez-Diaz, G. D. L. Torre, T. Torres, *Chem. Commun.*, 2010, **46**, 7090.

[17] T. T. Tasso, Y. Yamasaki, T. Furuyama, N. Kobayashi, *Dalton Trans.*, 2014, **43**, 5886.

[18] P. M Borsenberger, C. F Groner, M. T. Regan, *Photo conductive elements*, Eastman Kodak Company, 1984, EP 0109842 A2.

[19] M. J. Stillman, T. Nyokong, *in Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publishers, New York, 1989, vol. 1, Chapter 3.

[20] T. Nyokong, *Structure and Bonding, Functional Phthalocyanine Molecular Materials*, ed. J. Jiang and D. M. P. Mingos, *Electronic spectral and electrochemical behaviour of near infrared absorbing metallophthalocyanines*, London, Springer, 2010, vol.135, pp. 45–87.

[21] N. Kobayashi,. H. Ogata, N.;Nonaka, E. A. Luk'yanets, *Chem.Eur.,J.* 2003, **9**, 5123.

[22] A. B. Anderson, T. L. Gorden, M. E. Kenney, *J. Am. Chem. Soc.*, 1985, **107**, 192.

[23] M. Konami, M. Hatano, A. Tajiri, *Chem. Phys. Lett.*, 1990, **166**, 605.

[24] J. Mack, N. Kobayashi, *Chem. Rev.*, 2011, **111**, 281.

[25] A. M. Master, M. E. Rodriguez, M. E. Kenney, N. L. Oleinick, A.S. Gupta, *J. Pharm. Sci.*, 2009, **99**, 2386.

[26] S.C.H. Leung, P-C Lo, D.K.P. Ng, W-K Liu, K-P Fung, W-P Fong, *Brit. J. Pharmacol.*, 2008, **154**, 4.

[27] J. He, H. E. Larkin, Y-S. Li, B.D. Rihter, S. I. A. Zaidi, M.A. J. Rodgers, H. Mukhtar, M. E. Kenney, N. L. Oleinick, *Photochem. Photobiol.*, 1997, **65**(3),581.

[28] R. Decreau, M.J. Richard, P. Verrando, M. Chanon, M. Julliard, *J. Photochem. Photobiol. B: Biol.*, 1999, **48**, 48.

[29] M. Çamur, M. Durmuş, M. Bulut, *J. Photochem. Photobiol. A: Chem.* 2011, **222**, 266.

[30] M. Durmuş, T. Nyokong, *Polyhedron*, 2007, **26**, 2767.

[31] Y. Zorlu, F. Dumoulin, M. Durmuş, V. Ahsen, *Tetrahedron*, 2010, **66**, 3248.

[32] D. M. Maree, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol*., 2001, **140**, 117.

[33] A. Tuhl, W. Chidawanayika, H. M. Ibrahim, N. Al-Awadi, C. Litwinski, T. Nyokong, H. Behbehani, H. Manaa, S. Makhseed, *J. Porphyr. Phthalocya.*, 2012, **16**, 163.

[34] P. Zimcik, V. Novakova, K. Kopecky, M. Miletin, R. Z. U. Kobak , E. Svandrlikova, L. Váchová, K. Lang, *Inorg. Chem.*, 2012, **51**, 4215.

[35] N. Kobayashi, H. Ogata, N. Nonaka, E. A. Luk'yanets, *Chem. Eur. J.*, 2003, **9**, 5123.

[36] S. D'Souza, S. Moeno, T. Nyokong, *Polyhedron*, 2015, **85**, 476.

[37] M. Durmuş, T. Nyokong, *Tetrahedron*, 2007, **63**, 1385.

[38] M. Durmuş, T. Nyokong, *Spectrochim. Acta Part A*, 2008, **69**, 1170.

[39] V. Chauke, M. Durmuş, T. Nyokong, *J. Photochem. Photobiol. A*, 2007, **192**, 179.

[40] M. Pişkin, M. Durmuş, M. Bulut, *Inorg. Chim. Acta*, 2011, **373**, 107.

[41] A. Nas, Ü. Demirbaş, M. Pişkin, M. Durmuş, H. Kantekin, *J. Lumin.*, 2014, **145**, 635.

[42] E. N. Kaya, M. Durmuş, M. Bulut, *J. Organomet. Chem.*, 2014, **774**, 94.

[43] M. Durmuş, *Photochemical and Photophysical Characterization*, in ed. T .Nyokong, V. Ahsen, *Photosensitizers in Medicine, Environment, and Security*, Springer, New York, 2012, pp.135.

[44] G. Schnurpfeil, A. K. Sobbi, W. Spiller, H. Kliesch, D.Wöhrle, *J. Porphyr. Phthalocya.*, 1997, **1**, 159.