Journal of Organometallic Chemistry 696 (2011) 3807–3815

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, photophysical and photochemical properties of highly soluble phthalocyanines substituted with four 3,5-dimethylpyrazole-1-methoxy groups

Rıza Bayrak[a], Hakkı Türker Akçay[b], Mahmut Durmuş[c,*], İsmail Değirmencioğlu[a]

[a] *Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey*
[b] *Department of Chemistry, Faculty of Arts and Sciences, Rize University, 53050 Rize, Turkey*
[c] *Gebze Institute of Technology, Department of Chemistry, P.O.Box 141, 41400, Gebze, Kocaeli, Turkey*

ARTICLE INFO

Article history:
Received 12 July 2011
Received in revised form
28 August 2011
Accepted 1 September 2011

Keywords:
Phthalocyanine
Pyrazole
Photophysical
Photochemical
Quenching

ABSTRACT

The synthesis and characterization of new peripherally tetra-3,5-dimethylpyrazole-1-methoxy substituted metal-free (**4**), zinc (**5**), nickel (**6**), cobalt (**7**), copper (**8**) and lead (**9**) phthalocyanines are described for the first time in this study. The photophysical (fluorescence quantum yields and fluorescence lifetimes) and photochemical (photodegradation and singlet oxygen quantum yields) properties of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanines are studied in dimethylsulfoxide (DMSO). Nickel (**6**), cobalt (**7**) and copper (**8**) phthalocyanines (**6**–**8**) did not evaluate for this purpose due to transition metal and paramagnetic behavior of central metals in the phthalocyanine cavity. The fluorescence quenching behavior of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanines are also investigated. The fluorescence emissions of these phthalocyanines are effectively quenched by 1,4-benzoquinone in DMSO.

1. Introduction

Phthalocyanines (Pcs) have been actively explored for various technological applications since their discovery [1]. Substituted phthalocyanine derivatives have been used in areas such as catalysis [1], chemical sensors [2], liquid crystals [3], semiconductors [4], non-linear optics [5] and photodynamic therapy (PDT) of cancer [6]. The solubility of phthalocyanine derivatives is very important for these applications, because many phthalocyanines are not soluble in organic solvents and aqueous medium. The substitution improves the useful properties of phthalocyanines and usually enhances their solubility. Generally, tetra-substituted phthalocyanines are more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomer mixture [7,8].

Phthalocyanine derivatives have proved to be highly promising as photosensitizers for PDT due to their intense absorption in the long wavelength region of the visible light, high triplet state quantum yields and long triplet lifetime values which are required for an efficient sensitization. The photophysical properties of the phthalocyanine dyes are strongly influenced by the presence and nature of the central metal ion. Complexation of phthalocyanine molecules with transition metals or paramagnetic ions gives dyes short triplet lifetimes. Closed shell or diamagnetic ions, such as Zn^{2+}, Al^{3+} and Si^{4+}, give phthalocyanine complexes both high triplet yields and singlet oxygen generation [9]. Zinc phthalocyanines (ZnPcs) in particular have been extensively studied because of d^{10} configuration of the central Zn^{2+} ion results in optical spectra that are not complicated by additional bands, as in transition-metal Pc complexes. ZnPcs have intensive red-visible region absorption, high singlet and triplet quantum yields. These properties make them important candidates as photosensitizers for PDT applications.

Heterocyclic compounds have so far been synthesized mainly due to the wide range of biological activities. Pyrazoles are one of the most important classes of heterocyclic compounds and they are very significant for medicinal chemistry [10]. Pyrazoles exhibit antiarrhythmic [11], antipyretic [12], analgesic and anti-inflammatory [13], neuroleptic [14], sedative-hypnotic effect [15] and antimicrobial activity [16]. They are inhibitors and deactivators of liver alcohol dehydrogenase [17]. The 3,5-substituted pyrazoles show hypoglycemic activity [13] in glucose primed and diabetic rats. Heterocyclic compounds are also used as intermediaries in the industry of the dyes [18].

There is no research in literature about the PDT activities of pyrazole substituted phthalocyanines and investigation of these properties is compulsory due to the wide range of biological activities of the 3,5-substituted pyrazoles [10–18]. Therefore in this study, 4-[(3,5-dimethyl-1H-pyrazol-1-yl)methoxy]phthalonitrile and its corresponding metal-free and metallophthalocyanine (zinc,

---

[*] Corresponding author. Tel.: +90 262 6053075; fax: +90 262 6053101.
E-mail address: durmus@gyte.edu.tr (M. Durmuş).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.09.002

nickel, cobalt, copper and lead) derivatives synthesized with high yield. The structures of the new compounds were characterized by IR, ^{1}H and ^{13}C NMR, UV–Vis, mass spectroscopies and elemental analysis. Metal-free and metallophthalocyanines show excellent solubility in variety of solvents, which improves the possible applications (such as PDT) of these compounds.

A mixture of phthalocyanine and quinone should be a good mimicker of the natural photosynthetic systems; with the phthalocyanine being the light harvester, and the quinone, the energy transducer. An investigation into the light-harvesting and energy-transducing tendencies of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanine-benzoquinone systems is presented in this work. Quinones are known to quench the excited singlet states of phthalocyanines under red light excitation. This work also explores the effects of substituents and nature of the central metal ions on the fluorescence properties of the phthalocyanines and on the quenching of the phthalocyanines by 1,4-benzoquinone (BQ) using the Stern–Volmer relationship.

2. Experimental

2.1. Materials

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and purified as described by Perrin and Armarego [19]. 1,3-diphenylisobenzofuran (DPBF) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. (3,5-dimethyl-1*H*-pyrazol-1-yl)methanol (**1**) [20] and 4-nitrophthalonitrile (**2**) [21] were prepared according to the literature procedures.

2.2. Equipment

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum FT-IR spectrometer using KBr pellets. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer using chloroform–methanol solvent system. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument and the obtained values agreed with the calculated ones. UV–Vis spectra were recorded by Unicam UV2-100 and Shimadzu 2001 spectrophotometers using 1 cm pathlength cuvettes at room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Melting points were measured on an electrothermal apparatus and are uncorrected.

Photo-irradiations were done using a General Electric quartz line lamp (300 W) for metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanine derivatives. A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample solution. Light intensities were measured using a POWER MAX5100 (Molelectron detector incorporated) power meter.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using equation (1) [22,23].

$$\Phi_F = \Phi_F(\text{Std})\frac{F\cdot A_{\text{Std}}\cdot n^2}{F_{\text{Std}}\cdot A\cdot n_{\text{Std}}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4**, **5** and **9**) and the standard, respectively. A and A_{Std} are the relative absorbance of the samples (**4**, **5** and **9**) and standard at the excitation wavelength, respectively. n and n_{std} are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.20$) [24] was employed as the standard in DMSO. The concentrations of the samples and standard were arranged at 1×10^{-6} M in DMSO.

Natural radiative (τ_0) lifetimes were determined using Photochem CAD program using Strickler–Berg equation [25]. The fluorescence lifetimes (τ_F) were evaluated using equation (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out by using the experimental set-up described in literatures [26–28]. Typically, 3 cm^3 portion of the respective metal-free (**4**), zinc (**5**) or lead (**9**) phthalocyanine solutions ($C = 1\times10^{-5}$ M) containing the DPBF which singlet oxygen quencher was irradiated in the Q band region with the photoirradiation set-up described in references [26–28]. Φ_Δ was determined in air using the relative method with unsubstituted ZnPc as a reference in DMSO. Equation (3) was employed for the calculations of Φ_Δ values:

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}}\frac{R\cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}}\cdot I_{\text{abs}}} \tag{3}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_\Delta^{\text{Std}} = 0.67$ in DMSO) [29]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**4**, **5** and **9**) and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples (**4**, **5** and **9**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quencher was lowered to $\sim3\times10^{-5}$ M [30]. Solutions of sensitizers containing DPBF were prepared in the dark and irradiated in the Q band region using the photoirradiation set-up. DPBF degradation at 417 nm was monitored. The light intensity was 6.54×10^{15} photons s^{-1} cm^{-2} for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

Determination of photodegradation quantum yields (Φ_d) of Pc derivatives were carried out as described in the literatures [26–28]. Φ_d values were determined using equation (4),

$$\Phi_d = \frac{(C_0 - C_t)\cdot V\cdot \text{N}_\text{A}}{I_{\text{abs}}\cdot S\cdot t} \tag{4}$$

where C_0 and C_t are the samples (**4**, **5** and **9**) concentrations before and after irradiation, respectively. V is reaction volume, N_A is the Avogadro's constant, S is irradiated cell area, t is irradiation time and I_{abs} is the overlap integral of the radiation source light intensity. A light intensity of 2.18×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the substituted phthalocyanine compounds (**4**, **5** and **9**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the samples. The concentrations of BQ solutions in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence emission spectra of substituted phthalocyanine derivatives (**4**, **5** and **9**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [31] was shown in equation (5):

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \tag{5}$$

where I_0 and I are the fluorescence intensities of fluorophore (phthalocyanines in this study) in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Stern–Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F. K_{SV} is expressed in equation (6).

$$K_{SV} = k_q \cdot \tau_F \tag{6}$$

The ratios of I_o/I were calculated and plotted against [BQ] according to equation (5), and K_{SV} is determined from the slope.

2.5. Synthesis

2.5.1. 4-[(3,5-dimethyl-1H-pyrazol-1-yl)methoxy]phthalonitrile (3)

3,5-dimethylpyrazole-1-methanol (**1**) (2.52 g, 0.02 mol) was added to a solution of 4-nitrophthalonitrile (**2**) (3.46 g, 0.02 mol) in dry DMF (50 cm^3), and the mixture was stirred at 55–60 °C. Powdered K_2CO_3 (2.76 g, 0.02 mol) was added to this solution in eight equal portions at 15 min intervals with efficient stirring and the reaction system was stirred at the same temperature for 5 days. Then the solution poured into ice-water (150 cm^3). The precipitate was filtered off, washed with water until the filtrate neutral, then diethyl ether and dried in vacuum over P_2O_5. The crude product crystallized from ethyl acetate/petroleum ether (1:1) solvent system to give light brown crystalline powder. Yield: 3.34 g, (66%), mp: 134–136 °C. Anal. Calc. for $C_{14}H_{12}N_4O$: C 66.65, H 4.79, N 22.21; Found: C 66.52, H 4.68, N 22.17. IR [(KBr) ν_{max}/cm^{-1}]: 3091 υ(Ar–CH), 2923–2875 υ(Aliph. CH), 2231 (C≡N), 1624–1601 υ(C=C), 1567–1550 υ(CH=N), 1277–1253 υ(C–O–C)/(C–N), 1140 δ(C–N), 1095–1010 δ(C–O–C), 991 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 7.74–7.70 (d, J = 8.2 Hz, 1H/Ar-H), 7.61–7.57 (d, J = 8.1 Hz, 2H/Ar–H), 5.96 (s, 2H/CH_2), 5.83 (s, 1H/$CH_{pyrazole}$), 2.34 (s, 3H/CH_3(a)), 2.21 (s, 3H/CH_3(b)). ^{13}C NMR ($CDCl_3$), (δ: ppm): 163.34, 148.86, 144.28, 135.44, 123.14, 120.54, 117.65, 115.48 (C≡N), 112.79, 105.14, 101.80 ($CH_{pyrazole}$), 79.67 (CH_2), 13.23 (CH_3(a)), 11.45 (CH_3(b)). MS (ESI), (m/z): Calculated: 252.10; Found: 252.75 $[M]^+$.

2.5.2. Synthesis of metal-free phthalocyanine (4)

The solution of 4-[(3,5-dimethyl-1H-pyrazol-1-yl)methoxy] phthalonitrile (**3**) (0.20 g, 0.79 mmol) in dry n-hexanol (4 cm^3) was heated to 90 °C in a glass tube and DBU (0.44 cm^3, 0.80 mmol) was added to this solution at this temperature. The mixture was heated to 160 °C for 24 h. Then it was cooled to room temperature and diluted with n-hexane (ca. 30 cm^3) and stirred for 12 h. The precipitated product was filtered and then washed with methanol, hot ethanol, and diethyl ether and dried in vacuum over P_2O_5. The solid product was purified with column chromatography on silica gel with chloroform/methanol (50:0.5) solvent system as eluent to give dark green product. Yield: 0.05 g, (25%), mp >300 °C. Anal. Calc. for $C_{56}H_{50}N_{16}O_4$: C 66.52, H 4.98, N 22.16; Found: C 66.34, H 4.77, N 22.25. IR [(KBr) ν_{max}/cm^{-1}]: 3294 (–NH), 3092 υ(Ar–CH), 2925–2871 υ(Aliph. CH), 1721–1614 υ(C=C), 1565 υ(CH=N), 1264–1251 υ(C–O–C)/(C–N), 1135 δ(C–N), 1091–1001 δ(C–O–C), 982 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 7.70 (bs, 4H/Ar–H), 7.56–7.48 (d, J = 7.7 Hz, 8H/Ar–H), 6.08 (s, 8H/CH_2), 5.95 (s, 4H/$CH_{pyrazole}$), 2.35 (s, 12H/CH_3(a)), 2.23 (s, 12H/CH_3(b)). ^{13}C NMR ($CDCl_3$), (δ: ppm): 161.35, 148.21, 147.45, 145.11, 143.17, 133.34, 121.78, 119.45, 118.36, 106.55, 102.71 ($CH_{pyrazole}$), 77.21 (CH_2), 12.85 (CH_3(a)), 12.02 (CH_3(b)). UV/Vis (chloroform): λ_{max} nm (log ε) 700 (5.21), 662 (5.13), 636 (4.83), 600 (4.59), 338 (5.03). MS (ESI), (m/z): Calculated: 1010.42; Found: 1011.58 $[M + H]^+$.

2.5.3. The general procedure for synthesis of metallophthalocyanines (5–8)

The solution of 4-[(3,5-dimethyl-1H-pyrazol-1-yl)methoxy] phthalonitrile (**3**) (0.20 g, 0.790 mmol) and anhydrous metal salts [$Zn(Ac)_2$ (0.036 g, 0.198 mmol), $Ni(Ac)_2$ (0.035 g, 0.198 mmol), $CoCl_2$ (0.025 g, 0.198 mmol), $CuCl_2$ (0.027 g, 0.198 mmol) and $Pb(Ac)_2$ (0.075 g, 0.198 mmol)] in dry n-hexanol (4 cm^3) heated to 90 °C in a glass tube and DBU (0.44 cm^3, 0.8 mmol) was added to this solution. Then the temperature of the mixture was increased to 160 °C and stirred at this temperature for 24 h. Then the mixture was cooled to room temperature and diluted with n-hexane (ca. 30 cm^3) and stirred for 12 h. The precipitated product was filtered and then washed with methanol, hot ethanol, diethyl ether and dried in vacuum over P_2O_5. Finally pure metallophthalocyanines were obtained by column chromatography on silica gel with chloroform/methanol (20:0.5) for compound **5**, (25:0.5) for compound **6**, (23:0.5) for compound **7**, (18:0.5) for compound **8**, and (22:0.5) for compound **9** solvent system as eluents.

*2.5.3.1. Zn(II) phthalocyanine (**5**).* Yield: 0.067 g, (32%), mp >300 °C. Anal. Calc. for $C_{56}H_{48}N_{16}O_4Zn$: C 62.60, H 4.50, N 20.86; Found: C 62.41, H 4.33, N 20.67. IR [(KBr) ν_{max}/cm^{-1}]: 3073 υ(Ar–CH), 2942–2862 υ(Aliph. CH), 1735–1601 υ(C=C), 1572 υ(CH=N), 1252–1217 υ(C–O–C)/(C–N), 1130 δ(C–N), 1099–1005 δ(C–O–C), 972 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 7.72–7.69 (d, J = 7.4 Hz, 4H/Ar–H), 7.54–7.39 (d, J = 8.2 Hz, 8H/Ar–H), 5.93 (s, 8H/CH_2), 5.88 (s, 4H/$CH_{pyrazole}$), 2.31 (s, 12H/CH_3(a)), 2.21 (s, 12H/CH_3(b)). ^{13}C NMR ($CDCl_3$), (δ: ppm): 160.41, 146.78, 145.87, 145.08, 142.15, 131.52, 120.98, 118.78, 116.63, 105.84, 101.32 ($CH_{pyrazole}$), 76.41 (CH_2), 12.53 (CH_3(a)), 11.05 (CH_3(b)). UV/Vis (chloroform): λ_{max} nm (log ε) 682 (5.17), 618 (4.46), 356 (4.92). MS (ESI), (m/z): Calculated: 1072.33; Found: 1072.45 $[M]^+$.

*2.5.3.2. Ni(II) phthalocyanine (**6**).* Yield: 0.055 g, (26%), mp >300 °C. Anal. Calc. for $C_{56}H_{48}N_{16}O_4Ni$: C 62.99, H 4.53, N 20.99; Found: C 62.83, H 4.39, N 20.86. IR [(KBr) ν_{max}/cm^{-1}]: 3088 υ(Ar–CH), 2917–2867 υ(Aliph. CH), 1630–1617 υ(C=C), 1585–1547 υ(CH=N), 1245 υ(C–O–C)/(C–N), 1125 δ(C–N), 1085–1015 δ(C–O–C), 985 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 7.72 (bs, 4H/Ar–H), 7.55–7.37 (d, J = 7.2 Hz, 8H/Ar–H), 5.90 (bs, 12H/CH2 + CHpyrazole), 2.29 (s, 12H/CH_3(a)), 2.20 (s, 12H/CH_3(b)). ^{13}C NMR ($CDCl_3$), (δ: ppm): 163.32, 147.14, 144.28, 144.08, 141.56, 130.96, 121.46, 119.62, 116.54, 104.25, 102.03 (CHpyrazole), 76.79 (CH_2), 11.59 (CH_3(a)), 10.23 (CH_3(b)). UV/Vis (chloroform): λ_{max} nm (log ε) 673 (5.15), 606 (4.38), 334 (4.67). MS (ESI), (m/z): Calculated: 1066.34; Found: 1067.96 $[M + H]^+$.

*2.5.3.3. Co(II) phthalocyanine (**7**).* Yield: 0.068 g, (32%), mp >300 °C. Anal. Calc. for $C_{56}H_{48}N_{16}O_4Co$: C 62.98, H 4.53, N 20.98; Found: C 62.77, H 4.35, N 20.77. IR [(KBr) ν_{max}/cm^{-1}]: 3086 υ(Ar–CH), 2913–2869 υ(Aliph. CH), 1622–1615 υ(C=C), 1587–1553 υ(CH=N), 1251 υ(C–O–C)/(C–N), 1147 δ(C–N), 1074–1010 δ(C–O–C), 992 δ(CH). UV/Vis (chloroform): λ_{max} nm (log ε) 676 (5.21), 608 (4.43), 350 (4.82). MS (ESI), (m/z): Calculated: 1067.34; Found: 1068.63 $[M + H]^+$.

*2.5.3.4. Cu(II) phthalocyanine (**8**).* Yield: 0.038 g, (18%), mp >300 °C. Anal. Calc. for $C_{56}H_{48}N_{16}O_4Cu$: C 62.71, H 4.51, N 20.89; Found: C 62.61, H 4.38, N 20.75. IR [(KBr) ν_{max}/cm^{-1}]: 3094 υ(Ar–CH), 2923–2884 υ(Aliph. CH), 1615–1605 υ(C=C), 1575–1541 υ(CH=N), 1248 υ(C–O–C)/(C–N), 1132 δ(C–N), 1064–1018

δ(C–O–C), 978 δ(CH). UV/Vis (chloroform): λ_{max} nm (log ε) 678 (5.19), 610 (4.52), 338 (4.81). MS (ESI), (m/z): Calculated: 1071.33; Found: 1071.85 $[M]^+$.

*2.5.3.5. Pb(II) phthalocyanine (**9**).* Yield: 0.055 g, (23%), mp >300 °C. Anal. Calc. for $C_{56}H_{48}N_{16}O_4Pb$: C 55.30, H 3.98, N 18.43, Found: C 55.15, H 3.30, N 18.52. IR [(KBr) ν_{max}/cm^{-1}]: 3065 υ(Ar–CH), 2950–2851 υ(Aliph. CH), 1662–1614 υ(C=C), 1565–1471 υ(CH=N), 1273 υ(C–O–C)/(C–N), 1126 δ(C–N), 1082–1049 δ(C–O–C), 976 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 7.78–7.64 (m, 4H/Ar–H), 7.55–7.37 (d, $J = 7.8$ Hz, 8H/Ar–H), 5.96 (s, 8H/CH_2), 5.90 (s, 4H/$CH_{pyrazole}$), 2.34 (s, 12H/CH_3(a)), 2.21 (s, 12H/CH_3(b)). ^{13}C NMR ($CDCl_3$), (δ: ppm): 164.42, 148.55, 143.45, 142.26, 142.03, 131.75, 122.64, 120.19, 116.38, 104.82, 101.45 ($CH_{pyrazole}$), 75.19 (CH_2), 10.98 (CH_3(a)), 10.02 (CH_3(b)). UV/Vis (chloroform): λ_{max} nm (log ε) 712 (5.13), 643 (4.47), 359 (4.70). MS (ESI), (m/z): Calculated: 1216.38; Found: 1216.76 $[M]^+$.

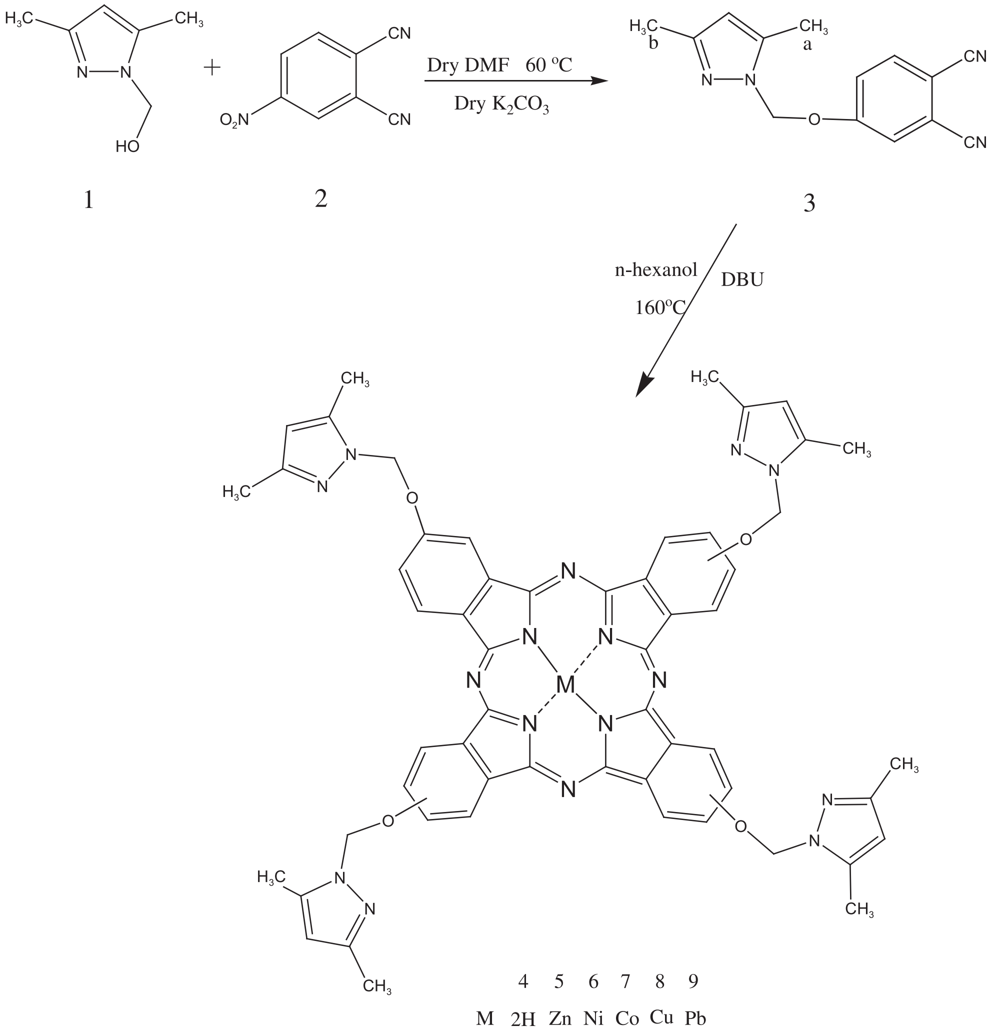
3. Results and discussion

3.1. Outlook of the synthesized compounds

The synthesis route of 3,5-dimethylpyrazole-1-methoxy substituted phthalonitrile (**3**), its target metal-free (**4**) and metallophthalocyanines (**5, 6, 7, 8** and **9**) is shown in Scheme 1. The structures of novel compounds have been characterized by a combination of ^1H and ^{13}C NMR, IR, UV-Vis spectroscopy, elemental analysis and mass spectral data.

*3.1.1. Synthesis of 3,5-dimethylpyrazole-1-methoxy substituted phthalonitrile (**3**)*

The preparation of phthalonitrile derivative **3** was achieved from the reaction of 3,5-dimethylpyrazole-1-methanol (**1**) and 4-nitrophthalonitrile (**2**) in the presence of anhydrous K_2CO_3 as base in DMF under N_2 atmosphere at 60 °C for 5 days. This is accomplished by base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with compound **1** [32–35]. The structure of the target compound was confirmed by spectral investigation. In the IR spectrum (KBr pellets) the formation of compound **3** clearly indicated by the disappearance of –OH stretching/deformation of compound **1** at 3349/1331 cm^{-1} and NO_2 stretching of compound **2** at 1519, 1333 cm^{-1} and by the appearance of C≡N absorption band at 2231 cm^{-1}. Its ^1H NMR spectrum (in $CDCl_3$) was also in good agreement with the structure of the synthesized compound. Phenolic (D_2O exchangeable) –OH at 7.81 ppm disappeared after condensation. In addition, compound **1** have no aromatic groups and of course have no aromatic signals, but after the condensation two doublets at ca. $\delta = 7.74–7.70$ and



Scheme 1. Synthetic route of novel phthalocyanine compounds.

7.61–7.57 appeared in the spectrum. Additionally, the ^{1}H NMR spectrum of **3** showed two singlet peaks at $\delta = 5.96$ (-CH$_2$), 5.83 (HC$_{\text{pyrazole}}$) as expected. Also two methyl groups (**a** and **b**) on the pyrazole moiety of compound **3** are not identical because of the electronegative oxygen and phthalonitrile group. So the signal of the methyl group **a** showed more downfield shift (2.34 ppm) than methyl group **b** (2.21 ppm). The proton-decoupled ^{13}C NMR spectrum indicated the presence of nitrile carbon atoms for compound **3** at 115.48 ppm. In addition, the mass spectrum of **3** showed a molecular ion peak at $m/z = 252.75$ [M]$^+$, supporting the proposed formula for this compound.

3.1.2. Syntheses of 3,5-dimethylpyrazole-1-methoxy substituted metal-free (*4*) and metallophthalocyanines (*5–8*)

The peripherally tetra-substituted metal-free phthalocyanine (**4**) was obtained by cyclotetramerization of compound **3** in n-hexanol in the presence of DBU under reflux for 24 h. Also, cyclotetramerization of substituted phthalonitrile compound (**3**) in the presence of the metal salts [Zn(CH$_3$COO)$_2$, Ni(CH$_3$COO)$_2$, CoCl$_2$, CuCl$_2$ and Pb(CH$_3$COO)$_2$] and DBU in dry n-hexanol at 160 °C for 24 h gave the tetra-substituted metallophthalocyanines (**5**, **6**, **7**, **8** and **9**), respectively.

The spectroscopic characterization of the novel phthalocyanine compounds includes ^{1}H NMR, IR, UV/Vis and mass spectral investigations, and the results are in accordance with the proposed structures. Cyclotetramerization of phthalonitrile compound (**3**) to metal-free Pc (**4**) was confirmed by the disappearance of the sharp C≡N vibration at 2231 cm^{-1} in their own IR spectra. The IR spectrum of the metal-free phthalocyanine (**4**) showed usual inner core –NH absorption at 3294 cm^{-1}, that is characteristic for metal-free phthalocyanines. The rest of the spectrum of **4** was similar to that of **3**. In the ^{1}H NMR spectrum of compound **4** shielded inner core –NH protons could not be observed due to the probable strong aggregation. The signals belong to aromatic and aliphatic protons of **4** represent the significant absorbance characteristics of the proposed structure. Furthermore, the ESI mass spectrum of compound **4** showed a molecular ion peak at $m/z = 1011.58$ [M]$^+$, supporting the proposed formula for this compound. In addition, elemental analysis values were also satisfactory.

The disappearance of the C≡N vibration of phthalonitrile compound (**3**) at 2231 cm^{-1} in the IR spectra of metallophthalocyanines (**5–9**) proves the formation of these phthalocyanine compounds. The ^{1}H NMR spectra of **7** and **8** could not be determined because of the presence of paramagnetic cobalt and copper atoms [36] in the phthalocyanine core. The ^{1}H NMR spectra of the compounds **5** and **6** were almost similar to those of the metal-free phthalocyanine **4**. In the mass spectra of compounds **5–9**, the parent molecular ion peaks were observed at $m/z = 1072.45$ [M]$^+$ for **5**, 1067.96 [M + 1]$^+$ for **6**, 1068.63 [M + 1]$^+$ for **7**, 1071.85 [M]$^+$ for **8** and 1216.76 [M]$^+$ for **9** confirmed the proposed structures.

3.1.3. UV–Vis absorption spectra

The metal-free (**4**) and metallophthalocyanines (**5–9**) exhibit typical electronic spectra with two strong absorption regions, one around ca. 300 nm is called as the "B" or Soret band because of electronic transitions from deeper π-HOMO to n*-LUMO energy levels, while the other one at 600–750 nm is called as the "Q" band, due to electronic transitions from π-HOMO to π*-LUMO energy levels [37]. One of the best indicators of the formation of phthalocyanines is their UV–Vis spectra in dilute solution (Figs. 1 and 2). The Q band of the metal-free phthalocyanine was observed as splitted two bands due to D$_{2h}$ symmetry, as Q$_x$ and Q$_y$ bands [38,39]. The electronic absorption spectrum of compound **4** in chloroform solution at room temperature is shown in Fig. 1. The splitting Q band was observed at $\lambda_{\max}$ 700 and 662 nm, indicating the structure with non-degenerate D$_{2h}$ symmetry [39–41].

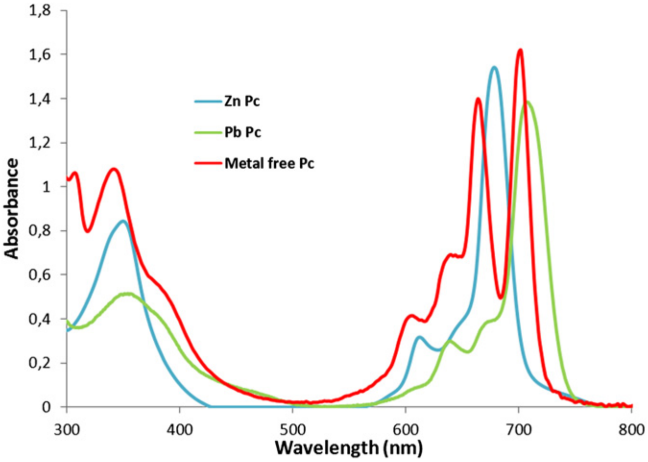


Fig. 1. Absorption spectra of compounds **4**, **5** and **9** in CHCl$_3$ at 1×10^{-5} M.

The UV–Vis absorption spectra of metallophthalocyanines (**5–9**) (Figs. 1 and 2) showed strong Q absorption bands between 673 and 712 nm with shoulders at 606–643 nm -sign of the degenerate D$_{4h}$ symmetry- and B bands at ca. 340 nm [42] in chloroform. The sharp bands in Figs. 1 and 2 are evidence of the presence of non-aggregated species at measured concentration. It has been well established that non-aggregated Pcs are extremely important for their various applications [43]. The Q band of the lead phthalocyanine complex (**9**) was red-shifted when compared to the corresponding other studied phthalocyanine complexes (**4–8**), suggesting that the non-planar effect of the bigger lead as central atom.

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, type of the complexed metal ions and temperature. In this study, the aggregation behavior of the studied phthalocyanine compounds (**4–9**) was investigated at different concentrations in DMSO. In DMSO, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species for the studied phthalocyanine compounds (**4–9**), (Fig. 3 as an example for compound **9**). Beer–Lambert law was obeyed for these compounds in the concentrations ranging from 1.2×10^{-5} to $2 \text{ x } 10^{-6}$ M in DMSO.

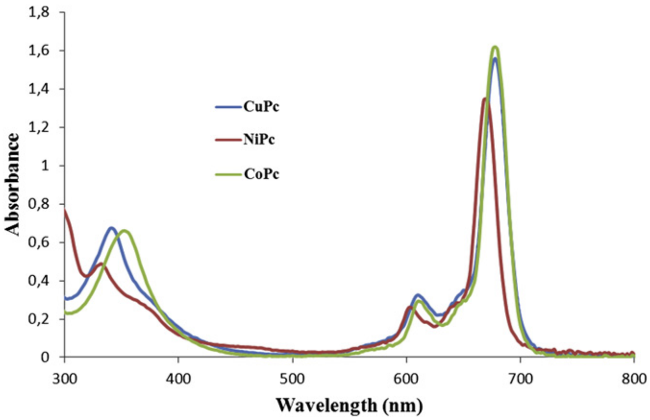


Fig. 2. Absorption spectra of compounds **6**, **7** and **8** in CHCl$_3$ at 1×10^{-5} M.

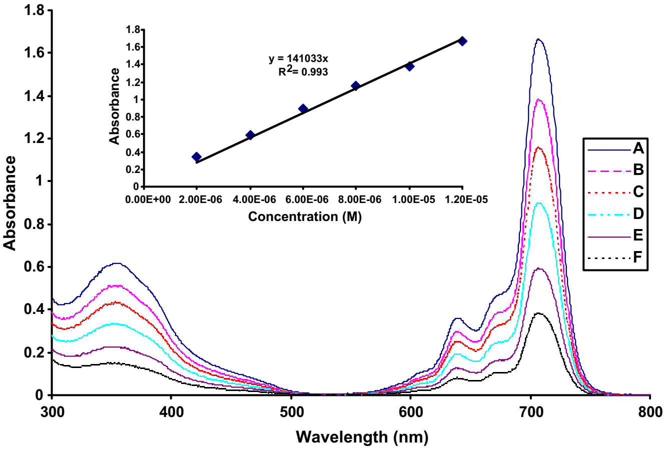


Fig. 3. Absorption spectra changes of compound **9** in DMSO at different concentrations: 12×10^{-6} (A),10×10^{-6} (B), 8×10^{-6} (C), 6×10^{-6} (D), 4×10^{-6} (E), 2×10^{-6} (F) M. (Inset: Plot of absorbance versus concentration).

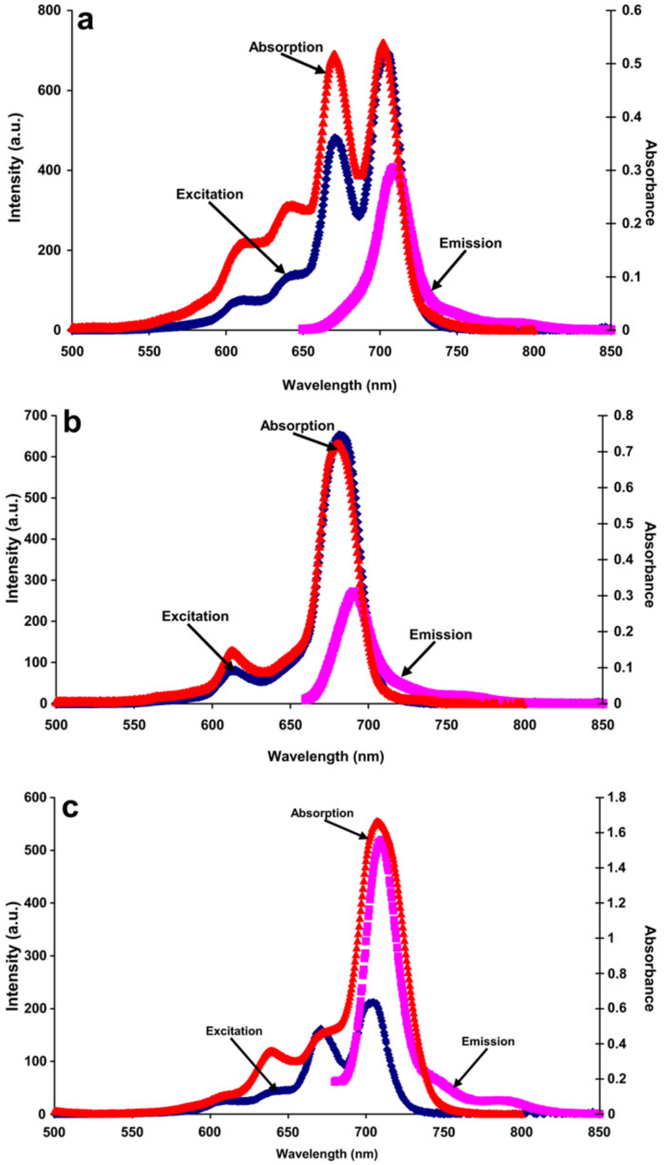


Fig. 4. Absorption, fluorescence, emission and excitation spectra for: (a) compound **4**, (b) compound **5** and (c) compound **9** in DMSO. Excitation wavelengths = 640 nm for **4**, 650 nm for **5** and 670 nm for **9**.

3.1.4. Fluorescence spectra

The fluorescence behavior of the metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanines were studied in DMSO. Fig. 4 shows the absorption, fluorescence emission and excitation spectra of these complexes in DMSO. The shapes of the excitation spectra were similar to absorption spectra for the metal-free (**4**) and zinc phthalocyanine (**5**) compounds (Fig. 4a and b) suggesting that the proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for phthalocyanine derivatives **4** and **5** suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation. However, for the lead phthalocyanine compound (**9**), the shape of excitation spectra was different from the absorption spectra in that the Q band of the former showed two peaks in the Q band region, Fig. 4c, unlike the narrow Q band of the latter. This attribute that there are changes in the molecule following excitation most likely due to the larger lead metal being out of the plane of the phthalocyanine ring.

Fluorescence emission and excitation peaks for compounds **4**, **5** and **9** in DMSO are listed in Table 1. Fluorescence emission peaks were observed at 710 nm for **4**, 692 nm for **5** and 710 nm for **9** in DMSO. While the observed Stokes shift of the substituted zinc phthalocyanine complex (**5**) is higher, the metal-free (**4**) and lead (**9**) phthalocyanine compounds are lower than unsubstituted ZnPc (**Std-ZnPc**), (Table 1). The nickel (**6**), cobalt (**7**) and copper (**8**) phthalocyanine compounds did not show fluorescence in DMSO.

3.2. Photophysical properties of metal-free (4), zinc (5) and lead (9) phthalocyanines

3.2.1. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanine compounds are typical of Pc compounds in DMSO, but the Φ_F values of lead phthalocyanine compound (**9**) is lower than for other studied phthalocyanine compounds (**4** and **5**) in DMSO (Table 2) suggesting that there are more changes in the molecule following excitation in DMSO most likely due to the larger lead metal being out of the plane of the phthalocyanine ring. While the Φ_F values of the substituted metal-free and lead phthalocyanine compounds are lower than unsubstituted ZnPc (**Std-ZnPc**), the Φ_F value of zinc phthalocyanine complex is similar with experimental error. A decrease in fluorescence intensity (hence yield) may occur in the presence of substituted groups which increase of the fluorescence quenching. Thus the decrease in the Φ_F values for substituted phthalocyanine compounds in the presence of the ring substituents suggests that the substituents more quench the excited singlet state. The substituted metal-free complex (**4**) shows higher Φ_F values than other studied Pc compounds in DMSO (Table 2).

Fluorescence lifetime (τ_F) is the average time a molecule stays in its excited state before fluorescence, and its value is directly related

Table 1
Absorption, excitation and emission spectral data for unsubstituted and substituted phthalocyanines in DMSO.

Compound	Q band λ_{max}, (nm)	(log ε)	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
4	671, 702	4.55, 4.58	671, 703	710	8
5	680	4.72	681	692	12
9	708	5.10	671, 705	710	2
Std-ZnPc[a]	672	5.14	672	682	10

[a] Data from Ref. [50].

Table 2
Photophysical and photochemical parameters of unsubstituted and substituted phthalocyanines in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	k_F (s^{-1}) (x10^7)[a]	Φ_d (x 10^{-5})	Φ_Δ
4	0.19	3.95	20.79	4.81	8.08	0.17
5	0.17	2.99	17.63	5.68	6.76	0.78
9	0.13	1.07	8.21	12.14	36.24	0.22
Std-ZnPc[b]	0.20	1.22	6.80	1.47	2.61	0.67

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Data from Ref. [50].

to that of Φ_F. The longer the lifetime means the higher the fluorescence quantum yield. Any factor that shortens the fluorescence lifetime of a fluorophore (phthalocyanine in this study) indirectly reduces the value of Φ_F. Such factors include internal conversion and intersystem crossing. As a result, the nature and the environment of a fluorophore determine its fluorescence lifetime. Lifetimes of fluorescence (τ_F, Table 2) were calculated using the Strickler—-Berg equation. Using this equation, a good correlation has been found between experimentally and the theoretically determined lifetimes for the unaggregated molecules [23]. Thus we suggest that the τ_F values obtained using this equation are an appropriate measure of fluorescence lifetimes. Generally, the τ_F values of the studied phthalocyanine compounds (**4**, **5** and **9**) are within the range reported for Pc compounds [44]. While the τ_F values are higher for substituted metal-free (**4**) and zinc (**5**) phthalocyanine compounds, the τ_F value of lead phthalocyanine compound (**9**) is lower when compared to unsubstituted ZnPc (**Std-ZnPc**) (Table 2). For the substituted complexes, longer τ_F value is obtained for the metal-free (**4**) phthalocyanine compound compared to other studied phthalocyanine complexes (**5** and **9**).

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 2. τ_0 values of the studied phthalocyanine compounds (**4**, **5** and **9**) are longer than **Std-ZnPc** in DMSO. The substituted metal-free phthalocyanine compound (**4**) showed the longest τ_0 values when compared to other substituted complexes (**5** and **9**) in DMSO. The rate constants for fluorescence (k_F) values of studied phthalocyanine compounds (**4**, **5** and **9**) are also higher than **Std-ZnPc** in DMSO. The k_F value of substituted lead phthalocyanine compound (**9**) is highest among the studied phthalocyanine compounds in DMSO.

*3.3. Photochemical properties of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanines*

3.3.1. Singlet oxygen quantum yields

An effective photosensitizer must be very productive in generating singlet oxygen for photocatalytic reactions such as PDT. Energy transfer between the triplet state of a photosensitizer (such as phthalocyanine) and the ground state of molecular oxygen leads to the production of singlet oxygen and must be highly efficient to generate large amounts of singlet oxygen. This is quantified by the singlet oxygen quantum yield (Φ_Δ) and this parameter can be give an indication of the potential of compounds to be used as photosensitizers in PDT applications. In this study, singlet oxygen quantum yields (Φ_Δ) of the studied phthalocyanine compounds (**4**, **5** and **9**) were determined in DMSO via chemical method using DPBF as a quencher. The disappearance of DPBF absorption was monitored using UV–vis spectrophotometer (Fig. 5 as an example for compound **5**). Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen such as triplet excited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. There was no change in the Q band intensity of studied phthalocyanine compounds (**4**, **5** and **9**) during the Φ_Δ determination, confirming that complexes were not decompose during singlet oxygen studies. It is believed that during photosensitization, the phthalocyanine is firstly excited to the singlet excited state and through intersystem crossing reaches the triplet state, then transfers its energy to ground state oxygen, $O_2(^3\sum_g)$, converted into its excited state (singlet oxygen), $O_2(^1\Delta_g)$. This singlet oxygen is the chief cytotoxic species, which subsequently oxidizes the surrounding substrates. This oxidation is the key of the Type II mechanism for PDT.

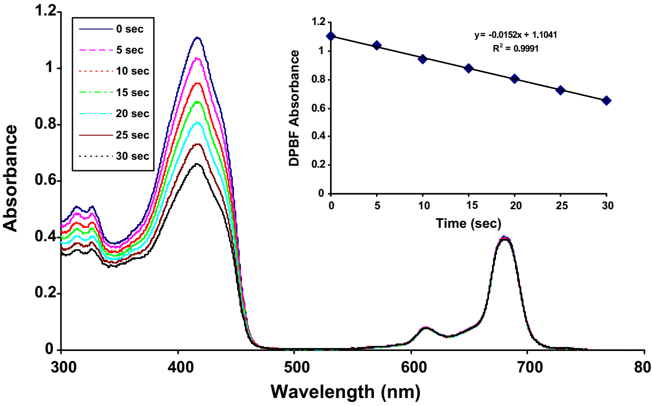


Fig. 5. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **5** in DMSO at a concentration of 1.0 × 10^{-5} M (Inset: Plots of DPBF absorbance versus time).

The value of Φ_Δ is higher for studied zinc phthalocyanine compound (**5**) when compared to respective **Std-ZnPc** complex in DMSO. But, the Φ_Δ values of studied metal-free (**4**) and lead (**9**) phthalocyanine compounds are lower than **Std-ZnPc** in DMSO (Table 2). When compared to the Φ_Δ values among the studied phthalocyanine compounds (**4**, **5** and **9**), substituted zinc phthalocyanine compound (**5**) shows highest Φ_Δ values in all studied compounds.

3.3.2. Photodegradation study

Photodegradation of the molecules under light irradiation can be used to study their stability and this is important for their application as photocatalytic reactions (such as photosensitization). Photodegradation is an oxidative degradation of a photosensitizer molecule with time into lower molecular weight fragments under

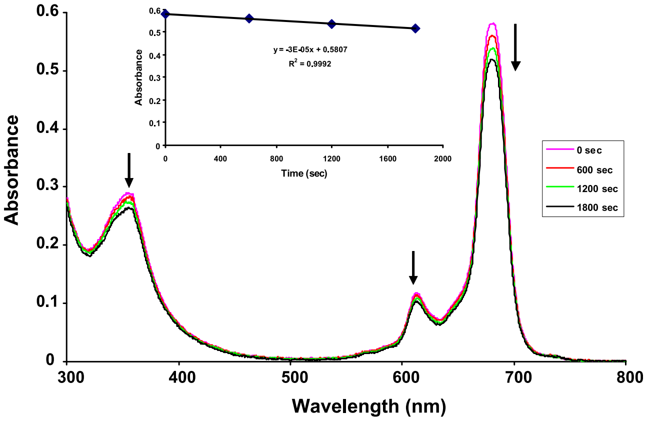


Fig. 6. The photodegradation of compound **5** in DMSO showing the disappearance of the Q band at 10 min intervals. (Inset: Plot of Q band absorbance versus time).

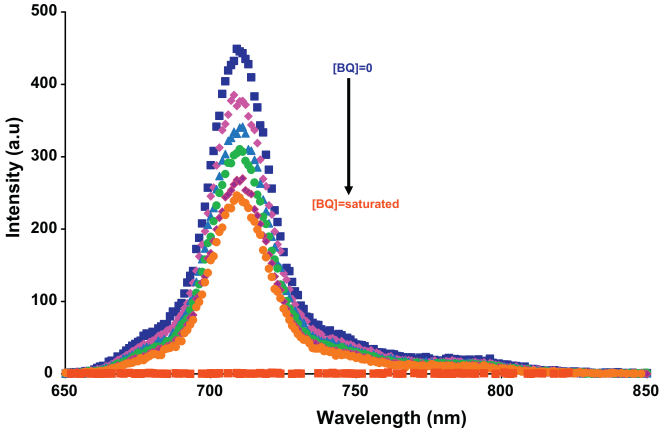


Fig. 7. Fluorescence emission spectral changes of compound **4** (1.00 × 10^{-5} M) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M and saturated with BQ.

light. Photodegradation generally depends on the structure of the molecule, concentration, solvent and light intensity [30].

The spectral changes observed for all the studied phthalocyanine compounds (**4**, **5** and **9**) during light irradiation are as shown in Fig. 6 (using complex **5** in DMSO as an example). The collapse of the absorption spectra without any distortion of the shape confirms photodegradation not associated with phototransformation for studies phthalocyanine compounds (**4**, **5** and **9**).

The photodegradation quantum yield (Φ_d) values of the studied phthalocyanine compounds (**4**, **5** and **9**) in DMSO are given in Table 2. Stable phthalocyanine molecules show the Φ_d values as low as 10^{-6} [44]. All studied phthalocyanine compounds (**4**, **5** and **9**) are less stable to degradation compared to **Std-ZnPc** in DMSO (Table 2) because the Φ_d values of all studied phthalocyanine compounds (**4**, **5** and **9**) are higher than **Std-ZnPc** in DMSO (Table 2). Thus the substitution of phthalocyanine compounds with 3,5-dimethylpyrazole-1-methoxy groups seems to decrease the stability of these complex in DMSO. The substituted lead phthalocyanine compound (**9**) is the lowest stable derivative among the studied phthalocyanine compounds suggesting that heavy atom effect of the lead atom.

3.4. *Fluorescence quenching studies of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanines by 1,4-benzoquinone (BQ)*

Phthalocyanine complexes may also be used as photosynthetic mimickers. An essential requirement for an effective photosynthetic mimicker is the ability to undergo excited state charge transfer with ease such as phthalocyanine-quinone systems have proved to be favored candidates for understanding of energy transfer process [27,45]. The fluorescence quenching of studied phthalocyanine compounds (**4**, **5** and **9**) by BQ in DMSO was found to obey Stern–Volmer kinetics. Fig. 7 shows the quenching of compound **4** by BQ in DMSO as an example. The slope of the plots shown at Fig. 8 gave K_{SV} values of the studied phthalocyanine compounds. The Stern–Volmer plots for all studied phthalocyanine compounds (**4**, **5** and **9**) gave straight lines, depicting diffusion-controlled quenching mechanisms. Quinones have high electron affinities and their involvement in electron transfer processes is well documented [46]. The energy of the lowest excited state for quinones is greater than the energy of the excited singlet state of phthalocyanine compounds [47]. Therefore, energy transfer from the excited phthalocyanine molecule to BQ is not likely to occur. Moreover, phthalocyanine compounds are known to be easily reduced. Therefore, fluorescence quenching of phthalocyanine compounds by BQ is via excited state electron transfer from the phthalocyanine to the BQ [48]. The K_{SV} and bimolecular quenching constant (k_q) values for the BQ quenching of phthalocyanine compounds in DMSO are listed in Table 3. The K_{SV} values of the substituted phthalocyanine compounds (**4**, **5** and **9**) are lower than **Std-ZnPc** in DMSO. When compared the substituted complexes, compound **4** showed the highest K_{SV} values, while compound **9** showed the lowest K_{SV} values in DMSO. The substitution of the phthalocyanine framework with 3,5-dimethylpyrazole-1-methoxy groups seems to decrease the K_{SV} values of the phthalocyanine compounds. The bimolecular quenching constant (k_q) values of the studied phthalocyanine compounds (**4**, **5** and **9**) were also lower than for **Std-ZnPc** in DMSO, thus substitution with 3,5-dimethylpyrazole-1-methoxy groups seems to decrease the k_q values of the complexes. The k_q values of the studied phthalocyanine compounds (**4**, **5** and **9**) were found to be close to the diffusion-controlled limits, ~ 10^{10} M^{-1} s^{-1}, which is in agreement with the Einstein–Smoluchowski approximation at room temperature for diffusion-controlled bimolecular interactions [49].

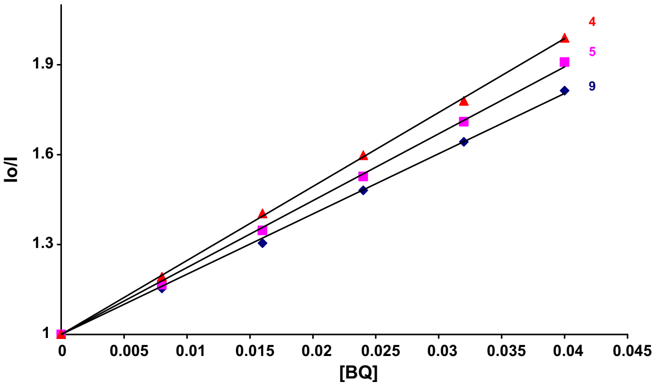


Fig. 8. Stern–Volmer plots for BQ quenching of **4**, **5** and **9** in DMSO. [MPc] ~1.00 × 10^{-5} M [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

Table 3
Fluorescence quenching data for unsubstituted and substituted phthalocyanines in DMSO.

Compound	K_{SV} (M^{-1})	$k_q/10^{10}$(dm^3 mol^{-1} s^{-1})
4	24.69	0.62
5	22.33	0.75
9	20.11	1.88
Std-ZnPc[a]	31.90	2.61

[a] Data from Ref. [50].

4. Conclusion

In this paper, the synthesis of new highly soluble tetrakis-3,5-dimethylpyrazole-1-methoxy substituted metal-free (**4**), zinc (**5**), nickel (**6**), cobalt (**7**), copper (**8**) and lead (**9**) phthalocyanines have been reported. The new compounds have been characterized by IR, UV–Vis, ^{1}H and ^{13}C NMR, mass spectroscopy and elemental analysis. The photophysical and photochemical properties of metal-free (**4**), zinc (**5**) and lead (**9**) phthalocyanine compounds have also been investigated in DMSO for comparison of the central metal effect on these properties. All the compounds show excellent solubility in most solvents such as chloroform, toluene, DMF, DMSO etc. In the UV–Vis spectra, while the metal-free complex (**4**) shows splitting Q band, the metallophthalocyanines (**5**–**9**) exhibit single narrow Q bands as expected and support the formation of phthalocyanine complexes. The substitution of the 3,5-dimethylpyrazole-1-methoxy substituents on the phthalocyanine ring increased the wavelength of the Q band. The fluorescence behavior of the studied phthalocyanine compounds (**4**, **5** and **9**) have been studied in DMSO. The fluorescence quantum yields of studied phthalocyanine compounds are typical for Pcs. The Φ_F values of the studied phthalocyanine compounds are lower than **Std-ZnPc**. The studied lead phthalocyanine compound (**9**) showed lowest Φ_F value could be due to the larger lead metal ion. In DMSO, the Φ_Δ values of studied phthalocyanine compounds ranged from 0.17 (for compound **9**) to 0.78 (for compound **5**) gives an indication of the potential of the compounds as photosensitizers (especially compound **5**) in photocatalytic applications such as PDT. While the studied metal-free (**4**) and zinc (**5**) phthalocyanine compounds showed similar stability, the lead phthalocyanine compound (**9**) exhibits lower stability than other studied phthalocyanine complexes most likely due to the larger lead metal atom. The fluorescence quenching behavior of the studied phthalocyanine compounds have been studied by BQ in DMSO. The studied phthalocyanine compounds (**4**, **5** and **9**) showed lower K_{SV} values when compared to the **Std-ZnPc**.

Acknowledgment

The authors thank to The Research Fund of Karadeniz Technical University, Projects No: 2010.111.002.3 and 2010.111.002.8. (Trabzon/Turkey).

References

[1] C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol:1–4, VCH Publishers, New York, 1989–1992–1993.
[2] G. Guillaud, J. Simon, J.P. Germain, Coord. Chem. Rev. 180 (1998) 1433–1484.
[3] J.A. Duro, G. de la Torre, J. Barber, J.L. Serrano, T. Torres, Chem. Mater. 8 (1996) 1061–1064.
[4] C.G. Classens, W.J. Blau, M. Cook, M. Hanack, R.J.M. Nolte, T. Torres, D. Wöhrle, Monatsh. Chem. 132 (2001) 3–11.
[5] M.A. Díaz-García, I. Ledoux, J.A. Duro, T. Torres, F. Agulló-López, J. Zyss, J. Phys. Chem. 98 (1994) 8761–8764.
[6] C.M. Allen, W.M. Sharman, J.E. van Lier, J. Porphyrins Phthalocyanines 5 (2001) 161–169.
[7] A. Beck, K.M. Mangold, M. Hanack, Chem. Ber. 124 (1991) 2315–2321.
[8] W. Eberhardt, M. Hanack, Synthesis-Stuttgart (1997) 95–100.
[9] H. Ali, J.E. van Lier, Chem. Rev. 99 (1999) 2379–2450.
[10] A.A. Bekhit, T. Abdel-Aziem, Bioorg. Med. Chem. 12 (2004) 1935–1945.
[11] R.W. Hamilton, J. Heterocyclic Chem. 13 (1976) 545–553.
[12] M. Windholz (Ed.), The Merck Index, 11th ed. Merck and Co, New Jersey, 1989.
[13] N.M. Abd-El Gawad, G.S. Hassan, G.S. Georgey, Med. Chem. Res. (2011). doi:10.1007/s00044-011-9606-4.
[14] D.J. Abraham, Burger's Medicinal Chemistry, Drug Discovery and Development. Wiley, New York, 1980.
[15] L.S. Goodman, A. Gilman, The pharmacological basis of therapeutics. Macmillan, New York, 1980.
[16] K. Ramalingam, G.X. Thyvelikakath, K.D. Berlin, R.W. Chesnul, R.P. Brown, N.N. Durham, S.E. Ealick, D. Vander Helm, J. Med. Chem. 20 (1977) 847–850.
[17] R.W. Fries, D.P. Bohlken, B.V. Plapp, J. Med. Chem. 22 (1979) 356–359.
[18] H.A. Lubs, The chemistry of synthetic dyes and pigments. American Chemical Society, Washington, 1970.
[19] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals. Pergamon, Oxford, 1989.
[20] I. Dvoretzky, G.H. Richter, J. Org. Chem. 15 (1950) 1285–1288.
[21] G.J. Young, W. Onyebuagu, J. Org. Chem. 55 (1990) 2155–2159.
[22] S. Fery-Forgues, D. Lavabre, J. Chem. Educ. 76 (1999) 1260–1264.
[23] M.D. Maree, T. Nyokong, K. Suhling, D. Phillips, J. Porphyrins Phthalocyanines 6 (2002) 373–376.
[24] A. Ogunsipe, J.Y. Chen, T. Nyokong, New J. Chem. 28 (2004) 822–827.
[25] H. Du, R.C.A. Fuh, J.Z. Li, L.A. Corkan, J.S. Lindsey, Photochem. Photobiol. 68 (1998) 141–142.
[26] J.H. Brannon, D. Madge, J. Am. Chem. Soc. 102 (1980) 62–65.
[27] A. Ogunsipe, T. Nyokong, J. Photochem. Photobiol. A: Chem. 173 (2005) 211–220.
[28] I. Seotsanyana-Mokhosi, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A: Chem. 140 (2001) 215–222.
[29] N. Kuznetsova, N. Gretsova, E. Kalmkova, E. Makarova, S. Dashkevich, V. Negrimovskii, O. Kaliya, E. Luk'yanets, Russ. J. Gen. Chem. 70 (2000) 133–140.
[30] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Roder, G. Schnurpfeil, J. Porphyrins Phthalocyanines 2 (1998) 145–158.
[31] J. Rose, Advanced physico-chemical experiments. Sir Isaac Pitman & Sons Ltd, London, 1964.
[32] İ Değirmencioğlu, R. Bayrak, M. Er, K. Serbest, Dyes Pigm. 83 (2009) 51–58.
[33] İ Değirmencioğlu, E. Atalay, M. Er, Y. Köysal, Ş Işık, K. Serbest, Dyes Pigm. 84 (2010) 69–78.
[34] K. Serbest, İ Değirmencioğlu, Y. Ünver, M. Er, C. Kantar, K. Sancak, J. Organomet. Chem. 692 (2007) 5646–5654.
[35] İ Değirmencioğlu, R. Bayrak, M. Er, K. Serbest, Polyhedron 30 (2011) 1628–1636.
[36] D. Kulac, M. Bulut, A. Altındal, A.R. Özkaya, B. Salih, Ö Bekaroğlu, Polyhedron 26 (2007) 5432–5440.
[37] Y. Gök, H. Kantekin, İ Değirmencioğlu, Supramol. Chem. 15 (2003) 335–343.
[38] B. Akkurt, E. Hamuryudan, Dyes Pigm. 79 (2008) 153–158.
[39] H.Y. Yenilmez, A.İ. Okur, A. Gül, J. Organomet. Chem. 692 (2007) 940–945.
[40] M. Durmuş, S. Yeşilot, B. Çoşut, A.G. Gürek, A. Kılıç, V. Ahsen, Synth. Met 160 (2010) 436–444.
[41] N. Nombona, W. Chidawanyika, T. Nyokong, Polyhedron 30 (2011) 654–659.
[42] I. Booysen, F. Matemadombo, M. Durmuş, T. Nyokong, Dyes Pigm. 89 (2011) 111–119.
[43] W.M. Sharman, S.V. Kudrevich, J.E. van Lier, Tetrahedron Lett. 37 (1996) 5831–5834.
[44] T. Nyokong, Coord. Chem. Rev. 251 (2007) 1707–1722.
[45] J.S. Connolly, J.R. Bolton, Photoinduced electron transfer reactions: Inorganic substrates and applications. in: M.A. Fox, M. Chanon (Eds.), Photoinduced electron transfer, Part D. Elsevier, Amsterdam, 1988.
[46] A. Ogunsipe, T. Nyokong, J. Porphyrins Phthalocyanines 9 (2005) 121–129.
[47] J.R. Darwent, I. McCubbin, D. Phillips, J. Chem. Soc. Faraday Trans. 78 (1982) 347–357.
[48] M. Idowu, T. Nyokong, J. Photochem. Photobiol. A: Chem. 204 (2009) 63–68.
[49] G.B. Dutt, N. Periasamy, J. Chem. Soc. Faraday Trans. 87 (1991) 3815–3820.
[50] I. Gürol, M. Durmuş, V. Ahsen, T. Nyokong, Dalton Trans. (2007) 3782–3791.