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Novel organosoluble metal-free and metallophthalocyanines bearing triazole moieties: Microwave assisted synthesis and determination of photophysical and photochemical properties

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ABSTRACT

The synthesis and characterization of new peripherally metal-free (**4**), nickel (**5**), zinc (**6**), cobalt (**7**), copper (**8**) and lead (**9**) phthalocyanines bearing tetra-2-(4-(4-methoxybenzylamino)-5-oxo-3-*p*-tolyl-4, 5-dihydro-1*H*-1, 2, 4-triazol-1-yl)ethoxy groups have been described for the first time in this study. These new phthalocyanine compounds have been characterized by several spectral methods such as FT-IR, ^{1}H NMR, ^{13}C NMR, electronic spectroscopy, mass spectra and elemental analyses. The thermal stabilities of these new phthalocyanines were determined by thermogravimetric analysis. The photophysical (fluorescence quantum yields and fluorescence lifetimes) and photochemical (singlet oxygen generations and photodegradation quantum yields) properties of metal-free (**4**), zinc (**6**) and lead (**9**) phthalocyanines were studied in dimethylsulfoxide (DMSO). The fluorescence quenching behavior of metal-free (**4**), zinc (**6**) and lead (**9**) phthalocyanines was also investigated.

1. Introduction

A compound that was called phthalocyanine (Pc) was discovered by happenstance in 1907 by Braun and Tcherniac as a highly colored by-product in the chemical conversion of some *orto*-(1,2)-disubstituted benzene derivatives [1]. The first conducted experiments astounded people who were not aimed to acquire the brand-new forms of this molecule. After that these happenstance based developments, Pc derivatives aroused a great deal of scientific interest. After the chain of events as the coincidence, even though scientists had dealt with spectacularly charming material for years, the structure of metal-free and metallophthalocyanines were firstly and elaborately illuminated by Linstead and his colleagues in 1934. Namely, the first observations of a molecule which was later called “phthalocyanine” date back to the aforementioned period. A phenomenon was proved and determined that it is plausible to place around seventy different elemental ions in the central cavity of Pc, and the choice of central metal cation can vigorously influence its chemical and physical properties [1].

Frequently, blue-green colored Pc derivatives are used as dyes and pigments [2] due to $\pi-\pi^*$ bands associated with the planar aromatic π-conjugation system. These blue-green compounds, which have high stability against light and air, have considerably attracted a good deal of interest in several application areas via 18 π electron macrocyclic conjugation systems [3].

The exploration of Pcs has affected every aspect of the inorganic and the other chemistry divisions. Aside from the use of dyes and pigments, phthalocyanines, which are completely synthetic compounds, have been used in many branches of industry and especially in the medical field at incremental speed. Phthalocyanines are also used in liquid crystal applications [4,5], chemical sensors [6–9], solar cells [10–12], corrosion inhibitors [13,14], gas sensors [15], optical data storage devices [16,17], light emitting diodes (LED) [18], semiconductors [19,20]. Particularly, the usage of Pcs attracts attention as light-sensitive material for the treatment of cancer cells with photodynamic therapy (PDT) and this vital issue is being investigated by many scientists for the health of human beings [21–24]. Photodynamic therapy is a sophisticated innovative treatment that uses special form of light-activated drugs, called

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as *photosensitizing/photosensitizer agents,* accompanied by light to detect and destroy cancer cells. This therapy method (PDT), which is also called phototherapy or photochemotherapy, takes minutes to complete and the absolute results provide incentives for researchers to develop new and useful photosensitizer agents.

In general, two different methods are used for synthesis of Pc compounds: one of them is microwave processing and the other one is classical thermal method in a high-boiling solvent with metal salts [25]. Microwave processing technique has a good number of advantages over the other technique which is already known. One of the most preferable advantages is that accelerate the reaction time ultimately [26]. The other inherent advantages of microwave processing are selective, direct, controllable and internal [27].

Our understanding of the Pc has advanced very rapidly over the last years. Hereafter, Pcs should be investigated and developed as much as possible that will benefit many implementation area of tomorrow's modern science just as above mentioned.

Symmetrically substituted metal-free (**4**) and metallophthalocyanines (**5**–**9**) containing tetra-triazole moieties which were synthesized by the classical and microwave irradiation technique have been described in this study. These new phthalocyanine compounds have been characterized using several spectral methods and elemental analyses, as well. Metal-free (**4**) and metallophthalocyanines (**5**–**9**) show excellent solubility in a variety of solvents, which improves on the possible applications of these compounds. The thermal behavior of these phthalocyanine compounds was determined by thermogravimetric analysis (TGA). The photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties of metal-free (**4**), zinc (**6**) and lead (**9**) phthalocyanines were investigated in DMSO.

2. Experimental

2.1. Materials

All reagents and solvents were dried and purified before use as described by Perrin and Armarego [28]. All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. 1-(2-Hydroxyethyl)-4-(4-methoxybenzylamino)-3-p-tolyl-1H-1,2,4-triazol-5(4H) one (**1**) [29] and 4-nitrophthalonitrile (**2**) [30] were prepared according to the reported procedures.

2.2. Equipments

All reactions were carried under a dry nitrogen atmosphere using standard Schlenk techniques. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer using KBr pellets. Electronic spectra were recorded by Unicam UV2-100 and Shimadzu 2101 spectrophotometers using 1 cm path length cuvettes at the room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at the room temperature. Mass spectra were performed on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (δ) relative to TMS as an internal standard. Elemental analyses and metal contents of novel compounds were performed on a Vario MICRO Elemental Analyzer at Anadolu University in Turkey. Melting points were measured on an electrothermal apparatus. Domestic microwave oven was used for carrying out the synthesis of all metallophthalocyanines. A Seiko II Exstar 6000 thermal analyzer was performed in order to record the DTA curves under a nitrogen atmosphere with a heating rate of 20 °C min^{-1} in the temperature range of 30–900 °C using platinum crucibles.

Photo-irradiations were done using a General Electric quartz line lamp (300 W) for metal-free (**4**), zinc (**6**) 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 Eq. (1) [31,32].

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4**, **6** and **9**) and the standard, respectively. A and A_{Std} are the relative absorbance of the samples (**4**, **6** 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 ($\Phi_F = 0.20$) [33] 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 PhotochemCAD program using Strickler-Berg equation [34]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (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 literature [35–37]. Typically, 3 mL portion of the respective metal-free (**4**), zinc (**6**) or lead (**9**) phthalocyanine solutions ($C = 1 \times 10^{-5}$ M) containing the 1,3-diphenylisobenzofuran (DPBF) which singlet oxygen quencher was irradiated in the Q band region with the photoirradiation set-up described in Refs. [35–37]. Φ_Δ values were determined in air using the relative method with unsubstituted ZnPc as a reference in DMSO. Eq. (3) was employed for the calculations of Φ_Δ values:

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

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_\Delta^{\mathrm{Std}} = 0.67$ in DMSO) [38]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**4**, **6** and **9**) and standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the samples (**4**, **6** 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 $\sim 3 \times 10^{-5}$ M [39]. 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 6.57×10^{15} photons s^{-1} cm^{-2} for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

The photodegradation quantum yields (Φ_d) of Pc derivatives were carried out as described in the literature [35–37]. Φ_d values were determined using Eq. (4),

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

where C_0 and C_t are the samples (**4**, **6** 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 2.19×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.5. Synthesis

2.5.1. 4-(2-(4-(4-methoxybenzylamino)-5-oxo-3-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-1-yl)ethoxy)phthalonitrile (*3*)

1-(2-Hydroxyethyl)-4-(4-methoxybenzylamino)-3-p-tolyl-1H-1,2,4-triazol-5(4H) one (**1**) (1.51 g, 4.26 mmol) was dissolved in dry DMF (20 mL) at 50 °C under a nitrogen atmosphere and *4*-nitrophthalonitrile (**2**) (0.74 g, 4.26 mmol) was added to the solution with stirring. After stirring for 15 min, finely ground anhydrous K_2CO_3 (2.35 g, 17.04 mmol) was added portionwise over 2 h, with efficient stirring. The reaction mixture was stirred under a nitrogen atmosphere at 50 °C during 120 h. At the end of this period, the progress of reaction was checked by thin layer chromatography (TLC). Then, the obtained mixture was poured into 150 mL ice-water. The aqueous phase was extracted with chloroform (3 × 50 mL), and the extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was dried *in vacuo* and recrystallized from ethanol to give yellow precipitate. Yield: 1.4 g (68%), m.p.: 138–140 °C. Calc. for $C_{27}H_{24}N_6O_3$: % C 67.49, % H 5.03, % N 17.49. Found: % C 67.73, % H 5.07, % N 17.45. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3273 (N–H), 3043 (Ar–H), 2991–2835 (Aliph. C–H), 2226 (C≡N), 1703 (C=O), 1603 (C=N), 1564, 1512, 1402, 1394, 1297, 1248, 1104, 1028, 826, 739, 648, 525. ^1H NMR ($CDCl_3$) (δ: ppm): 7.82 (Ar–H, 2H, d), 7.78 (Ar–H, 1H, s), 7.73 (Ar–H, 2H, d), 7.69 (Ar–H, 2H, d), 7.31 (Ar–H, 2H, d), 7.16 (Ar–H, 2H, d), 4.87 (NH, 1H, s), 4.45 (OCH_2, 2H, t), 4.42 (N–CH_2, 2H, s), 4.08 (NH–CH_2, 2H, t), 2.42 (OCH_3, 3H, s), 1.65 (CH_3, 3H, s). ^{13}C NMR ($CDCl_3$) (δ: ppm): 161.64, 159.67, 153.41, 145.29, 140.96, 135.48, 130.85, 129.36, 127.62, 123.37, 120.04, 119.68, 115.34, 114.07, 112.58, 108.09, 66.18, 55.49, 54.46, 44.80, 21.77, 19.17. MS (ES^+), *m/z*: Calc.: 480.53; Found: 480.35 $[M]^+$.

2.5.2. Metal-free phthalocyanine (*4*)

A mixture of 4-(2-(4-(4-methoxybenzylamino)-5-oxo-3-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-1-yl)ethoxy)phthalonitrile (**3**) (0.2 g, 0.4162 mmol), and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry *n*-pentanol (2 mL) was stirred and heated at 160 °C in a sealed glass tube for 24 h under a nitrogen atmosphere and degassed several times. After cooling to the room temperature, the reaction mixture was precipitated by the addition of ethanol (10 mL) and this green product was filtered off. It was washed several times successively with hot ethanol, distilled water and diethyl ether in order to removing the unreacted organic impurities. After drying *in vacuo*, this compound was purified by preparative thin layer chromatography using chloroform–methanol (97:3) solvent system as eluent. The product is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO, benzene, pyridine. Yield: 36 mg (18%), m.p.: 418–442 °C (decomposition). Calc. for $C_{108}H_{98}N_{24}O_{12}$: % C 67.42, % H 5.13, % N 17.47. Found: % C, 67.88% H, 5.32% N 17.04. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3244 (N–H), 3032 (Ar–H), 2927–2862 (Aliph. C–H), 1704 (C=O), 1612, 1512, 1247, 1175, 1114, 1034, 942, 821, 742. ^1H NMR ($CDCl_3$) (δ: ppm): 7.89 (Ar–H, 8H, d), 7.76 (Ar–H, 4H, s), 7.71 (Ar–H, 8H, d), 7.58 (Ar–H, 8H, d), 7.34 (Ar–H, 8H, d), 7.15 (Ar–H, 8H, d), 5.39 (NH, 4H, s), 4.63–4.03 (N–CH_2, 16H, m), 4.21 (NH–CH_2, 8H, s), 2.28 (OCH_3, 12H, s), 1.27 (CH_3, 12H, s). ^{13}C NMR ($CDCl_3$) (δ: ppm): 178.36, 158.41, 152.88, 142.69, 142.05, 134.47, 130.89, 129.25, 127.83, 127.65, 123.76, 114.02, 100.93, 68.54, 55.42, 36.78, 22.47, 19.12. UV/vis ($CHCl_3$): λ, nm (log ε): 707 (5.26), 671 (5.26), 644 (5.09), 611 (4.90), 389 (4.95). MS (ES^+), *m/z*: Calc.: 1924.12; Found: 1924.53 $[M]^+$.

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

A mixture of 4-(2-(4-(4-methoxybenzylamino)-5-oxo-3-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-1-yl)ethoxy)phthalonitrile (**3**) (0.2 g, 0.4162 mmol), anhydrous metal salts [$NiCl_2$ (13.5 mg, 0.1041 mmol), $Zn(CH_3COO)_2$ (19 mg, 0.1041 mmol), $CoCl_2$ (13.5 mg, 0.1041 mmol), $CuCl_2$ (14 mg, 0.1041 mmol), PbO (23.2 mg, 0.1041 mmol)] and two drops of DBU in *2*-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W, for a few minutes. Then the reaction mixture was cooled to the room temperature, ethanol (30 mL) was added to the mixture and stirred overnight. At the end of this period, this mixture was filtered off. The green crude product was refluxed with ethanol for 5 h. Then it was filtered off again. Finally, obtained dark green product was washed several times successively with hot ethanol, distilled water and diethylether in order to removing the unreacted organic impurities and then dried *in vacuo* over P_2O_5. The crude product was purified by preparative thin layer chromatography using chloroform:methanol solvent system [(92:8) for compound **5**, (95:5) for compound **6**, (94:6) for compound **7**, (95:5) for compound **8**, (94:6) for compound **9**] as eluent. The metallophthalocyanine complexes are soluble in $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO, benzene, pyridine.

*2.5.3.1. Nickel(II) phthalocyanine (**5**).* Yield: 55 mg (27%), m.p.: 335–434 °C (decomposition). Calc. for $C_{108}H_{96}N_{24}NiO_{12}$: % C 65.49, % H 4.89, % N 16.97. Found: % C 64.87, % H 5.26, % N 15.44. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3246 (N–H), 3030 (Ar–H), 2928–2873 (Aliph. C–H), 1708 (C=O), 1611, 1512, 1419, 1246, 1175, 1095, 1033, 821, 739. ^1H NMR ($CDCl_3$) (δ: ppm): 7.71 (Ar–H, 8H, d), 7.69 (Ar–H, 4H, s), 7.56–7.51 (Ar–H, 24H, m), 7.15 (Ar–H, 8H, d), 5.08 (NH, 4H, s), 4.23–4.07 (N–CH_2, 16H, m), 4.20 (NH–CH_2, 8H, s), 2.03 (OCH_3, 12H, s), 1.26 (CH_3, 12H, s). ^{13}C NMR ($CDCl_3$) (δ: ppm): 168.07, 152.37, 136.07, 132.65, 131.17, 130.89, 129.06, 127.87, 125.06, 114.78, 68.40, 60.66, 30.53, 21.95, 19.43. UV/vis ($CHCl_3$): λ, nm (log ε): 677 (5.52), 620 (5.00), 386 (5.03). MS (ES^+), *m/z*: Calc. 1980.79; Found: 1981.72 $[M + H]^+$.

*2.5.3.2. Zinc(II) phthalocyanine (**6**).* Yield: 66 mg (32%), m.p.: 408–463 °C (decomposition). Calc. for $C_{108}H_{96}N_{24}O_{12}Zn$: % C 65.27, % H 4.87, % N 16.91. Found: % C 65.33, % H 5.00, % N 16.72. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3271 (N–H), 3027 (Ar–H), 2927–2873 (Aliph. C–H), 1708 (C=O), 1609, 1512, 1457, 1247, 1120, 821, 744.. ^1H NMR ($CDCl_3$) (δ: ppm): 7.86 (Ar–H, 8H, d), 7.79 (Ar–H, 4H, s), 7.73–7.69 (Ar–H, 16H, m), 7.27–7.12 (Ar–H, 16H, m), 5.15 (NH, 4H, s), 4.59–4.12 (N–CH_2, 16H, m), 4.10 (NH–CH_2, 8H, s), 2.28 (OCH_3, 12H, s), 1.26 (CH_3, 12H, s). ^{13}C NMR ($CDCl_3$) (δ: ppm): 159.17, 152.95, 144.67, 140.13, 139.92, 130.54, 128.92, 128.44, 127.51, 123.44, 113.70, 104.72, 67.24, 54.99, 35.17, 21.41, 19.14. UV/vis ($CHCl_3$): λ, nm (log ε): 684 (5.27), 617 (4.78), 356 (5.20). MS (ES^+), *m/z*: Calc.: 1987.49; Found: 1987.13 $[M]^+$.

*2.5.3.3. Cobalt(II) phthalocyanine (**7**).* Yield: 49 mg (24%), m.p.: 444–474 °C (decomposition). Calc. for $C_{108}H_{96}CoN_{24}O_{12}$: % C 65.48,

% H 4.88, % N 16.97. Found: % C 65.50, % H 4.96, % N 16.01. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3250 (N–H), 3024 (Ar–H), 2925–2857 (Aliph. C–H), 1704 (C=O), 1612, 1513, 1452, 1246, 1123, 1035, 821, 750. UV/vis ($CHCl_3$): λ, nm (log ε): 677 (5.16), 611 (4.74), 326 (5.11). MS (ES$^+$), *m/z*: Calc.: 1981.03; Found: 2005.55 $[M + H + Na]^+$.

*2.5.3.4. Copper(II) phthalocyanine (**8**).* Yield: 78 mg (38%), m.p.: 439–468 °C (decomposition). Calc. for $C_{108}H_{96}CuN_{24}O_{12}$: % C 65.33, % H 4.87, % N 16.93. Found: % C 65.54, % H 4.98, % N 15.79. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3253 (N–H), 3029 (Ar–H), 2931–2852 (Aliph. C–H), 1704 (C=O), 1609, 1512, 1496, 1247, 1177, 1034, 822, 748. UV/vis ($CHCl_3$): λ, nm (log ε): 687 (5.20), 628 (5.08), 350 (5.22). MS (ES$^+$), *m/z*: Calc.: 1985.65; Found: 1985.02 $[M]^+$.

*2.5.3.5. Lead(II) phthalocyanine (**9**).* Yield: 55 mg (25%), m.p.: 389–426 °C (decomposition). Calc. for $C_{108}H_{96}N_{24}O_{12}Pb$: % C 60.92, % H 4.54, % N 15.79. Found: % C 61.20, % H 4.71, % N 15.81. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3256 (N–H), 3012 (Ar–H), 2928–2862 (Aliph. C–H), 1705 (C=O), 1610, 1512, 1487, 1334, 1248, 1114, 1036, 821, 744. ^{1}H NMR ($CDCl_3$) (δ: ppm): 7.74–7.69 (Ar–H, 20H, m), 7.55–7.54 (Ar–H, 16H, m), 7.15 (Ar–H, 8H, d), 5.08 (NH, 4H, s), 4.24–4.08 ($N-CH_2$, 16H, m), 4.22 ($NH-CH_2$, 8H, s), 2.03 (OCH_3, 12H, s), 1.26 (CH_3, 12H, s). ^{13}C NMR ($CDCl_3$) (δ: ppm): 173.32, 158.24, 152.38, 149.63, 145.18, 136.63, 130.90, 129.26, 128.28, 124.75, 114.62, 107.40, 68.44, 55.42, 36.06, 29.96, 22.04, 19.41. UV/vis ($CHCl_3$): λ, nm (log ε): 720 (5.29), 654 (4.80), 367 (5.11). MS (ES$^+$), *m/z*: Calc.: 2129.30; Found: 2129.18 $[M]^+$.

3. Results and discussion

3.1. Synthesis and characterization

The initial step in the synthetic procedure, which was depicted in Scheme 1, was the formation of *4-(2-(4-(4-methoxybenzylamino)-5-oxo-3-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-1-yl)ethoxy)phthalonitrile* (**3**). The target compound (**3**) was synthesized by the reaction of *1-(2-hydroxyethyl)-4-(4-methoxybenzylamino)-3-p-tolyl-1H-1,2,4-triazol-5(4H) one* (**1**) with *4*-nitro phthalonitrile (**2**) in the presence of finely ground anhydrous potassium carbonate as a base [40] at 50 °C in dimethylformamide (DMF) for 120 h with the yield of 68% after crystallization from ethanol. The formation of compound **3** was obviously verified by the disappearance of the –OH band of compound **1** and the $-NO_2$ band of compound **2**, the appearance of considerably sharp C≡N stretching vibration band at 2226 cm^{-1} in the FT-IR spectrum of this compound. Furthermore, the intense vibration bands of compound **3** were observed at 3273 cm^{-1} corresponding to –NH (stretching) groups, at 1703 cm^{-1} corresponding to C=O groups, at 1603 cm^{-1}corresponding to C=N groups, at 1564 cm^{-1} corresponding to –NH (bending) groups, at 1248 cm^{-1} attributable to aromatic C–O–C groups. In the ^{1}H NMR spectrum of compound **3** in deuterated chloroform, the signal belonging to OH proton for the precursor compound **1** disappeared after formation of compound **3**. The aromatic protons were observed at $\delta = 7.82-7.16$ ppm, N–H proton was observed at $\delta = 4.87$ ppm and the aliphatic protons were observed at $\delta = 4.45-1.65$ ppm, respectively. ^{13}C NMR spectral data were in good agreement with the proposed structure. In the ^{13}C NMR spectrum of **3**, the characteristic signals were observed at $\delta = 115.34$ and 114.07 ppm related to dicyano carbon atoms. In the mass spectrum of compound **3**, the presence of characteristic molecular ion peak at *m/z*: 480.35 $[M]^+$ confirmed the proposed structure.

The conversion of compound **3** into the tetrasubstituted metal-free phthalocyanine (**4**) was achieved in the presence of a few drops of DBU as *N*-donor base in *n*-pentanol at 160 °C for 24 h under a nitrogen atmosphere by classical method in 18% yield (Scheme 1). The FT-IR spectrum of the metal-free phthalocyanine (**4**) considerably indicated the tetramerization of the dicyano derivative with the disappearance of the C≡N peak at 2226 cm^{-1} for compound **3**. The resonance at 3244 cm^{-1} was assigned to the N–H stretching vibration. The NH stretching absorption band of the inner core of the metal-free phthalocyanine (**4**) was not distinguished from NH stretching absorption band of triazole unit. In the ^{1}H NMR spectrum of compound **4**, the aromatic protons were observed at 7.89–7.15 ppm and the aliphatic protons were observed at 4.63–1.27 ppm. There was a broad signal at 5.39 ppm belonging to N–H proton of triazole unit. The typical shielding of inner core protons belonging to metal-free phthalocyanines, which are generally located at negative ppm region [41], were not observed in the ^{1}H NMR spectrum of compound **4** because of strong aggregation [42]. The ^{13}C NMR spectrum was almost identical for compound **4** by disappearance of the peaks belonging to dicyano carbons at 115.34 and 114.07 ppm. In the mass spectrum of compound **4**, the presence of characteristic molecular ion peak at *m/z*: 1924.53 $[M]^+$ confirmed the proposed structure.

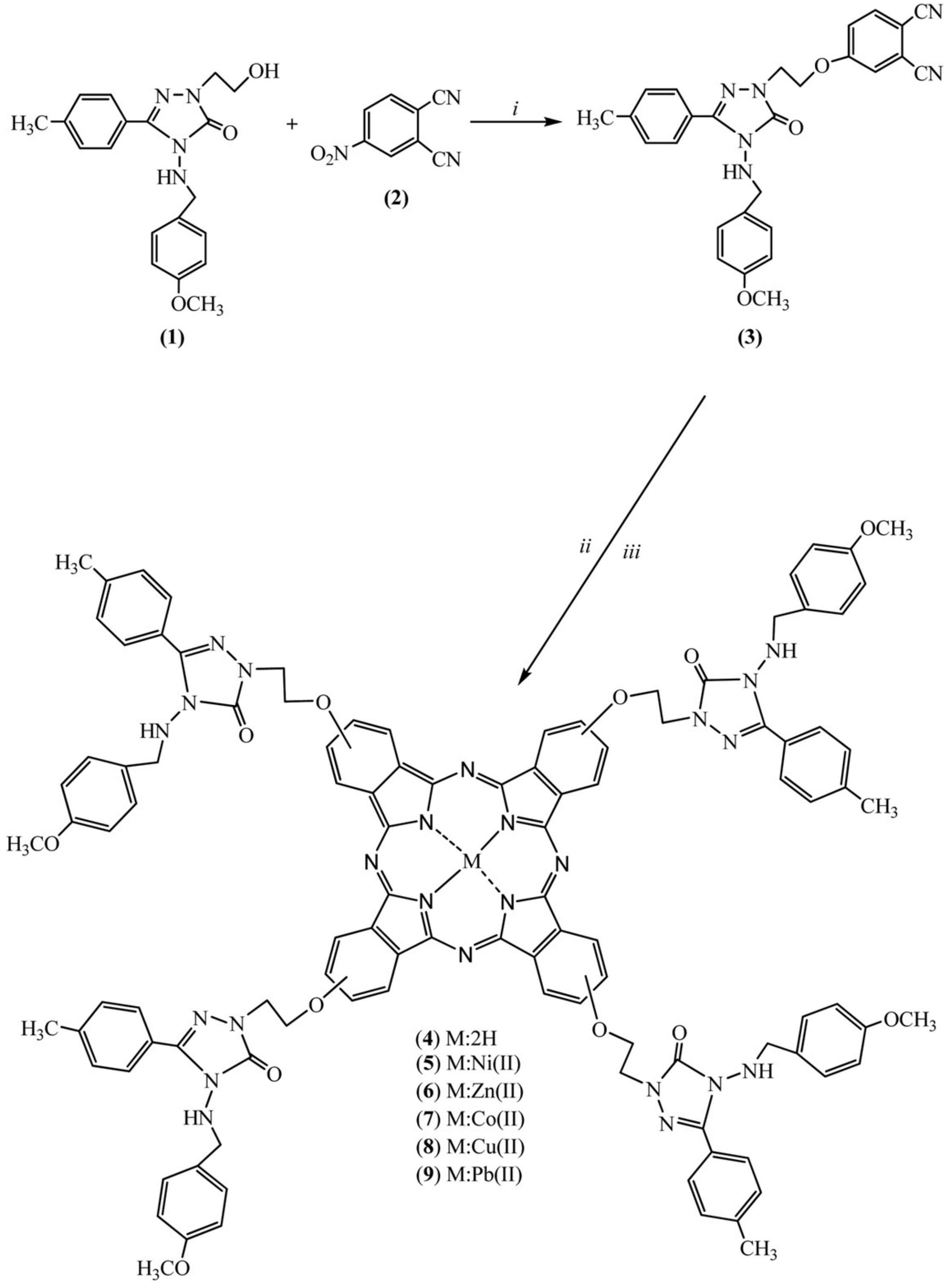
The syntheses of nickel, zinc, cobalt, copper, and lead metallophthalocyanines (**5**–**9**) were achieved directly by reacting of phthalonitrile derivative (**3**) with anhydrous metal salts ($NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$, PbO) and DBU in high-boiling solvent such as *2*-(dimethylamino)ethanol (DMAE) by microwave processing (Scheme 1). Obtained new metallophthalocyanines (**5**–**9**) were eluated by preparative thin layer chromatography method utilizing chloroform–methanol (92:8, 95:5, 94:6, 95:5 and 94:6 for compounds **5**–**9**, respectively) solvent system. The nickel, zinc, cobalt, copper and lead phthalocyanines (**5**–**9**) were obtained after purification by thin layer chromatography with the moderate yields. The FT-IR spectral results of novel phthalocyanine derivatives (**5**–**9**) were different from the phthalocyanine precursor **3**, so the sharp peak for the C≡N vibrations around 2226 cm^{-1} associated with nitrile groups disappeared after cyclotetramerization. The rest of FT-IR spectra of **5**–**9** were very similar to those of precursor dinitrile compound **3**. The ^{1}H NMR and ^{13}C NMR spectra of compound **5**, **6** and **9** showed almost identical chemical shifts. However, the ^{1}H NMR and ^{13}C NMR spectra of cobalt(II) (**7**) and copper(II) (**8**) phthalocyanines were precluded owing to their paramagnetic nature. Furthermore, in the mass spectra, the molecular ion peaks were observed at *m/z*: 1981.72 $[M + H]^+$ for compound **5**, *m/z*: 1987.13 $[M]^+$ for compound **6**, *m/z*: 2005.55 $[M + H + Na]^+$ for compound **7**, *m/z*: 1985.02 $[M]^+$ for compound **8**, *m/z*: 2129.18 $[M]^+$ for compound **9** which confirmed the proposed structures. Elemental analyses of the novel compounds (**3**–**9**) showed a good agreement with calculated values.

3.2. Thermal behavior of phthalocyanine compounds

The thermal behaviors of the metallophthalocyanines were investigated by TG/DTA. Although the potential thermal stabilities of phthalocyanines are well known, the obtained novel phthalocyanines (**4**–**9**) were observed not to be stable above 335 °C. The decomposition of compound **7** occurs in the 444.6–474 °C range, thus indicating that this structure presents higher stability than the other metal-free and metallophthalocyanines. The initial and main decomposition temperatures are given in Table 1. The initial decomposition temperatures decreased in the order of **7** > **8** > **4** > **6** > **9** > **5**.

3.3. Electronic absorption spectra

The absorption spectra of metallophthalocyanine complexes consist of an intense absorption band in the visible region traditionally near 670 nm called the Q band and a generally weaker band



Scheme 1. i: K_2CO_3, dry DMF; ii: *n*-pentanol, DBU; iii: DMAE, anhydrous $NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, $CuCl_2$ or PbO.

near 340 nm called the Soret or B band. The Q band is due to the transition from the ground state of A_{1g} symmetry to the first excited state which is of E_u symmetry [43]. The electronic absorption spectra of the metal-free phthalocyanine (**4**) and metallophthalocyanines (**5**–**9**) in chloroform are illustrated in Figs. 1 and 2. The metal-free phthalocyanine compound (**4**) showed two absorption bands in the Q band region due to D_{2h} symmetry of this compound in chloroform [40]. The absorption bands were observed at 389 nm in the UV region corresponding to the B band and at 707 and 671 nm with weaker absorptions at 644 and 611 nm corresponding to the Q band in the visible region. The UV–vis spectra of metallophthalocyanines **5**–**9** in chloroform showed intense Q absorption at $\lambda_{max} = 677$, 684, 677, 687 and 720 nm with a weaker absorption at 620, 617, 611, 628 and 654 nm, respectively (Figs. 1 and 2). B band absorptions of compounds **5**–**9** were observed at $\lambda_{max} = 386$, 356, 326, 350, 367 nm as expected, respectively. The Q

Table 1
Thermal properties of the studied phthalocyanines.

Compound	M	Initial decomposition temperature in °C	Main decomposition temperature in °C
4	2H	418.4	442.3
5	Ni	335.6	434.1
6	Zn	408.2	463.0
7	Co	444.6	474.0
8	Cu	439.6	468.8
9	Pb	389.4	426.7

band of the lead phthalocyanine complex (**9**) was red-shifted when compared to the corresponding other studied phthalocyanine complexes (**4**–**8**), suggesting that there is the non-planar effect of the bigger lead as central atom.

Aggregation of phthalocyanine molecules is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes in solution. It is dependent on the concentration, temperature, nature of the solvent, the substituents and type of the central metal ions. 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 in these compounds in the concentrations ranging from 1.2×10^{-5} to 2×10^{-6} M in DMSO.

3.4. Fluorescence spectra

The fluorescence behaviors of the metal-free (**4**), zinc (**6**) and lead (**9**) phthalocyanines were studied in DMSO. Fig. 4 shows the absorption, fluorescence emission and excitation spectra of metal-free Pc compound (**4**) in DMSO as an example. The shapes of the excitation spectra were similar to absorption spectra for the metal-free (**4**) and zinc phthalocyanine (**6**) compounds. The proximity of the wavelength of the Q band absorption and the Q band excitation spectra for phthalocyanine derivatives **4** and **6** were similar suggesting that the nuclear configurations of the ground and excited states were also similar and not affected by excitation. However, for the lead phthalocyanine compound (**9**), the shape of excitation spectrum was different from the absorption spectrum in that the Q band of the former showed two peaks in the Q band region, unlike the narrow Q band of the latter. This attributes that there were changes in the molecule following excitation most likely due to the larger lead metal being out of the plane of the phthalocyanine ring.

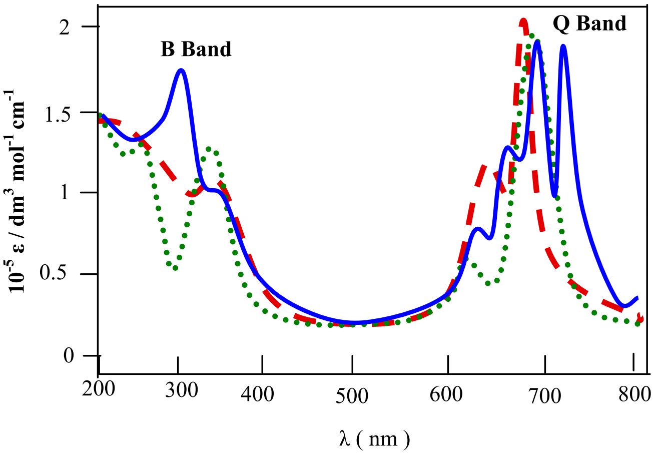


Fig. 1. UV/vis spectra of compounds **4** (—), **5** (- - -) and **6** (····) in chloroform.

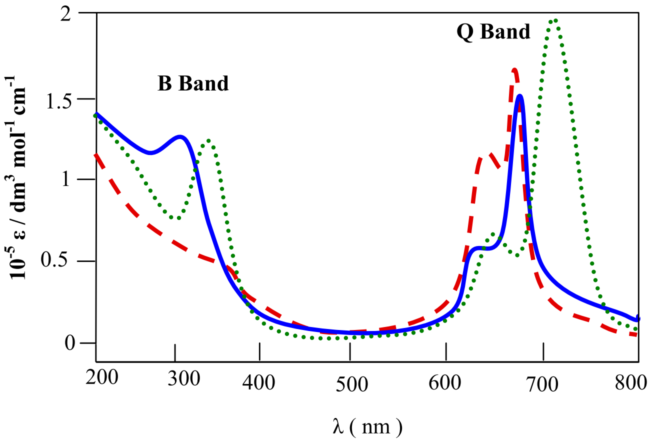


Fig. 2. UV/vis spectra of compounds **7** (—), **8** (- - -) and **9** (····) in chloroform.

Fluorescence emission and excitation peaks for compounds **4**, **6** and **9** in DMSO are listed in Table 2. Fluorescence emission peaks were observed at 713 nm for **4**, 691 nm for **6** and 712 nm for **9** in DMSO. The observed Stokes shift values of the substituted Pc compounds (**4**, **6** and **9**) are lower than unsubstituted ZnPc (**ZnPc**), (Table 2). The nickel (**5**), cobalt (**7**) and copper (**8**) phthalocyanine compounds did not show fluorescence in DMSO.

3.5. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of metal-free (**4**) and zinc (**6**) phthalocyanine compounds are higher than unsubstituted zinc phthalocyanine (**ZnPc**), but the Φ_F value of lead phthalocyanine compound (**9**) is lower than unsubstituted zinc phthalocyanine (**ZnPc**) in DMSO (Table 3) suggesting that there are more changes in the lead phthalocyanine (**9**) molecule following excitation in DMSO most likely due to the larger lead metal being out of the plane of the phthalocyanine ring. The substituted metal-free complex (**4**) shows higher Φ_F values than other studied Pc compounds in DMSO (Table 3).

Fluorescence lifetime (τ_F) is the average time a molecule stays in its excited state before fluorescence. Any factor can affect the fluorescence lifetime of a fluorophore (such as phthalocyanine in this study). 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 3) were calculated using the Strickler-Berg equation. Using this equation, a good correlation has been found between experimentally and theoretically determined lifetimes for the unaggregated molecules [32]. Thus we suggest that the τ_F values of studied phthalocyanines (**4**, **6** and **9**) obtained using this equation is an appropriate measure of fluorescence lifetimes. Generally, the τ_F values of the studied phthalocyanine compounds (**4**, **6** and **9**) are higher than reported Pc compounds [44]. For the substituted complexes, longer τ_F value is obtained for the lead phthalocyanine compound (**9**) compared to other studied phthalocyanine complexes (**4** and **6**).

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 3. τ_0 values of the studied phthalocyanine compounds (**4**, **6** and **9**) are longer than unsubstituted ZnPc (**ZnPc**) in DMSO. The substituted zinc phthalocyanine compound (**6**) showed the longest τ_0 values when

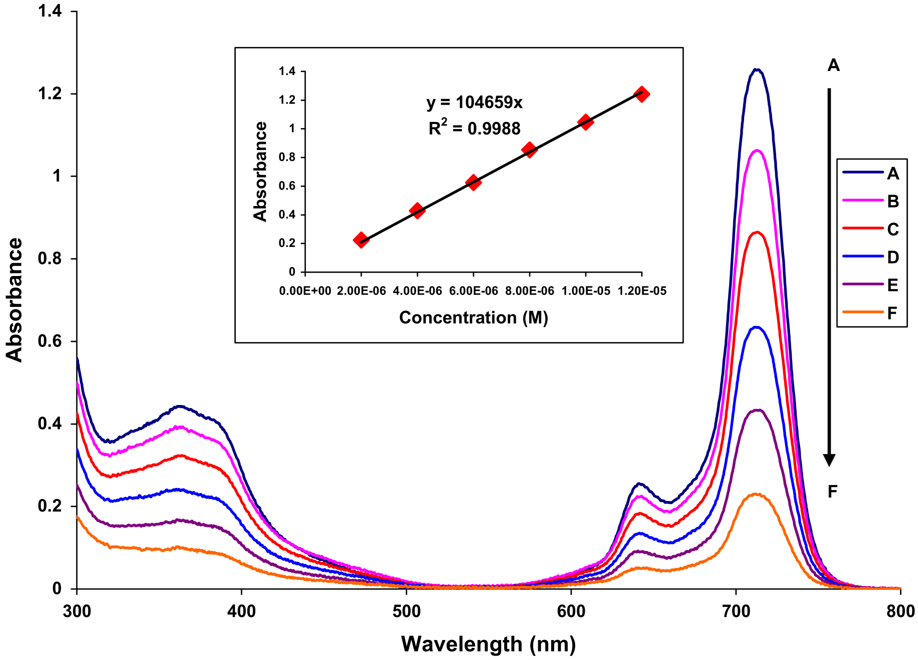


Fig. 3. Absorption spectra changes of compound **9** in DMSO at different concentrations: 12 × 10^{-6} (A), 10 × 10^{-6} (B), 8 × 10^{-6} (C), 6 × 10^{-6} (D), 4 × 10^{-6} (E), 2 × 10^{-6} (F) M (Inset: Plot of absorbance *versus* concentration).

compared to other substituted complexes (**4** and **9**) in DMSO. The rate constants for fluorescence (k_F) values of studied phthalocyanine compounds (**4**, **6** and **9**) are also higher than unsubstituted ZnPc (**ZnPc**) in DMSO. The k_F value of substituted lead phthalocyanine compound (**9**) is highest among the studied phthalocyanine compounds in DMSO.

3.6. Singlet oxygen quantum yields

An ideal photosensitizer must produce highly singlet oxygen for photocatalytic applications 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. The amount of generated singlet oxygen is quantified as singlet oxygen quantum yield (Φ_Δ) and this parameter can give an indication of the potential of compounds to be used as photosensitizers in PDT applications [45]. In this study, singlet oxygen quantum yields (Φ_Δ) of the studied phthalocyanine compounds (**4**, **6** 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

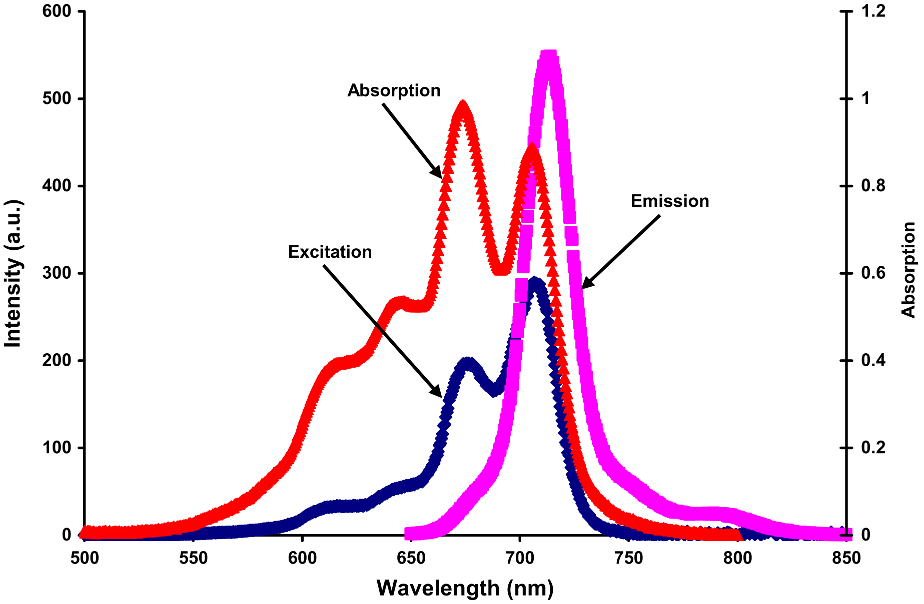


Fig. 4. Absorption, fluorescence emission and excitation spectra for compound **4** in DMSO. Excitation wavelengths = 640 nm. Concentration = 1 × 10^{-6} M for both absorption and fluorescence spectra.

Table 2
Absorption, excitation and emission spectral data for unsubstituted and substituted metal-free, zinc(II) and lead(II) 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	675, 705	4.83, 4.80	675, 708	713	5
6	681	4.92	684	691	7
9	712	5.02	675, 710	712	2
ZnPc[a]	672	5.14	672	682	10

[a] Data from Ref. [46].

as an example for compound **6**). Many factors are responsible for the generation of singlet oxygen such as triplet excited state energy, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen, ability of substituents and solvents to quench the singlet oxygen. There were no changes in the Q band intensities of studied phthalocyanine compounds (**4**, **6** and **9**) during the Φ_Δ determination, confirming that complexes were not decompose during singlet oxygen studies. It is believed that during photosensitization, the photosensitizer is firstly excited to its singlet excited state and through intersystem crossing reaches its 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 for PDT *via* Type II mechanism.

The Φ_Δ values of studied phthalocyanine compounds (**4**, **6** and **9**) are lower when compared to respective unsubstituted ZnPc (**ZnPc**) complex in DMSO. When compared to the Φ_Δ values among the studied phthalocyanine compounds (**4**, **6** and **9**), substituted zinc phthalocyanine compound (**6**) shows highest Φ_Δ value among all studied compounds. Generally, zinc phthalocyanine compounds possess high triplet yields and they can generate highly singlet oxygen since the d^{10} configuration of the central Zn^{2+} ion, which make them appropriate photosensitizers for PDT applications.

3.7. Photodegradation study

Degradation of the molecules under light irradiation can be used to study their stability and this is important for their applications such as photodynamic therapy. Photodegradation is an oxidative degradation of a photosensitizer molecule with time into lower molecular weight fragments under light. Photodegradation generally depends on the structure of the molecule, concentration, solvent and light intensity [39].

The spectral changes observed for all the studied phthalocyanine compounds (**4**, **6** and **9**) in DMSO during light irradiation are as shown in Fig. 6 (using complex **4** as an example). The collapse of the

Table 3
Photophysical and photochemical parameters of unsubstituted and substituted metal-free, zinc(II) and lead(II) phthalocyanines in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	[a]k_F (s^{-1}) ($\times 10^7$)	Φ_d($\times 10^{-5}$)	Φ_Δ
4	0.40	4.28	10.71	9.33	1.58	0.39
6	0.25	5.32	13.66	7.32	1.82	0.57
9	0.092	8.40	9.13	10.94	246.00	0.26
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. [46].

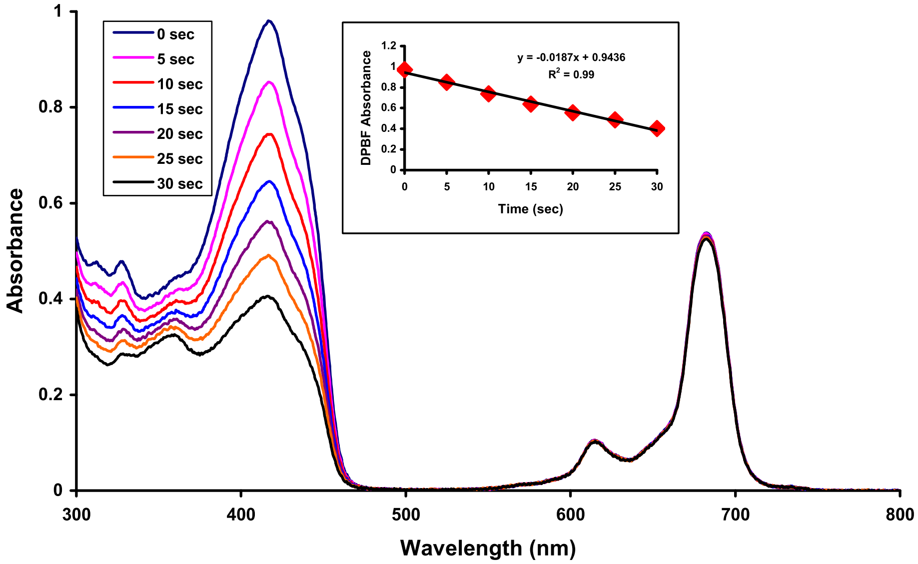


Fig. 5. Absorption changes during the determination of singlet oxygen quantum yield. This determination was for compound **6** in DMSO at a concentration of 1×10^{-5} M (Inset: Plot of DPBF absorbance *versus* time).

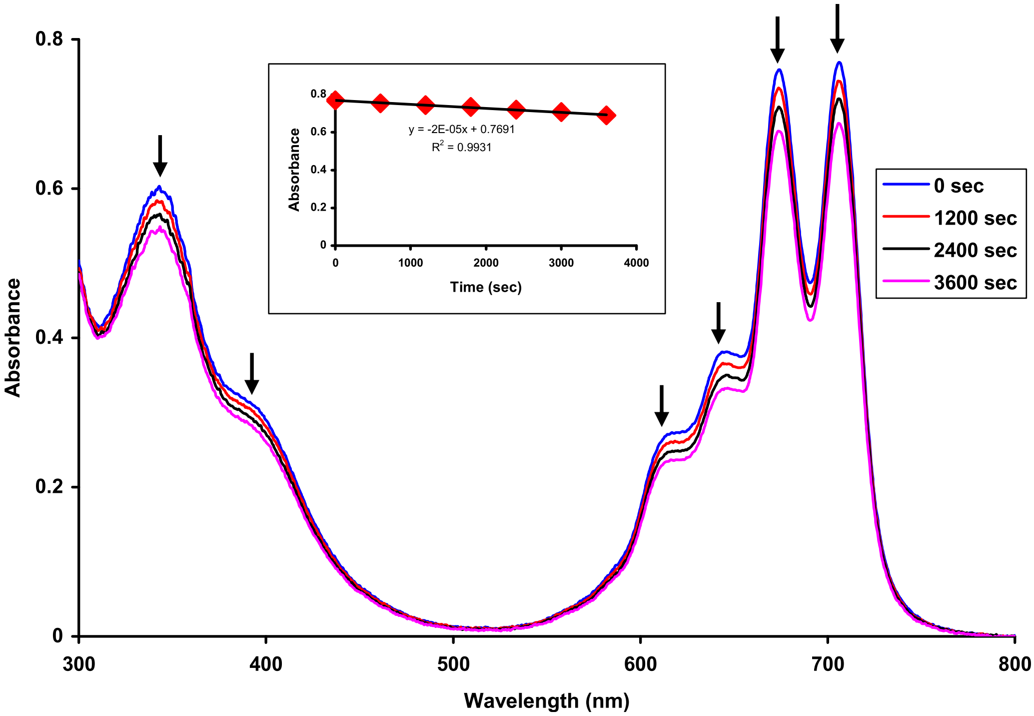


Fig. 6. Absorption changes during the photodegradation studies of compound **4** in DMSO showing the disappearance of the Q band at 20 min intervals (Inset: Plot of absorbance *versus* time).

absorption spectra without any distortion of the shape confirms photodegradation not associated with phototransformation for studied phthalocyanine compounds (**4**, **6** and **9**).

The photodegradation quantum yield (Φ_d) values of the studied phthalocyanine compounds (**4**, **6** and **9**) in DMSO are given in Table 3. Both studied metal-free (**4**) and zinc (**6**) phthalocyanine compounds are more stable to degradation compared to unsubstituted ZnPc (**ZnPc**) in DMSO because the Φ_d values of these studied phthalocyanine compounds (**4** and **6**) are lower than unsubstituted ZnPc (**ZnPc**) in DMSO (Table 3). The Φ_d value of the substituted lead phthalocyanine compound (**9**) is more higher than unsubstituted ZnPc (**ZnPc**) and other studied phthalocyanine compounds indicating that this compound is the lowest stable derivative among the studied phthalocyanine compounds suggesting that most likely due to the larger lead metal being out of the plane of the phthalocyanine ring due to light irradiation during photodegradation study.

4. Conclusions

In this work, the syntheses of 4-(2-(4-(4-methoxybenzylamino)-5-oxo-3-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-1-yl)ethoxy)phthalonitrile (**3**) and its new peripherally tetrasubstituted metal-free (**4**), Ni(II) (**5**), Zn(II) (**6**), Co(II) (**7**), Cu(II) (**8**) and Pb(II) (**9**) derivatives have been reported for the first time. Although the metal-free phthalocyanine compound was synthesized using conventional method, the metallophthalocyanines were synthesized using microwave irradiation technique. The new compounds were characterized by IR, UV–vis, ^{1}H and ^{13}C NMR, mass spectroscopy and elemental analysis. Although the potential thermal stabilities of phthalocyanines are well known, the obtained novel phthalocyanines (**4**–**9**) were observed not to be stable above 335 °C. Decomposition occurs in the 444.6–474 °C range for compound **7** and this compound showed higher stability than the other studied metal-free and metallophthalocyanines. All the compounds showed excellent solubility in most solvents such as chloroform, THF, DMF, DMSO etc. In the UV–vis spectra, while the metal-free complex (**4**) showed splitting Q band, the metallophthalocyanines (**5**–**9**) exhibited single narrow Q bands in chloroform. The Q band of the lead phthalocyanine complex (**9**) was red-shifted when compared to the corresponding other studied phthalocyanine complexes (**4**–**8**). The photophysical and photochemical properties of metal-free (**4**), zinc (**6**) and lead (**9**) phthalocyanine compounds were also investigated in DMSO for comparison of the central metal effect on these properties. The fluorescence quantum yields of studied metal-free (**4**) and zinc (**6**) phthalocyanine compounds are higher than unsubstituted ZnPc, but the Φ_F value of lead phthalocyanine complex is lower in DMSO. The singlet oxygen quantum yield values of studied phthalocyanine compounds are lower than unsubstituted ZnPc (ranged from 0.26 to 0.57), but these values still enough for potential of these compounds as photosensitizers in photocatalytic applications such as PDT. The substituted lead (**9**) phthalocyanine compound is approximately 100 times less stable than other substituted phthalocyanine compounds (**4** and **6**). It could be due to larger lead atom being out of the plane of the phthalocyanine cavity during photodegradation study.

Acknowledgement

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