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Novel triazole bearing zinc(II) and magnesium(II) metallophthalocyanines: Synthesis, characterization, photophysical and photochemical properties

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ABSTRACT

The synthesis and characterization of novel tetrakis *N*-(3,5-dichlorophenyl)-5-methyl-3H-1,2,4-triazol-3-one (**1**) and *N*-(3,5-dichlorophenyl)-5-ethyl-3H-1,2,4-triazol-3-one (**2**) substituted phthalonitrile derivatives and their new organosoluble peripherally tetra-substituted zinc(II) (**6** and **7**) and magnesium(II) (**8** and **9**) phthalocyanines were studied in this study. Photophysical and photochemical data of these compounds were measured in dimethysulfoxide (DMSO). The magnesium(II) phthalocyanine derivatives showed excellent fluorescent properties and the corresponding zinc(II) phthalocyanines generated efficient singlet oxygen. The fluorescence quenching behavior of the studied tetra-peripherally substituted zinc(II) and magnesium(II) phthalocyanine compounds by the addition of 1,4-benzoquinone were also studied in DMSO. These molecules can distinctly be employed in the field of photodynamic therapy in combination with fluorescence imaging.

1. Introduction

Although phthalocyanines (Pcs) are relatively old dye compounds, their potential applications are still extensively studied by many scientists because of their interesting optical, electrical properties and good thermal stability. The fully conjugated 18 π-electronic structure of Pcs gives to structure good thermal and optical stability. In addition, Pcs have intense absorption bands in visible area. Thanks to these special properties, Pcs play an important role in research of new high technological materials such as solar cells [1], semiconductors [2], optical data storage devices [3], laser dyes [4], photodynamic therapy agents [5], liquid crystals [6], nonlinear optics [7], electrochromic displaying systems [8] and molecular electronics [9].

Up to now, photophysical and photochemical behavior of Pc compounds have been extensively studied [10,11] but there are a few papers on photophysical and photochemical behavior of Pc bearing triazole moieties [12,13]. Because of this, in this study, the photophysical and photochemical behavior of novel triazole substituted Pc derivatives were investigated. The synthesis of triazole substituted Pcs is the same as with other substituted Pcs in literature [14–19].

In our study two different triazole containing phthalonitrile derivatives (**4** and **5**) were used for synthesis of the peripherally tetra-substituted Zn(II) (**6** and **7**) and Mg(II) (**8** and **9**) Pc macrocycles. The newly synthesized phthalonitrile derivatives and their Pcs counterparts were characterized spectroscopically. The photophysical properties including fluorescence quantum yields and lifetimes and photochemical properties including singlet oxygen and photodegradation quantum yields of these Pc compounds were investigated in DMSO. The quenching by fluorescence of newly synthesized Pc compounds was also studied using by 1,4-benzoquinone.

2. Experimental

2.1. Materials

All reactions were carried out under dry and oxygen free nitrogen atmosphere using Schlenk system. Dimethylformamide

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(DMF) was dried and purified as described by Perrin and Armarego [20]. *N*-(3,5-dichlorophenyl)-5-methyl-3H-1,2,4-triazol-3-one (**1**) [21] and *N*-(3,5-dichlorophenyl)-5-ethyl-3H-1,2,4-triazol-3-one (**2**) [21], 4-nitrophthalonitrile (**3**) [22] were prepared as described in the literature. 1,3-diphenylisobenzofuran (DPBF) and unsubstituted ZnPc were purchased from Fluka and Aldrich, respectively.

The used equipments, the photophysical and photochemical parameters were supplied as Supplementary information.

2.2. Synthesis

2.2.1. 4-[N-(3,5-dichlorophenyl)-5-methyl-5-oxo-3H-1,2,4-triazol-1-yl]phthalonitrile (**4**)

Compound (**1**) (2.44 g, 0.01 mol), 4-nitrophthalonitrile (**3**) (1.73 g, 0.01 mol) and dry K_2CO_3 (1.38 g, 0.01 mol) were mixed in dry DMF for 96 h. After evaporating the solvent, the compound (**4**) was purified by crystallization in acetone/petroleum ether (1:1) solvent system. Yield 2.96 g (80%). m.p: 214–215 °C Anal. calc. for $C_{17}H_9Cl_2N_5O$: C, 55.16; H, 2.45; N, 18.92; Found: C, 55.96; H, 2.22; N, 19.18. IR (KBr tablet) υ_{max}/cm^{-1}: 3099 υ(Ar–CH), 3073 υ(Ar–CH), 2992 υ(alip-CH), 2943 υ(alip-CH), 2227 (C≡N), 1719 υ(C=O), 1595 υ(C=N), 1584, 1570, 1497, 1436, 1417, 1399, 1380, 1303, 1266, 1190, 1161, 1113, 1044, 1023, 897, 874, 842, 801, 790, 731, 696, 668. ^1H NMR (DMSO-d_6), (δ: ppm): 8.50–8.48 (d, 1H/ArH), 8.40–8.37 (d, 1H/ArH), 8.26–8.24 (d, 1H/ArH), 7.86–7.83 (d, 1H/ArH), 7.81–7.76 (m, 2H/ArH), 2.24 (s, 3H/CH_3). ^{13}C NMR (DMSO-d_6), (δ: ppm): 157.40, 153.32, 142.20, 135.67, 134.60, 129.78, 125.11, 122.42, 121.52, 120.78, 116.82, 115.53, 114.96, 110.11, 21.56. MS (ESI), (*m*/*z*): Calculated: 369; Found: 370 $[M + H]^+$.

2.2.2. 4-[N-(3,5-dichlorophenyl)-5-ethyl-5-oxo-3H-1,2,4-triazol-1-yl]phthalonitrile (**5**)

Compound (**2**) (2.58 g, 0.01 mol), 4-nitrophthalonitrile (**3**) (1.73 g, 0.01 mol) and dry K_2CO_3 (1.38 g, 0.01 mol) were mixed in dry DMF for 96 h. After evaporating the solvent, the compound (**5**) was purified by crystallization in acetone/petroleum ether (1:1) solvent system. Yield 2.96 g (77%). m.p: 225–228 Anal. calc. for $C_{18}H_{11}Cl_2N_5O$: C, 56.27; H, 2.89; N, 18.23%; Found: C, 56.48; H, 2.71; N, 18.36. IR (KBr tablet) υ_{max}/cm^{-1}: 3093 υ(Ar–CH), 2985 υ(alip-CH), 2943 υ(alip-CH), 2227 (C≡N), 1721 υ(C=O), 1595 υ(C=N), 1573, 1493, 1450, 1420, 1387, 1370, 1339, 1277, 1192, 1167, 1148, 1104, 1071, 1059, 979, 900, 858, 843, 803, 735, 710, 666. ^1H NMR (DMSO-d_6), (δ: ppm): 8.45–8.39 (m, 2H/ArH), 8.24–8.22 (d, 1H/ArH), 7.83–7.78 (m, 3H/ArH), 2.95–2.89 (q, 2H/CH_2), 1.43–1.38 (t, 3H/CH_3). ^{13}C NMR (DMSO-d_6), (δ: ppm): 156.14, 152.78, 141.32, 134.82, 134.51, 129.63, 124.03, 122.96, 121.44, 121.08, 116.14, 115.84, 115.12, 109.72, 26.22, 11.93. MS (ESI), (*m*/*z*): Calculated: 383; Found: 384 $[M + H]^+$.

2.2.3. Synthesis of phthalocyanines (**6–9**)

The same procedure was used for the synthesis of the Pcs (**6–9**) with literature [13]. MetalloPcs (**6–9**) were synthesized with addition of 0.2 g of substituted phthalonitrile compounds (**4** or **5**) and stoichiometric amounts of related anhydrous metal salts ($Zn(CH_3COO)_2$; $MgCl_2$) to the reaction media at reflux temperature in n-pentanol (3 mL) and by the catalyst of DBU (3 drops) for 24 h. After precipitating the crude products in methanol, the solid residues were purified by column chromatography, using silica gel as support material.

6: Eluent for column chromatography: THF:methanol (100:2). Yield: 51 mg (24.5%), mp > 300 °C. Anal. calc. for $C_{68}H_{36}Cl_8N_{20}O_4Zn$:C, 52.82; H, 2.35; N, 18.12; Found: C, 52.66; H, 2.52; N, 18.21. IR (KBr tablet) υ_{max}/cm^{-1}: 3097 υ(Ar–CH), 2982 υ(alip-CH), 1722 υ(C=O), 1593 υ(C=N), 1568, 1493, 1412, 1377, 1186, 1045, 1021. ^1H NMR (DMSO-d_6), (δ: ppm): 8.45–8.36 (m, 8H/ArH), 8.22–8.14 (bd, 4H/ArH), 7.82–7.75 (m, 12H/ArH), 2.21 (s, 12H/CH_3). UV–vis (DMSO) λ_{max}/nm: [(10^{-5} ε, dm^3 mol^{-1} cm^{-1})]: 689 (5.19), 622 (4.57), 360 (4.83). MS (ESI), (*m*/*z*): Calculated: 1544 Found: 1545 $[M + H]^{+\cdot}$

7: Eluent for column chromatography: THF:methanol (100:2). Yield: 58 mg (27.9%), mp > 300 °C. Anal. calc. for $C_{72}H_{44}Cl_8N_{20}O_4Zn$:C, 53.97; H, 2.77; N, 17.48%; Found: C, 54.15; H, 2.59; N, 17.63%. IR (KBr tablet) υ_{max}/cm^{-1}: 3096 υ(Ar–CH), 2980 υ(alip-CH), 1716 υ(C=O), 1591 υ(C=N), 1564, 1493, 1411, 1381, 1185, 1021. ^1H NMR (DMSO-d_6), (δ: ppm): 8.41–8.27 (bm, 12H/ArH), 7.86–7.76 (m, 12H/ArH), 2.93–2.81 (q, 8H/CH_2), 1.41–1.35 (t, 12H/CH_3). UV–vis (DMSO) λ_{max}/nm: [(10^{-5} ε, dm^3 mol^{-1} cm^{-1})]: 690 (5.28), 623 (4.54), 363 (4.83). MS (ESI), (*m*/*z*): Calculated: 1602 Found: 1625 $[M + Na]^+$.

8: Eluent for column chromatography: THF:methanol (100:2.5). Yield: 62 mg (30.6%), mp > 300 °C. Anal. calc. for $C_{68}H_{36}Cl_8N_{20}O_4Mg$:C, 54.26; H, 2.41; N, 18.61. Found: C, 54.13; H, 2.53; N, 18.72%. IR (KBr tablet) υ_{max}/cm^{-1}: 3085 υ(Ar–CH), 2993 υ(alip-CH), 1715 υ(C=O), 1590 υ(C=N), 1571, 1493, 1411, 1370, 1185, 1044, 1020. ^1H NMR (DMSO-d_6), (δ: ppm): 8.44–8.33 (m, 8H/ArH), 8.21–8.16 (d, 4H/ArH), 7.80–7.73 (m, 12H/ArH), 2.24 (s, 12H/CH_3). UV–vis (DMSO) λ_{max}/nm: [(10^{-5} ε, dm^3 mol^{-1} cm^{-1})]: 689 (5.19), 623 (4.57), 362 (4.86). MS (ESI), (*m*/*z*): Calculated: 1504, Found: 1543 $[M + K]^{+\cdot}$

9: Eluent for column chromatography: THF:methanol (100:2.5). Yield: 52 mg (25.6%), mp > 300 °C. Anal. calc. for $C_{72}H_{44}Cl_8N_{20}O_4Mg$:C, 55.39; H, 2.84; N, 17.94. Found: C, 55.53; H, 3.03; N, 17.85. IR (KBr tablet) υ_{max}/cm^{-1}: 3099 υ(Ar–CH), 2995 υ(alip-CH), 1717 υ(C=O), 1593 υ(C=N), 1570, 1495, 1410, 1370, 1186, 1045, 1023. ^1H NMR (DMSO-d_6), (δ: ppm): 8.42–8.23 (bm, 12H/ArH), 7.93–7.69 (bm, 12H/ArH), 2.90–2.82 (q, 8H/CH_2), 1.42-1.34 (t, 12H/CH_3). UV–vis (DMSO) λ_{max}/nm: [(10^{-5} ε, dm^3 mol^{-1} cm^{-1})]: 690 (5.33), 623 (4.57), 364 (4.88). MS (ESI), (*m*/*z*): Calculated: 1560, Found: 1561 $[M + H]^+$.

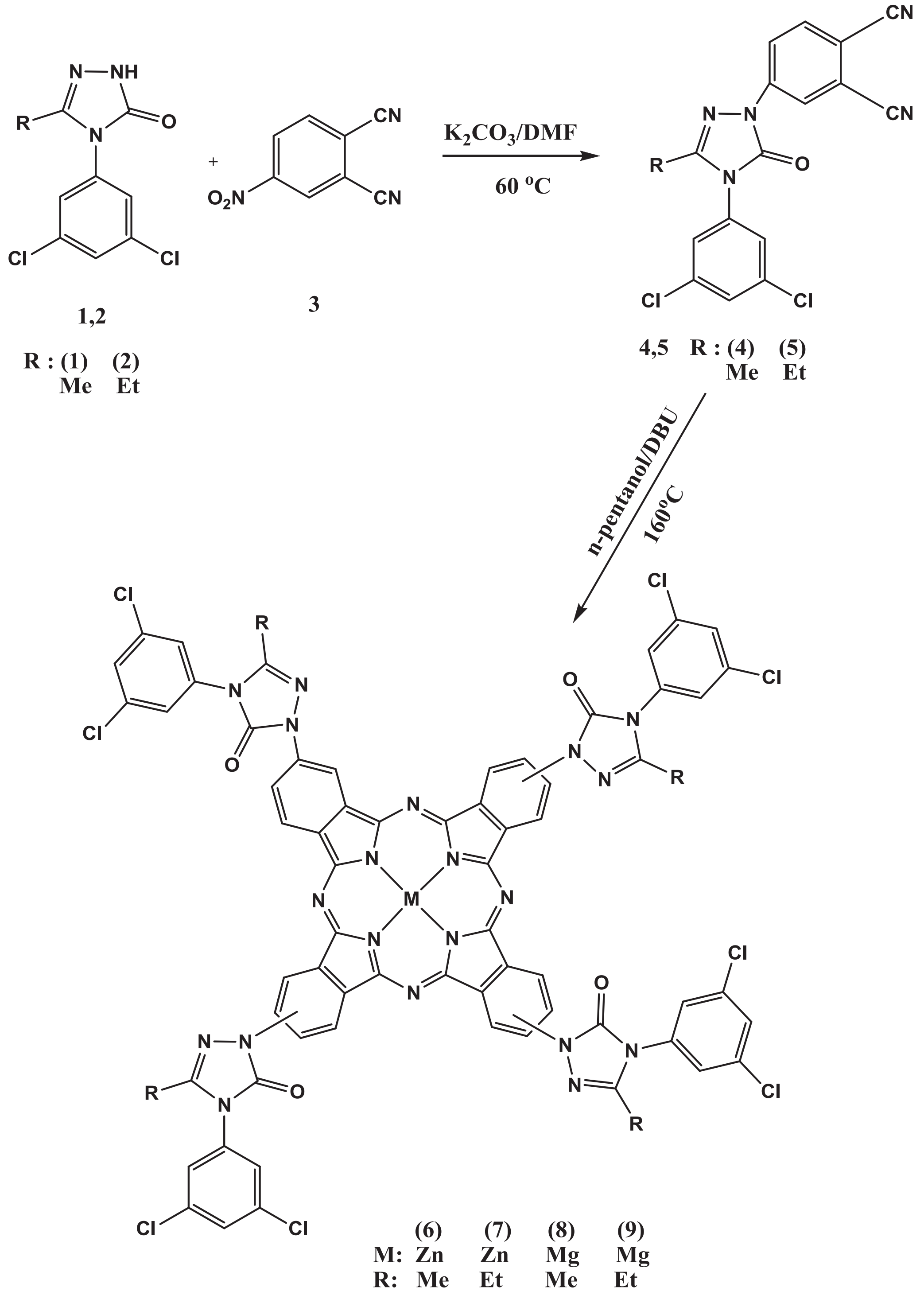
3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathway of the novel compounds is shown in Scheme 1. The dinitrile compounds (**4** and **5**) were prepared from the reactions between 4-nitrophthalonitrile and compounds **1** and **2**, respectively, that have active –NH groups, by the catalyst of K_2CO_3 [12]. All spectral data support the proposed structures of compounds **4** and **5**. According to IR spectroscopy data, new vibration appeared at 2227 cm^{-1}, which belongs to the C≡N groups, supported the proposed structures of compounds **4** and **5**. Two different tautomeric structures are possible for compounds **1** and **2** (Fig. 1). In the IR spectra of the compound **4** and **5**, C=O stretching vibrations were obtained at 1719 and 1721 cm^{-1} indicated that the “keto” forms are more stable than “enol” forms.

In ^1H NMR spectra of phthalonitrile compounds (**4** and **5**), the –NH signals at 11.73 and 11.75 ppm for compounds **1** and **2**, respectively disappeared [21]. Presence of additional aromatic protons indicated that substitution was accomplished. Stable molecular ion $[M + H]^+$ peaks *m*/*z* at 370 and 384 in the mass spectra of compounds **4** and **5** were showed that target compounds were successfully prepared. Also elemental analysis data of these compounds (**4** and **5**) were satisfactory.

Researchers generally use substituted phthalonitriles or 1,3-diimino-1*H*-isoindoles as starting materials for synthesis of Pcs. In this work, phthalonitrile compounds (**4** and **5**) were also used as starting compounds for synthesis of the metallo-Pcs (Zn, Mg) due to mild reaction conditions. Characterization of new Pc compounds was performed using by IR, ^1H NMR, elemental



Scheme 1. The synthetic route of the novel phthalonitrile (**4** and **5**) and phthalocyanine compounds (**6**–**9**).

analysis and UV/Vis, mass spectrometry. All spectral data support the proposed structures (**6**–**9**). The IR spectra of all Pcs were in good agreement with the proposed structures. The most important proof of the cyclotetramerization of nitrile groups is the absence of the $-C\equiv N$ vibrations at 2227 cm^{-1} in IR spectra of the substituted phthalonitrile compounds (**4** and **5**). The rest of the spectra were not very different from that of the corresponding phthalonitrile compounds (**4** and **5**).

The signals in the ^1H NMR spectra of Pcs (**6**–**9**) that were recorded in DMSO-d_6 were broad because of the isomeric mixture and probable aggregation at measured concentration. The spectra of the compounds were very similar and the integral ratio of the aromatic protons to aliphatic protons was similar to corresponding phthalonitrile compounds (**4** and **5**). In addition, elemental analysis results and mass spectra of the compounds **6**–**9** were good agreement with proposed structure.

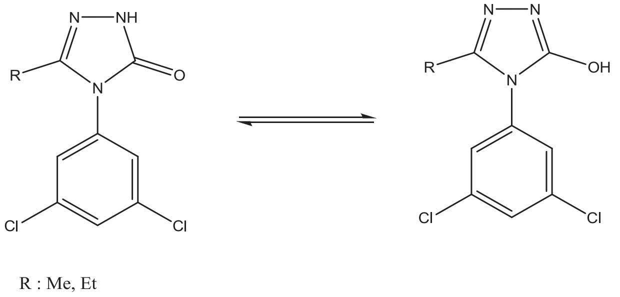


Fig. 1. The possible tautomeric structures of compounds **1** and **2**.

3.2. *UV–vis absorption spectra*

Electronic spectra were mainly used for characterization of the Pc compounds. Pcs display typical electronic spectra with two absorption regions, one is called Q-band and observed at around 600–700 nm and arise from π–π^* transitions from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring, other one is called B-band and observed at around 300–350 nm results from deeper π levels-LUMO transitions.

All substituted metalloPcs were soluble in most of organic solvents such as tetrahydrofuran, dichloromethane, chloroform, *N*,*N*-dimethylformamide, dimethylsulfoxide (DMSO) and pyridine. In UV–vis spectra of the metalloPcs (**6**–**9**) that were measured in DMSO at 1×10^{-5} M the Q-bands were observed at around 690 nm with the shoulders at around 660 nm and the B-bands were observed at around 362 nm (Figs. 2 and 3). The sharp absorption bands were the evidence of non-aggregated species at measured concentration [13].

Fig. 4 shows fluorescence emission, absorption and excitation spectra of Pc compounds (**6**–**9**) in DMSO. Fluorescence emission and excitation maximum peaks of compounds (**6**–**9**) in DMSO were listed in Table 1. The triazole containing Pc compounds (**6**–**9**) exhibited red-shifted Q-bands by approximately 18 nm compared to the corresponding bands of the unsubstituted ZnPc. The observed Stokes shifts of the studied Pc compounds (**6**–**9**) were slightly lower than unsubstituted zinc Pc and typical of MPc compounds in DMSO (Table 1). Fluorescence emission peaks were observed at approximately 700 nm for Pc compounds in DMSO (Table 1).

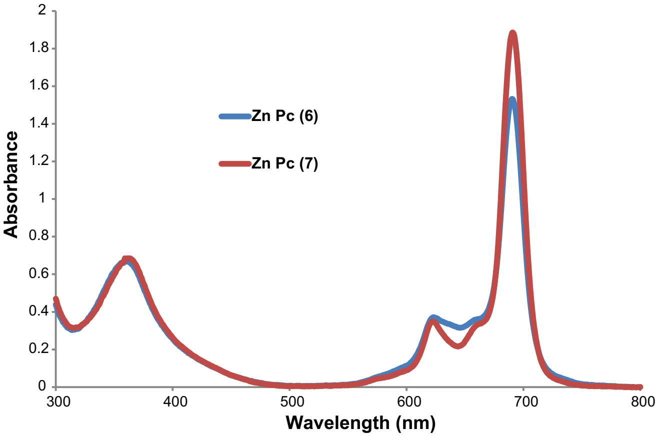


Fig. 2. Electronic absorption spectra of phthalocyanine compounds **6** and **7** in DMSO at 1×10^{-5} M.

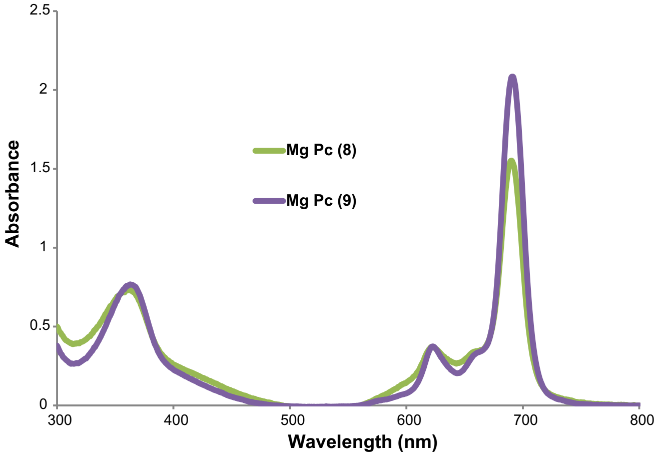


Fig. 3. Electronic absorption spectra of phthalocyanine compounds **8** and **9** in DMSO at 1×10^{-5} M.

The excitation spectra of the triazole containing Pc compounds were similar to absorption spectra of these compounds and both were mirror images of the fluorescent spectra in DMSO. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for all compounds suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation in DMSO.

3.3. *Fluorescence quantum yields and lifetimes*

The fluorescence quantum yields (Φ_F) and lifetimes of triazole containing substituted zinc(II) and magnesium(II) Pcs (**6**–**9**) were measured in DMSO and data were given in Table 2. The calculated values were typical of MPc compounds. Although the Φ_F values of magnesium(II) Pcs were higher, the Φ_F values of zinc(II) Pcs were lower than unsubstituted zinc(II) Pcs. The substituted magnesium(II) Pcs (**8** and **9**) showed higher Φ_F values than substituted zinc(II) Pcs (**6** and **7**). Due to size of magnesium (II) cation is smaller than that of zinc (II), MgPcs have more fluorescenece property than Zn(II)Pcs. The fluorescence lifetime can be introduced the average staying time of a molecule in its excited state before emission and this value is directly related to that of fluorescence quantum yield values. The studied magnesium(II) Pcs showed higher fluorescence lifetimes values than the studied zinc(II) Pcs, thus should be accompanied by corresponding high fluorescence quantum yield values of magnesium(II) Pcs.

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values in DMSO were also measured and given in Table 2. The τ_0 values of the tetra-triazole containing substituted zinc(II) and magnesium(II) Pc compounds (**6**–**9**) were longer than unsubstituted zinc(II) Pc compound in DMSO. On the contrary, these substituted Pc compounds (**6**–**9**) showed lower k_F values than unsubstituted zinc(II) Pc.

3.4. *Singlet oxygen quantum yields*

Singlet oxygen quantum yields (Φ_Δ) were established in DMSO using 1,3-diphenylisobenzofuran (DBPF) as a chemical quencher. The decreasing of the absorbances of DPBF at 417 nm was monitored using UV–vis spectrometer. Any changes did not observe in the Q-band intensities of the studied Pcs during the Φ_Δ determinations (Fig. 5, using compound **7** as an example in DMSO), indicating that the studied Pc compounds were not degraded under

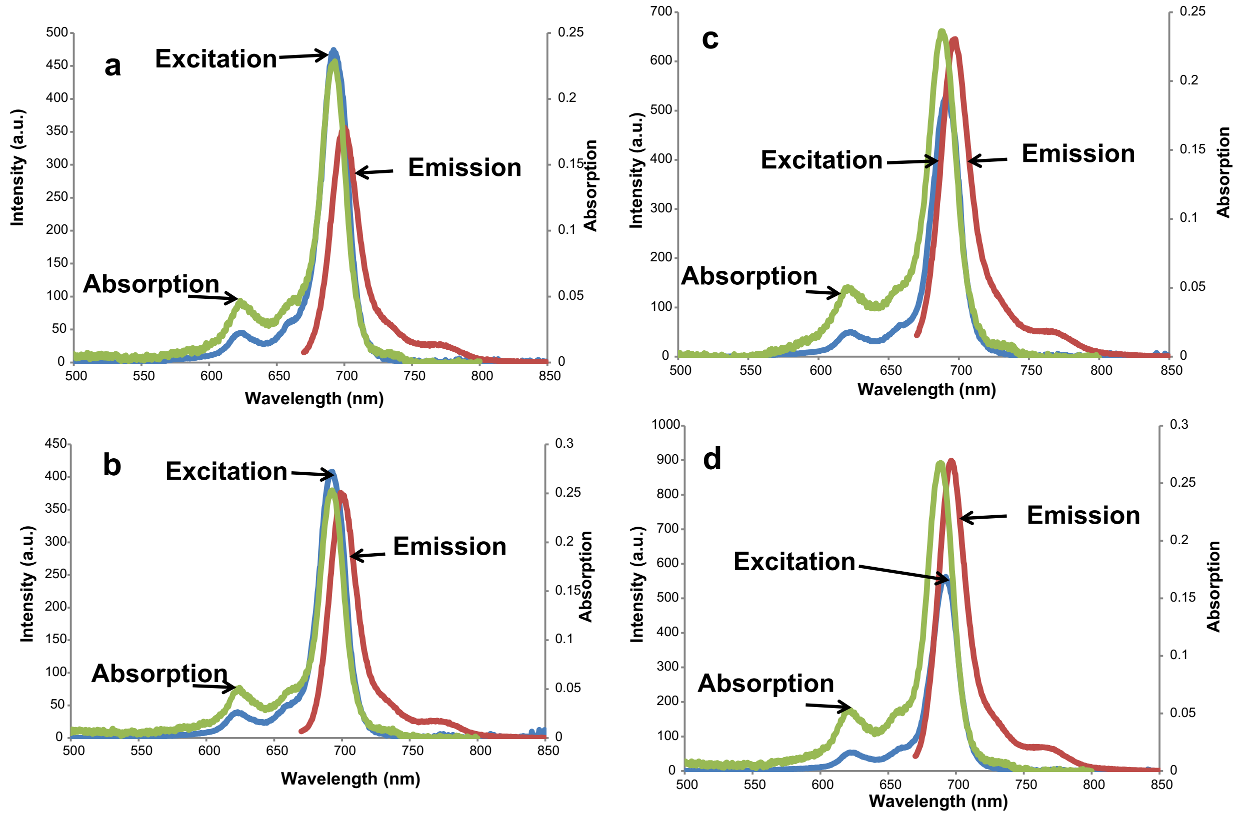


Fig. 4. Electronic absorption, excitation and emission spectra of (a) for compound **6**, (b) for compound **7**, (c) for compound **8** and (d) for compound **9** in DMSO ($\lambda_{ex} = 660$ nm).

light irradiation (30 Volt) during singlet oxygen determinations. The Φ_Δ values of the newly synthesized substituted Pc compounds (**6**–**9**) and unsubstituted zinc(II) Pc were given in Table 2. The studied Pc compounds showed lower Φ_Δ values than unsubstituted zinc(II) Pc except for zinc(II) Pc compound **7**. The substituted zinc(II) Pc compounds (**6** and **7**) showed higher Φ_Δ values than magnesium(II) Pc counterparts mostly due to the lower Φ_F values of zinc(II) Pcs than magnesium counterparts as explained above. The length of alkyl chain (methyl or ethyl) on the triazole group was also effected singlet oxygen generation of studied Pc compounds. When the ethyl group substituted on the triazole group, higher singlet oxygen production was observed among the studied Pc compounds.

3.5. *Photodegradation studies*

Degradation of the molecules under light irradiation can be given hints about their photostability and the determination of the photostability of the molecules is especially important for use their photocatalytic applications.

The photodegradation cause some spectral changes in UV–vis spectra of the Pcs (6–9). An example of these spectral changes is shown in Fig. 6 (using compound **8** in DMSO). Although decreasing the absorption bands of Pcs (6–9) in the electronic spectra, there is no change in the form of the absorption bands refers photodegredation instead of phototransformation. The degradation degree of the molecules under light irradiation is confirmed as photodegradation quantum yield (Φ_d) and these values of studied Pc compounds (**6**–**9**) in DMSO were given in Table 2. All the compounds showed about the same stability with Φ_d of the order of 10^{-5}. While the stable Pc compounds show Φ_d values as low as 10^{-6}, the order of 10^{-3} had been reported for the unstable Pc compounds [11]. The Φ_d values for the triazole containing zinc(II) and magnesium(II) Pcs were similar with Pc derivatives having different substituents on the Pc ring in the literature [11]. The studied zinc(II) (**6**, **7**) and magnesium(II) (**8**, **9**) Pc compounds showed lower Φ_d values compared to unsubstituted zinc(II) Pc (**ZnPc**). It means the substitution of the Pc framework with triazole

Table 1
Absorption, excitation and emission spectral data for the unsubstituted and the substituted phthalocyanine compounds in DMSO.

Compound	Q-band λ_{max}, (nm)	log ε	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
6	689	5.19	692	700	8
7	690	5. 28	692	700	8
8	689	5.19	692	697	9
9	690	5.33	692	697	9
ZnPc[a]	672	5.14	672	682	10

[a] Data from Ref. [23].

Table 2
Photophysical and photochemical data of the unsubstituted and the substituted phthalocyanine compounds in DMSO.

Compound	Φ_F	τ_F (ns)	τ_0 (ns)	k_F[a] (s^{-1}) ($\times 10^8$)	Φ_d ($\times 10^{-5}$)	Φ_Δ
6	0.18	1.79	9.93	1.01	0.98	0.55
7	0.16	1.35	8.28	1.21	1.99	0.74
8	0.27	2.44	8.90	1.12	2.42	0.27
9	0.38	2.62	6.90	1.45	2.53	0.60
ZnPc	0.20[b]	1.22[c]	6.80[c]	1.47[c]	2.61[c]	0.67[d]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Data from Ref. [24].
[c] Data from Ref. [23].
[d] Data from Ref. [25].

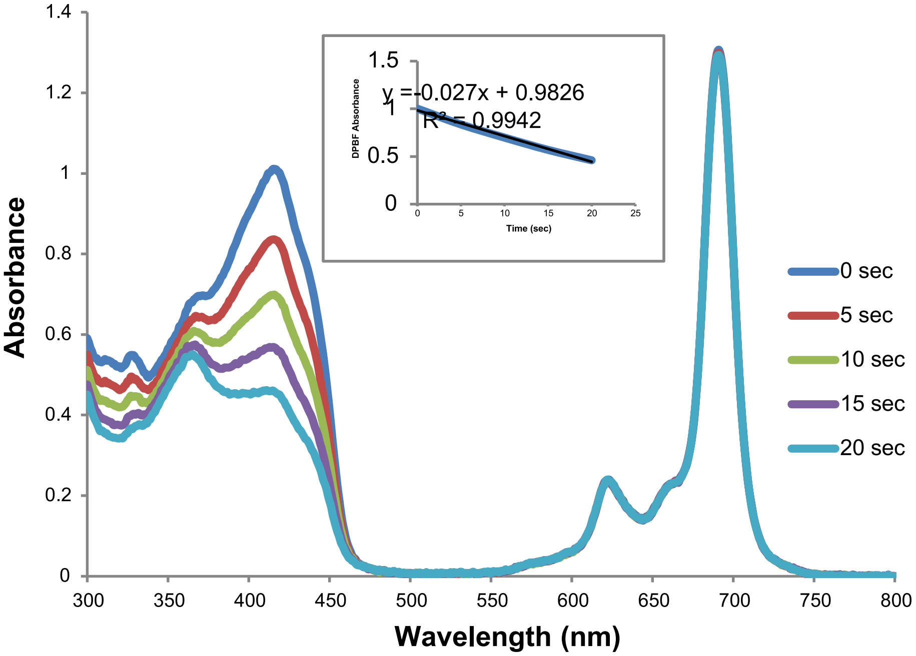


Fig. 5. UV–vis spectra changes during the determination of singlet oxygen quantum yield. This determination was for compound **7** in DMSO at a concentration of 1 × 10^{-5} M (Inset: Plot of DPBF absorbance versus time).

containing substituents increased the photostability of the compounds under light irradiation. The studied substituted zinc(II) Pcs (**6** and **7**) showed lower Φ_d values compared to magnesium(II) counterparts (**8** and **9**) in DMSO. For this reason, the studied Pcs containing zinc(II) as central metal ion in the Pc cavity are more stable compared to magnesium containing Pcs due to more sensitive of magnesium atom against to light irradiation.

3.6. Fluorescence quenching studies by 1,4-benzoquinone [BQ]

The quenching of fluorescence for the tetra-substituted zinc(II) and magnesium (II) Pc compounds containing triazole groups was determined decreasing of the emission spectra of these compounds by addition of increasing amounts of 1,4-benzoquinone (BQ) in DMSO. The quenching between Pcs and BQ was found to obey Stern–Volmer kinetics, which is consistent with diffusion controlled bimolecular reactions. Fig. 7 shows the reducing of the emission spectra for compound **8** due to the quenching by BQ in DMSO as an example. The slope of the plots shown in Fig. 8 gave Stern–Volmer constant (K_{SV}) values and these values were listed in Table 3. The K_{SV} values of the triazole containing substituted zinc Pc compounds (**6** and **7**) were lower than unsubstituted ZnPc in DMSO. The zinc(II) compounds (**6** and **7**) showed lower K_{SV} value than the magnesium(II) counterparts (**8** and **9**) in DMSO could be

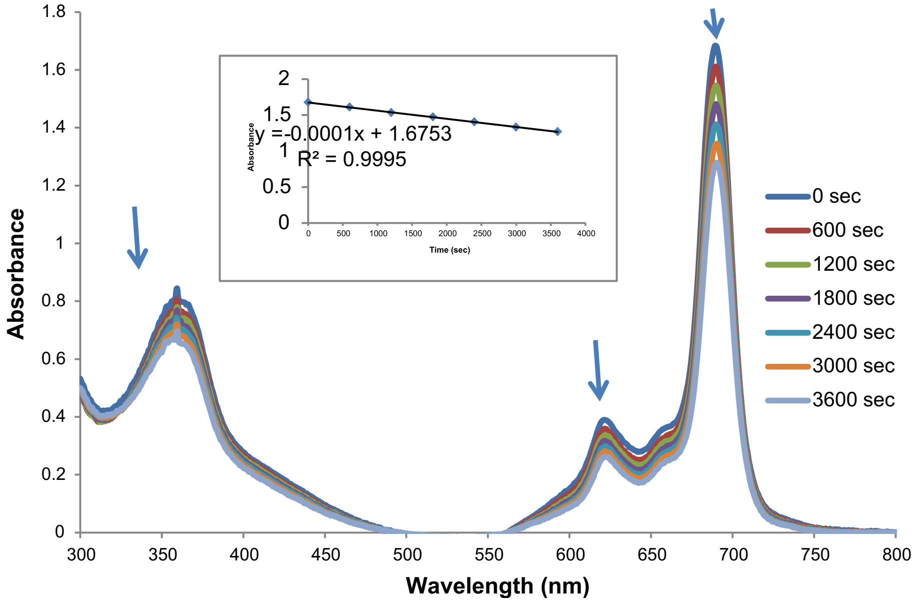


Fig. 6. UV–vis spectral changes during the photodegradation studies of the compound **8** in DMSO showing the disappearance of the Q-band at 10 min intervals. (Inset: Plot of absorbance versus time). 300 W General Electric quartz line lamp was used as a light source. Power density was 18 mW/cm^2 and used energy was 100 W.

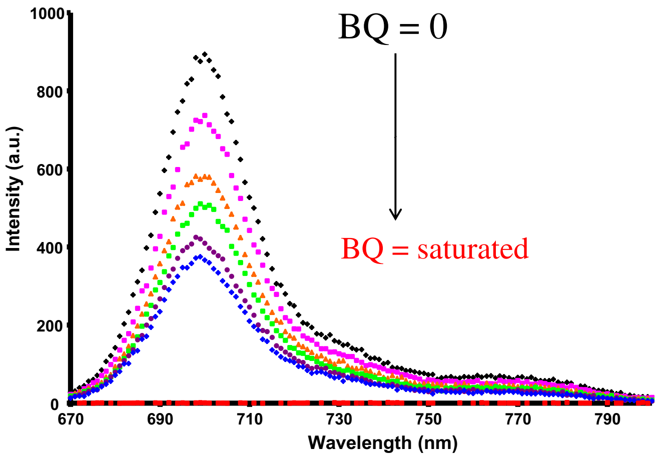


Fig. 7. Fluorescence emission spectral changes of the compound **8** (1×10^{-5} M) by addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.04 M.

due to lower metal size of magnesium than zinc. The obtained bimolecular quenching constant (k_q) values for all studied Pc compounds (**6**–**9**) were lower than unsubstituted zinc(II) Pc (**ZnPc**). When compared to k_q values among the studied Pcs, magnesium(II) Pc compounds had higher values than zinc(II) Pcs. The increase of the length of the alkyl chain from methyl to ethyl on the substituents decreased both the K_{SV} and k_q values of the studied compounds. The bimolecular quenching rate constants were obtained to be close to the diffusion-controlled limits, $\sim 10^{10}$ M^{-1} s^{-1}.

4. Conclusions

This work described the synthesis, spectral characterization, photophysical and photochemical properties of newly synthesized peripherally tetra-substituted zinc(II) and magnesium(II) Pc compounds containing *N*-(3,5-dichlorophenyl)-5-methyl-3H-1,2,4-triazol-3-one (**1**) or *N*-(3,5-dichlorophenyl)-5-ethyl-3H-1,2,4-triazol-3-one (**2**) groups. Elemental analyses, IR, UV/VIS, ^{1}H NMR and mass spectra confirmed the proposed structure of the compounds. The substitution of Pc framework with *N*-(3,5-dichlorophenyl)-5-methyl-3H-1,2,4-triazol-3-one (**1**) or *N*-(3,5-dichlorophenyl)-5-ethyl-3H-1,2,4-triazol-3-one (**2**) groups increased the wavelength of the Q-band. The fluorescence quantum yield and fluorescence lifetime values were found higher for magnesium(II) Pcs (**8**–**9**) compared to zinc(II) Pcs (**6**–**7**) in DMSO due to the smaller nature of the Mg atom than Zn atom in the Pc cavity. The amount of the singlet oxygen is very important for the prediction of PDT activity of photosensitizers. All studied triazole containing Pc compounds generated quite lot singlet oxygen in DMSO. Especially, the zinc(II) Pc compound **7** showed highest Φ_Δ value among the studied Pcs. The studied zinc(II) (**6**–**7**) Pc compounds were stable to degradation under light irradiation compared to unsubstituted zinc Pc (ZnPc) and the substituted zinc(II) Pc compounds (**6** and **7**) were more stable than magnesium(II) Pcs in DMSO. The Stern–Volmer constant (K_{SV}) and the bimolecular quenching constant (k_q) values of the substituted magnesium(II) Pc compounds (**8** and **9**) were found higher than the substituted zinc(II) Pc compounds in DMSO. The fluorescence quenching between studied Pcs and BQ was proceed via diffusion-controlled mechanism since bimolecular quenching rate constants were obtained to be close to the limits to 10^{10} M^{-1} s^{-1}. These properties give an indication of the potential of the compounds as photosensitizers in applications where singlet oxygen is required, especially compound (**7**) can be good candidate as a photosensitizer for PDT application.

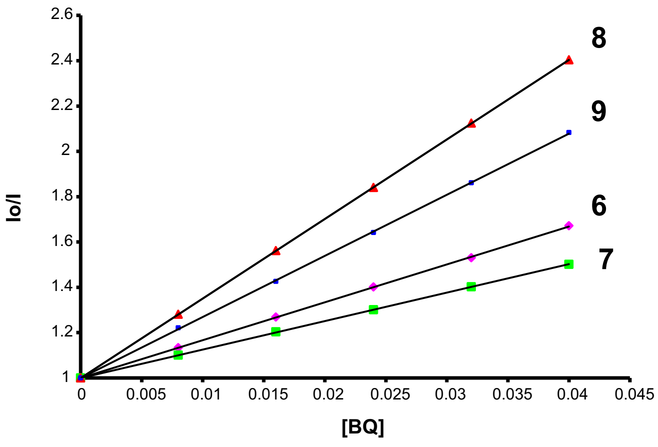


Fig. 8. Stern–Volmer plots for BQ quenching of substituted phthalocyanines (**6**–**9**) at a concentration of $\sim 1 \times 10^{-5}$ M in DMSO.

Table 3
Fluorescence quenching data for the unsubstituted and the substituted phthalocyanine compounds in DMSO.

Compound	K_{SV} (M^{-1})	$k_q/10^{10}$(dm^3 mol^{-1} s^{-1})
6	16.71	0.94
7	12.55	0.93
8	35.09	1.44
9	26.95	1.03
ZnPc[a]	31.90	2.61

[a] Data from Ref. [23].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.08.029.

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