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Synthesis, photochemical, bovine serum albumin and DNA binding properties of tetrasubstituted zinc phthalocyanines and their water soluble derivatives



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ABSTRACT

Tetra-substituted zinc (II) phthalocyanines (**2a**, **3a**, **5a** and **6a**) were synthesized by cyclotetramerization of phthalonitrile derivatives (**2**, **3**, **5** and **6**). These zinc phthalocyanines (**2a**, **3a**, **5a** and **6a**) were converted into their water-soluble quaternized derivatives (**2b**, **3b**, **5b** and **6b**) by reaction with methyl iodide. The photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties of these novel compounds were investigated in dimethylsulfoxide for both non-ionic and quaternized ionic complexes and in phosphate buffer saline (PBS) for only quaternized ionic complexes. The effect of the two type substituents with different positions on the photophysical and photochemical properties of these phthalocyanines were compared in this study.

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1. Introduction

Phthalocyanines (Pcs) comprise a remarkably robust and versatile class of chemical compounds. Recent investigations on phthalocyanines (Pcs) bearing discrete redox-active, ion-active and photo-active units has been rapidly expanding into several applied fields including electrochromic displays [1], Langmuir–Blodgett films [2], optical data storage [3], solar cell [4], liquid crystals [5], chemical sensors [6] and catalysis [7–9]. Phthalocyanine derivatives are also useful agent for photodynamic therapy (PDT) applications [10] because they exhibit relatively high triplet yields and long lifetimes [11].

Photodynamic therapy is gaining acceptance as a technique for cancer treatment. PDT utilizes a photosensitizer, working as a light-sensitive drug, to treat the target tissue locally upon the irradiation of light with appropriate wavelengths. It is generally accepted that the mechanism of PDT is based on the interaction between the excited photosensitizer and surrounding molecules, generating reactive oxygen species (ROS), such as singlet oxygen

(¹O₂). ROS can cause oxidative damage to biological substrates and ultimately cell death [12].

The main disadvantages of phthalocyanine compounds as photosensitizer in PDT are their solubility problem and strong tendency for aggregation in water and other polar solvents due to the hydrophobic nature of the phthalocyanine macrocycle. Phthalocyanine aggregation decreases their fluorescence and singlet oxygen quantum yields and as a result their photosensitizing activity [13]. In order to reduce phthalocyanine aggregation and to increase their solubility and biological efficacy, phthalocyanine compounds are quaternized via amine groups on substituents at the phthalocyanine macrocycle [14–16].

In this paper, novel zinc (II) phthalocyanine derivatives containing 2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethanol groups bearing quaternizable nitrogen atom were designed and synthesized. These zinc (II) phthalocyanines were converted to their quaternized cationic derivatives. The obtained quaternized cationic zinc (II) phthalocyanines showed excellent solubility in aqueous media which is very important for biological cell studies on PDT. The photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation quantum yields) properties of newly synthesized both peripherally and non-peripherally tetra substituted zinc (II) phthalocyanine complexes (**2a**, **3a**, **5a** and **6a**) and their

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quaternized derivatives (**2b**, **3b**, **5b** and **6b**) were investigated in DMSO for all complexes and in PBS for water soluble quaternized zinc phthalocyanine complexes for the determination of PDT activity of the these zinc(II) phthalocyanines. The bovine serum albumin (BSA) and DNA binding behavior of the studied water soluble zinc (II) phthalocyanines were also described in PBS solutions.

2. Experimental

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

2.1. Synthesis

Experimental procedures were given as supplementary information.

2.1.1. 3-(2-{2-[3-(Dimethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile (**3**)

IR (KBr pellet): ν (cm^{-1}): 3084 (Ar–H), 2924–2874 (Aliph. C–H), 2230 ($\text{C}\equiv\text{N}$), 1611, 1582, 1502, 1449, 1354, 1292, 1238, 1171, 1153, 1129, 1063, 998, 935, 887, 822, 796, 754, 687. ^1H NMR (CDCl_3): δ (ppm): 7.53 (m, 1H, Ar–H), 7.31–7.25 (m, 1H, Ar–H), 7.09 (m, 2H, Ar–H), 6.34–6.26 (m, 3H, Ar–H), 4.07 (m, 2H, $-\text{CH}_2-\text{O}$), 3.80–3.62 (m, 4H, $-\text{CH}_2-\text{O}$), 3.37 (s, 2H, $-\text{CH}_2-\text{O}$), 2.89 (s, 6H, CH_3). ^{13}C NMR (CDCl_3): δ (ppm): 160.67, 159.16, 151.35, 142.70, 134.28, 129.73, 129.18, 124.75, 116.97, 112.67, 110.83, 105.39, 101.40, 99.11, 72.64, 68.77, 66.59, 61.01, 40.05. Calc. for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_3$: C 68.36, H 6.02, N 11.96%; found: C 68.58, H 5.86, N 11.77%. MS (ESI-MS) m/z : 352 [$\text{M} + \text{H}$] $^+$.

2.1.2. 3-(2-{2-[3-(Diethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile (**6**)

IR (KBr pellet): ν (cm^{-1}): 3086 (Ar–H), 2972–2872 (Aliph. C–H), 2232 ($\text{C}\equiv\text{N}$), 1611, 1584, 1566, 1504, 1463, 1396, 1376, 1357, 1274, 1216, 1197, 1139, 1071, 1025, 997, 832, 795, 758, 685. ^1H NMR (CDCl_3): δ (ppm): 7.57–7.13 (m, 3H, Ar–H), 6.58 (d, 1H, Ar–H), 6.33–6.17 (m, 3H, Ar–H), 4.34 (m, 2H, $-\text{CH}_2-\text{O}$), 4.12 (m, 2H, $-\text{CH}_2-\text{O}$), 4.01–3.94 (m, 4H, $-\text{CH}_2-\text{O}$), 3.36 (m, 4H, $-\text{CH}_2-\text{N}$), 1.16 (m, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ (ppm): 161.70, 155.26, 150.07, 134.53, 131.05, 126.70, 120.68, 117.73, 115.60, 113.24, 109.52, 106.52, 103.58, 99.23, 70.76, 70.03, 69.71, 67.45, 44.68, 12.70. Calc. for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_3$: C 69.64, H 6.64, N 11.07%; found: C 69.82, H 6.35, N 10.82%. MS (ESI-MS) m/z : 380 [$\text{M} + \text{H}$] $^+$.

2.1.3. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) (**2a**)

IR (KBr pellet): ν (cm^{-1}): 3071 (Ar–H), 2915–2869 (Aliph. C–H), 1608, 1573, 1488, 1447, 1393, 1337, 1279, 1237, 1120, 1091, 1060, 997, 956, 821, 744, 685. ^1H NMR (CDCl_3): δ (ppm): 8.45 (m, 4H, Ar–H), 8.13 (m, 4H, Ar–H), 7.28 (m, 8H, Ar–H), 6.91 (m, 4H, Ar–H), 6.25 (m, 8H, Ar–H), 4.11 (m, 32H, CH_2-O), 2.28 (s, 24H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ (ppm): 159.46, 151.24, 150.64, 140.17, 139.54, 130.61, 129.37, 123.04, 118.78, 111.25, 105.75, 104.12, 102.11, 99.78, 69.89, 67.45, 67.10, 62.47, 40.29. UV–vis (DMSO), λ_{max} nm (log ϵ): 356 (4.86), 615 (4.47), 683 (5.11). Calc. for $\text{C}_{80}\text{H}_{84}\text{N}_{12}\text{O}_{12}\text{Zn}$: C 65.32, H 5.76, N 11.43%; found: C 65.51, H 5.58, N 11.24%. MS (MALDI-TOF) m/z : 1472 [$\text{M} + \text{H}$] $^+$.

2.1.4. 1(4),8(11),15(18),22(25)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) (**3a**)

IR (KBr pellet): ν (cm^{-1}): 3068 (Ar–H), 2921–2869 (Aliph. C–H), 1609, 1585, 1488, 1446, 1334, 1268, 1234, 1125, 1067, 997, 884,

800, 743, 685. ^1H NMR (CDCl_3): δ (ppm): 8.87 (m, 4H, Ar–H), 8.00–7.92 (m, 8H, Ar–H), 7.71 (m, 4H, Ar–H), 7.46 (m, 4H, Ar–H), 6.71 (m, 8H, Ar–H), 4.36 (m, 16H, CH_2-O), 4.06 (m, 16H, CH_2-O), 2.21 (s, 24H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ (ppm): 159.50, 156.10, 153.11, 150.97, 141.35, 130.58, 129.41, 127.09, 125.66, 116.72, 113.44, 106.09, 103.38, 100.18, 70.85, 69.75, 68.39, 67.38, 40.60. UV–vis (DMSO): λ_{max} nm (log ϵ): 310 (4.79), 375 (4.68), 633 (4.64), 703 (5.38). Calc. for $\text{C}_{80}\text{H}_{84}\text{N}_{12}\text{O}_{12}\text{Zn}$: C 65.32, H 5.76, N 11.43%; found: C 65.58, H 5.42, N 11.18%. MS (MALDI-TOF) m/z : 1472 [$\text{M} + \text{H}$] $^+$.

2.1.5. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(trimethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) iodide (**2b**)

IR (KBr pellet): ν (cm^{-1}): 3008 (Ar–H), 2922–2866 (Aliph. C–H), 1606, 1488, 1451, 1393, 1335, 1277, 1230, 1118, 1090, 1056, 957, 875, 744, 684. UV–vis (DMSO): λ_{max} nm (log ϵ): 356 (4.82), 615 (4.42), 683 (5.10). Calc. for $\text{C}_{84}\text{H}_{96}\text{I}_4\text{N}_{12}\text{O}_{12}\text{Zn}$: C 49.49, H 4.75, N 8.24%; found: C 49.61, H 4.52, N 8.48%. MS (MALDI-TOF) m/z : 383 [$\text{M} + \text{H} - \text{I}$] $^{+4}$.

2.1.6. 1(4),8(11),15(18),22(25)-Tetrakis-(2-{2-[3-(trimethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) iodide (**3b**)

IR (KBr pellet): ν (cm^{-1}): 3016 (Ar–H), 2922–2868 (Aliph. C–H), 1588, 1487, 1453, 1332, 1301, 1251, 1230, 1118, 1063, 942, 881, 801, 744, 684. UV–vis (DMSO): λ_{max} nm (log ϵ): 322 (4.70), 377 (4.62), 633 (4.57), 702 (5.31). Calc. for $\text{C}_{84}\text{H}_{96}\text{I}_4\text{N}_{12}\text{O}_{12}\text{Zn}$: C 49.49, H 4.75, N 8.24%; found: C 49.68, H 4.44, N 8.56%. MS (MALDI-TOF) m/z : 384 [$\text{M} + 2\text{H} - \text{I}$] $^{+4}$.

2.1.7. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) (**5a**)

IR (KBr pellet): ν (cm^{-1}): 3071 (Ar–H), 2969–2862 (Aliph. C–H), 1606, 1568, 1496, 1471, 1395, 1375, 1336, 1275, 1220, 1136, 1078, 1024, 989, 965, 824, 746, 687. ^1H NMR (CDCl_3): δ (ppm): 8.14 (m, 8H, Ar–H), 7.22 (m, 4H, Ar–H), 6.53–6.31 (m, 16H, Ar–H), 4.22–4.10 (m, 32H, $-\text{CH}_2-\text{O}$), 3.27 (m, 16H, $-\text{CH}_2-\text{N}$), 1.10 (m, 24H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ (ppm): 163.43, 152.72, 152.25, 143.18, 133.70, 133.21, 126.93, 123.53, 114.22, 110.75, 108.80, 106.46, 104.28, 102.74, 73.24, 70.51, 47.84, 15.91. UV–vis (DMSO): λ_{max} nm (log ϵ): 356 (4.96), 616 (4.61), 683 (5.26). Calc. for $\text{C}_{88}\text{H}_{100}\text{N}_{12}\text{O}_{12}\text{Zn}$: C 66.76, H 6.37, N 10.62%; found: C 66.92, H 6.12, N 10.88%. MS (MALDI-TOF) m/z : 1584 [$\text{M} + \text{H}$] $^+$.

2.1.8. 1(4),8(11),15(18),22(25)-Tetrakis-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) (**6a**)

IR (KBr pellet): ν (cm^{-1}): 3082 (Ar–H), 2968–2868 (Aliph. C–H), 1608, 1567, 1498, 1481, 1374, 1335, 1274, 1244, 1200, 1171, 1125, 1089, 1025, 988, 880, 801, 745, 685. ^1H NMR (CDCl_3): δ (ppm): 8.10 (m, 8H, Ar–H), 7.68 (m, 4H, Ar–H), 7.45 (m, 4H, Ar–H), 7.11–6.88 (m, 8H, Ar–H), 6.48 (m, 4H, Ar–H), 4.30–4.17 (m, 32H, $-\text{CH}_2-\text{O}$), 3.20 (m, 16H, $-\text{CH}_2-\text{N}$), 1.14 (m, 24H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ (ppm): 160.52, 158.22, 153.58, 149.93, 141.27, 132.38, 131.43, 130.43, 117.60, 107.69, 106.84, 103.87, 101.47, 98.76, 69.88, 67.64, 44.45, 13.07. UV–vis (DMSO): λ_{max} nm (log ϵ): 318 (4.80), 372 (4.73), 632 (4.68), 702 (5.43). Calc. for $\text{C}_{88}\text{H}_{100}\text{N}_{12}\text{O}_{12}\text{Zn}$: C 66.76, H 6.37, N 10.62%; found: C 66.98, H 6.09, N 10.94%. MS (MALDI-TOF) m/z : 1584 [$\text{M} + \text{H}$] $^+$.

2.1.9. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(diethylmethylamino)phenoxy]ethoxy}ethoxy)phthalocyaninato zinc (II) iodide (**5b**)

IR (KBr pellet): ν (cm^{-1}): 3010 (Ar–H), 2925–2868 (Aliph. C–H), 1602, 1486, 1465, 1451, 1392, 1333, 1240, 1117, 1087, 1045, 952, 746, 689. UV–vis (DMSO): λ_{max} nm (log ϵ): 357 (4.87), 614 (4.51), 680 (5.17). Calc. for $\text{C}_{92}\text{H}_{112}\text{I}_4\text{N}_{12}\text{O}_{12}\text{Zn}$: C 51.37, H 5.25, N 7.81%; found: C 51.53, H 5.02, N 8.06%. MS (MALDI-TOF) m/z : 411 [$\text{M} + \text{H} - \text{I}$] $^{+4}$.

2.1.10. 1(4),8(11),15(18),22(25)-Tetrakis-(2-[2-[3-(diethylmethylamino)phenoxy]ethoxy]ethoxy)phthalocyaninato zinc (II) iodide (**6b**)

IR (KBr pellet): ν (cm^{-1}): 3009 (Ar–H), 2924–2854 (Aliph. C–H), 1605, 1578, 1480, 1448, 1391, 1327, 1235, 1166, 1113, 1080, 1046, 985, 868, 745, 687. UV–vis (DMSO): λ_{max} nm (log ϵ): 328 (4.81), 372 (4.78), 627 (4.72), 695 (5.48). Calc. for $\text{C}_{92}\text{H}_{112}\text{I}_4\text{N}_{12}\text{O}_{12}\text{Zn}$: C 51.37, H 5.25, N 7.81%; found: C 51.61, H 5.06, N 8.12%. MS (MALDI-TOF) m/z : Calc. 2156; found: 410 $[\text{M}-4\text{I}]^{+4}$.

3. Results and discussion

3.1. Synthesis and characterization

General synthetic route for the synthesis of new tetra-substituted zinc (II) phthalocyanines (**2a**, **3a**, **5a** and **6a**) and their water soluble derivatives (**2b**, **3b**, **5b** and **6b**) are given in Figs. 1–3, respectively. The cyclotetramerization of the phthalonitrile derivatives **2** and **5** in the presence of anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ in *n*-pentanol and a few drops 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under a nitrogen atmosphere afforded the peripherally zinc phthalocyanines (**2a**

and **5a**). Cyclotetramerization of the phthalonitrile derivatives **3** and **6** to the non-peripherally tetra-substituted zinc (II) phthalocyanines (**3a** and **6a**) were accomplished in the presence of anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ in *n*-pentanol and DBU. Quaternized amphiphilic zinc (II) phthalocyanines (**2b**, **3b**, **5b** and **6b**) were synthesized from the reaction of corresponding zinc (II) phthalocyanines (**2a**, **3a**, **5a** and **6a**) with methyl iodide as a quaternization agent in chloroform. After reaction with methyl iodide, the quaternized zinc phthalocyanines (**2b**, **3b**, **5b** and **6b**) showed excellent solubility in water. The new compounds were characterized by using FT-IR, ^1H NMR, ^{13}C NMR, UV–vis, MS spectroscopic data and elemental analysis.

In the FT-IR spectra of phthalonitrile derivatives **2** and **5**, the characteristic $\text{C}\equiv\text{N}$ stretching vibrations were observed at 2230 and 2231 cm^{-1} , respectively. After the reaction of cyclotetramerization, these sharp peaks disappeared in FT-IR spectra of **2a** and **5a**. Thus, we obtained the peripherally tetra-substituted zinc phthalocyanines bearing four 2-[2-[3-(dimethylamino)phenoxy]ethoxy]ethoxy (for complex **2a**) and 2-[2-[3-(diethylamino)phenoxy]ethoxy]ethoxy (for complex **5a**) groups. In the ^1H NMR spectra of peripherally tetra-substituted zinc (II) phthalocyanines (**2a** and **5a**), the aromatic protons appeared in the range between 7.53–6.25 ppm (for complex **2a**) and 8.14–6.31 ppm (for complex

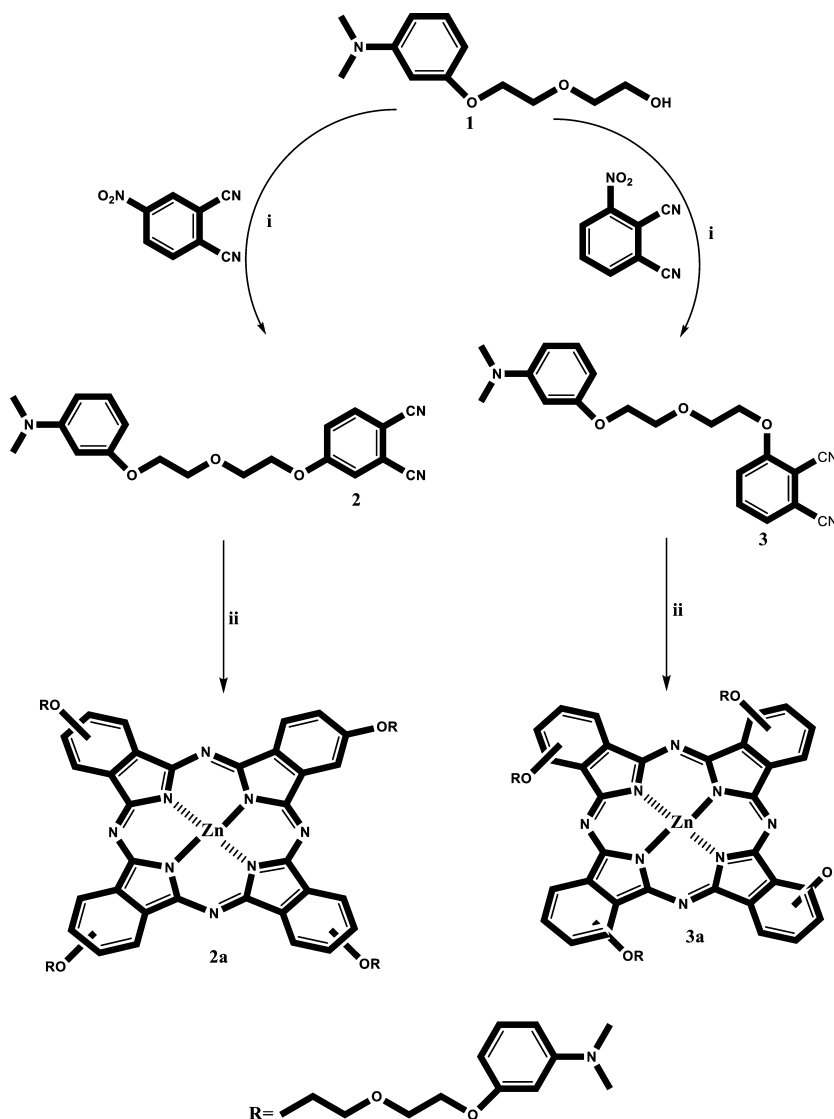


Fig. 1. The synthesis of the zinc (II) phthalocyanines **2a** and **3a**. (i) K_2CO_3 , N_2 , DMF and (ii) $\text{Zn}(\text{CH}_3\text{COO})_2$, *n*-pentanol, DBU, 160 °C.

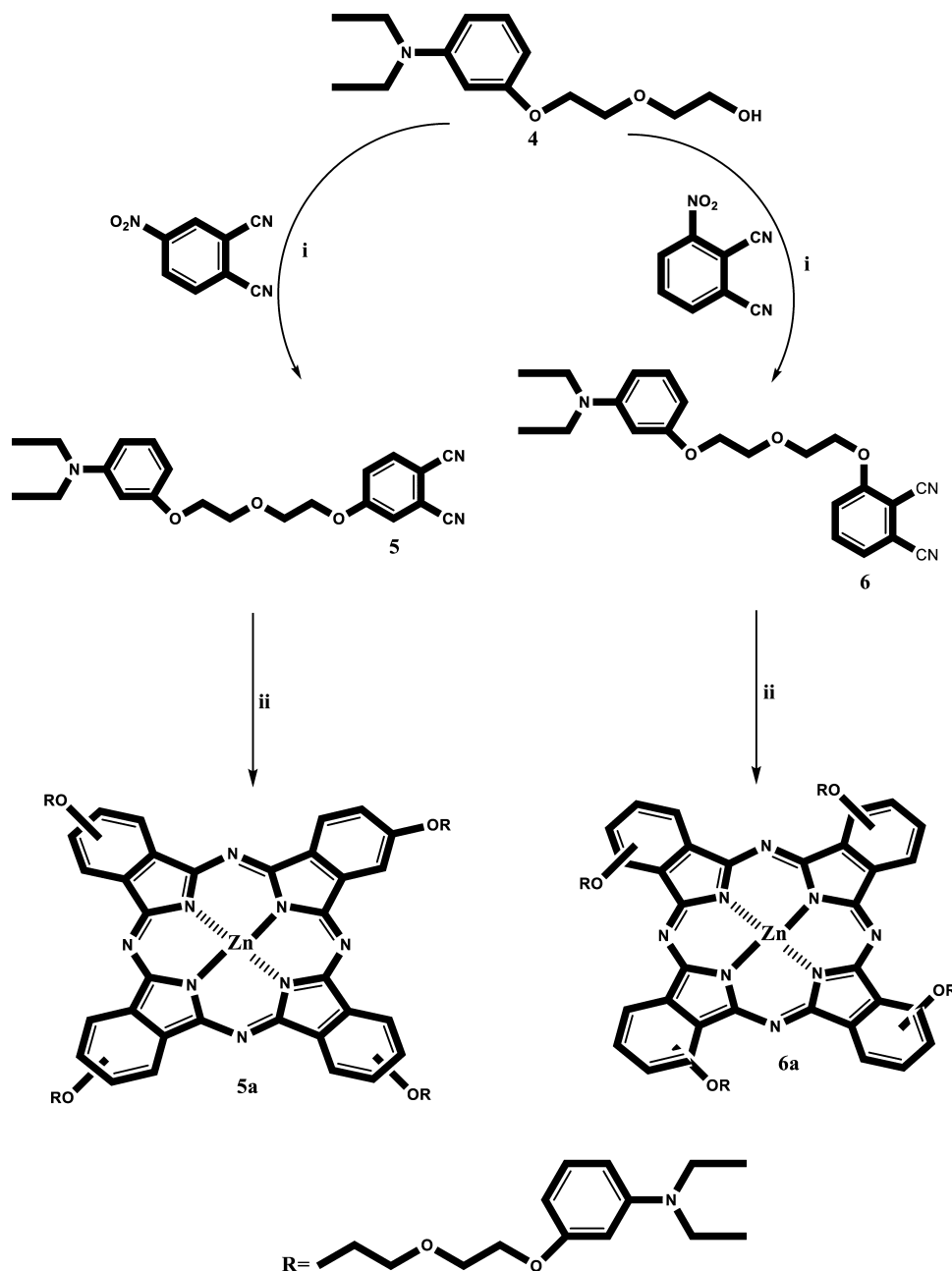


Fig. 2. The synthesis of the zinc (II) phthalocyanines **5a** and **6a**. (i) K_2CO_3 , N_2 , DMF and (ii) $\text{Zn}(\text{CH}_3\text{COO})_2$, *n*-pentanol, DBU, 160°C .

5a). Examining the ^1H NMR spectra of zinc phthalocyanine complexes **2a** and **5a** in CDCl_3 exhibited the expected chemical shifts. In the MALDI-TOF mass spectra of compounds **2a** and **5a** the molecular ion peaks were observed at $m/z = 1472 [\text{M} + \text{H}]^+$ and $1584 [\text{M} + \text{H}]^+$, respectively, and these peaks were confirmed the proposed structures. Electronic spectra are especially useful to identify the structure of the phthalocyanines. In general, phthalocyanines show characteristic electronic spectra, with two strong absorptions around 300–350 nm (B band) and 600–700 nm (Q band) [17–19].

In the FT-IR spectra of phthalonitrile derivatives **3** and **6**, the characteristic $\text{C}\equiv\text{N}$ stretching vibrations were observed at 2230 and 2232 cm^{-1} , respectively. After conversion of the phthalonitriles **3** and **6** to the phthalocyanines **3a** and **6a**, the sharp $\text{C}\equiv\text{N}$ vibrations at 2230 and 2232 cm^{-1} disappeared. The ^1H NMR spectra of non-peripherally tetra-substituted zinc (II) phthalocyanines **3a** and **6a** in CDCl_3 harmonizes with the ^1H

NMR spectra of peripherally tetra-substituted zinc (II) phthalocyanines **2a** and **5a**. In the MALDI-TOF mass spectra of compounds **3a** and **6a**, the molecular ion peaks were observed at $m/z = 1472 [\text{M} + \text{H}]^+$ and $1584 [\text{M} + \text{H}]^+$, respectively.

No major change in the FT-IR spectra was observed after quaternization of zinc phthalocyanine compounds. The MALDI-TOF mass spectra of quaternized zinc (II) phthalocyanines (**2b**, **3b**, **5b** and **6b**) confirmed the proposed structure, with the molecular ion being easily identified at $383 [\text{M} + \text{H} - 4\text{I}]^{+4}$, $384 [\text{M} + 2\text{H} - 4\text{I}]^{+4}$, $411 [\text{M} + \text{H} - 4\text{I}]^{+4}$ and $410 [\text{M} - 4\text{I}]^{+4}$ for complexes **2b**, **3b**, **5b** and **6b**, respectively.

3.2. Photophysical and photochemical studies

3.2.1. Ground state electronic absorption spectra

Ground state electronic absorption spectroscopy is one of the useful method for characterization of phthalocyanine compounds.

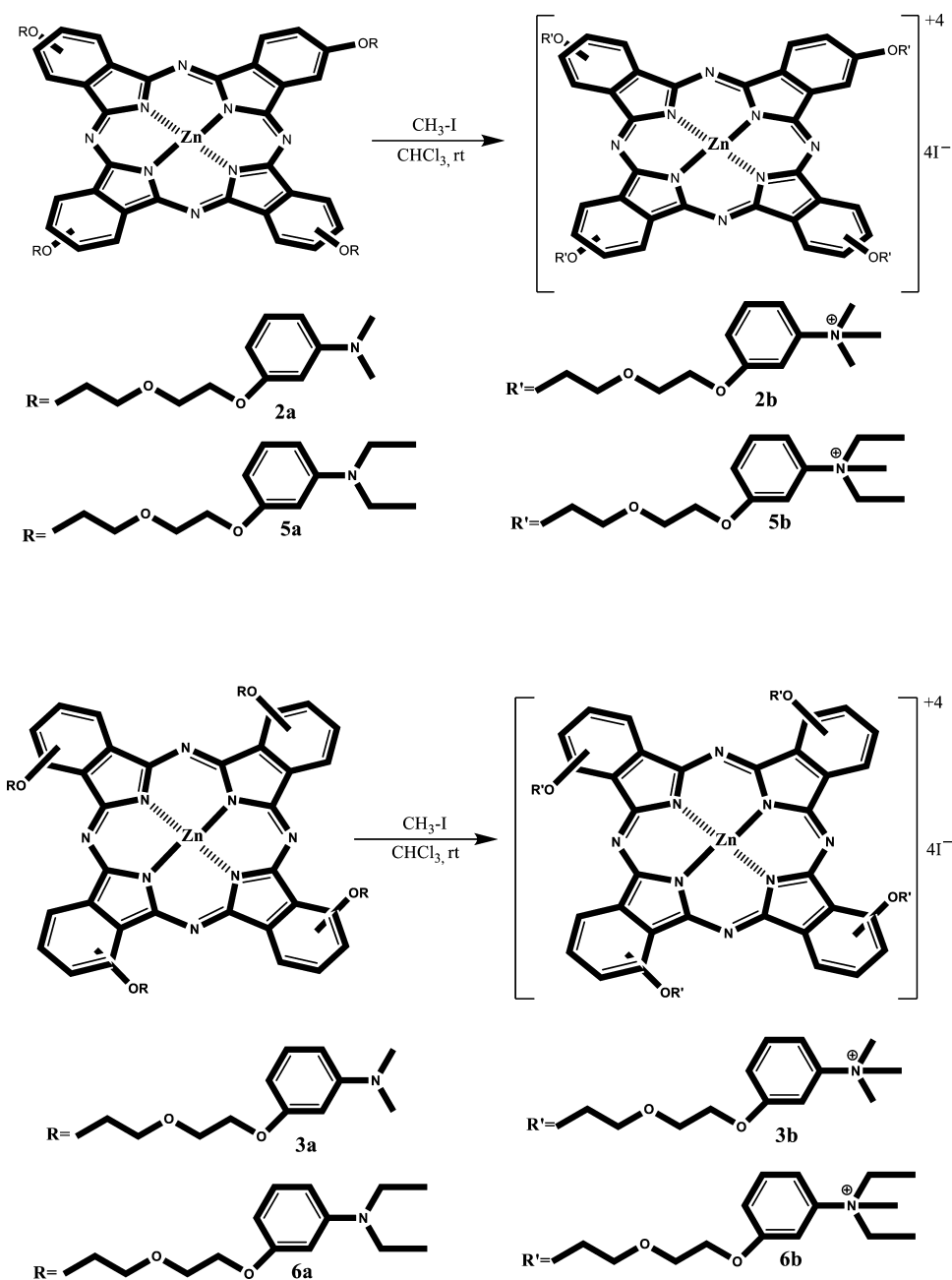


Fig. 3. The synthesis of the water soluble zinc (II) phthalocyanines **2b**, **3b**, **5b** and **6b**.

Phthalocyanine derivatives show two absorption bands in their ground state electronic absorption spectra. One of them is observed in the visible region of spectrum at around 600–750 nm due to the $\pi \rightarrow \pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring and known as Q band. The other one is observed in the ultraviolet region of spectrum at around 300–450 nm arising from deeper π levels \rightarrow LUMO and known as B band. While the metallated phthalocyanine derivatives exhibit single narrow Q band due to D_{4h} symmetry, the metal-free phthalocyanine derivatives exhibit splitted two Q-bands due to D_{2h} symmetry.

The electronic absorption behaviors of studied zinc (II) phthalocyanine compounds were examined by UV-vis spectroscopy. The spectra of the studied peripherally (**2a**, **5a**) and non-peripherally (**3a**, **6a**) substituted zinc (II) phthalocyanine

complexes showed characteristic absorption in the Q band region at around 680–700 nm in DMSO, Table 1. The spectra of tetra-peripherally (**2a**, **5a**) and non-peripherally (**3a**, **6a**) substituted zinc (II) Pc complexes and their quaternized derivatives (**2b**, **3b**, **5b** and **6b**) showed monomeric behavior evidenced by a single (narrow) Q band in the Q band region DMSO. The changing of the variety of the substituents did not significant effect on the electronic spectra of studied zinc (II) phthalocyanine compounds (Fig. 4).

In the UV-vis spectra of tetra-peripherally substituted complexes **2a** and **5a** in DMSO, the Q band absorptions were observed at 683 nm. In addition, B band absorptions of the zinc phthalocyanine complexes **2a** and **5a** were observed at 356 nm. The electronic spectra of non-peripherally substituted phthalocyanines **3a** and **6a** showed intense Q absorption at 703 and 702 nm, respectively, in DMSO. B band absorptions of compounds

Table 1

Absorption, excitation and emission spectral data for unsubstituted and substituted zinc (II) phthalocyanine complexes in DMSO.

Compound	Solvent	Q band λ_{max} (nm)	$\log \varepsilon$	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift $\Delta\lambda_{\text{Stokes}}$ (nm)
2a	DMSO	683	5.11	683	693	10
2b	DMSO	683	5.10	681	692	11
	PBS	634, 680	4.47, 4.27	–	–	–
3a	DMSO	703	5.38	704	713	9
3b	DMSO	702	5.32	702	711	9
	PBS	655, 709	4.69, 4.83	–	–	–
5a	DMSO	683	5.26	685	693	8
5b	DMSO	680	5.17	682	693	11
	PBS	632, 680	4.64, 4.55	–	–	–
6a	DMSO	702	5.43	705	717	15
6b	DMSO	695	5.49	696	705	9
	PBS	646, 686	4.88, 4.85	–	–	–
Std ZnPc	DMSO ^a	672	5.14	672	682	10

^a Data from Ref. [31].

3a and **6a** were observed at 310, 375 nm and 318, 372 nm, respectively. The electronic spectra of the peripherally (**2a**, **2b**, **5a** and **5b**) and non-peripherally (**3a**, **3b**, **6a** and **6b**) tetra-substituted zinc (II) Pc complexes showed characteristic Q band absorptions in DMSO, Fig. 4. The non-peripherally substitution on the Pc ring induces red-shift of the Q band, which is the consequence of a smaller HOMO–LUMO gap, compared to the peripherally substitution [20].

The ground state electronic spectra of the quarternized zinc phthalocyanines (**2b**, **3b**, **5b** and **3b**) showed characteristic absorptions in the Q band region at 683 nm for **2b**, 702 nm for **3b**, 680 nm for **5b** and 695 nm for **6b** in DMSO. B band absorptions were observed at 356, 377, 357 and 372 nm, respectively.

The novel zinc (II) phthalocyanine complexes (**2a**, **3a**, **5a**, and **6a**) showed good solubility in most organic solvents, in addition quaternized zinc (II) phthalocyanine complexes (**2b**, **3b**, **5b**, and

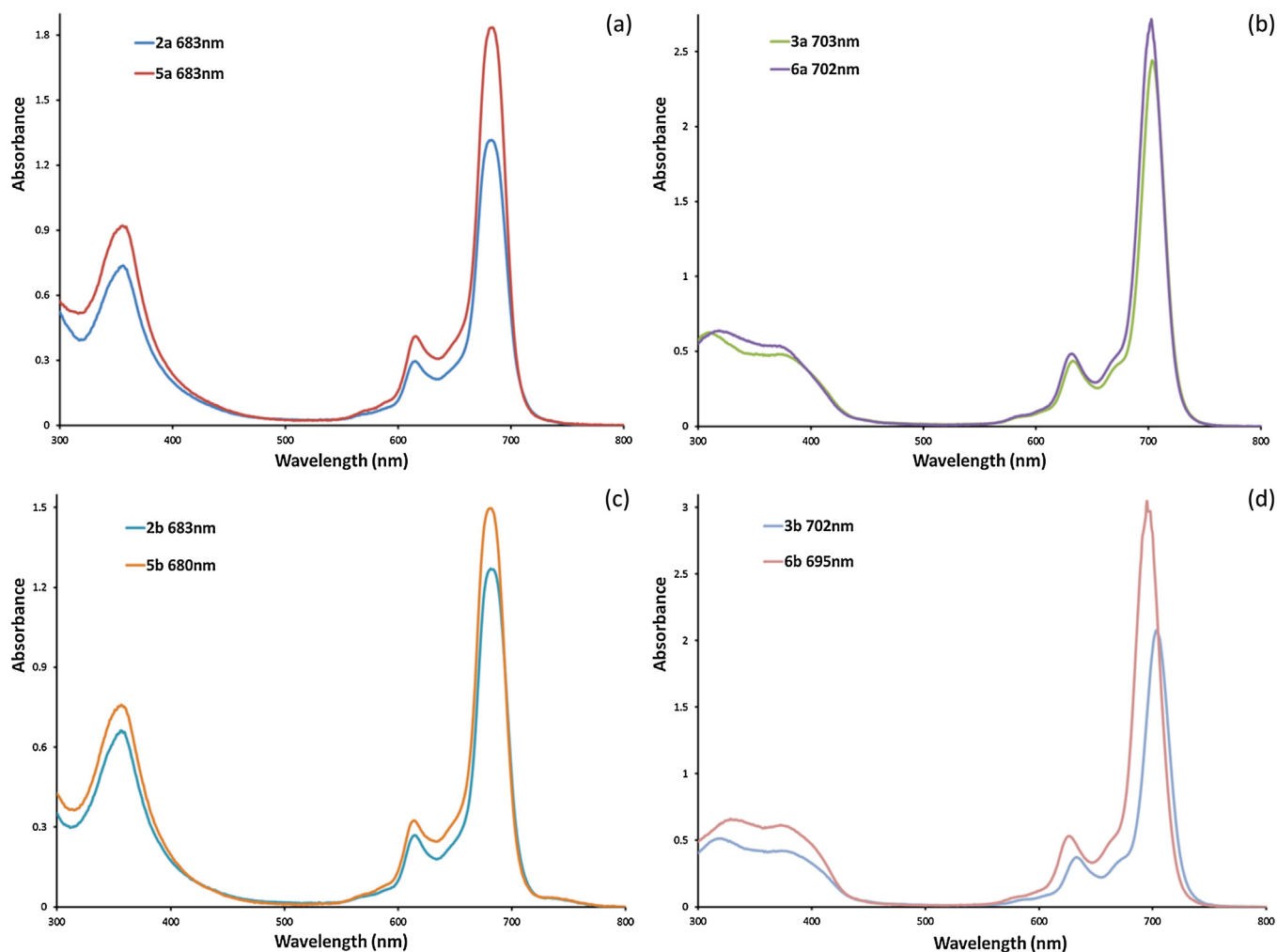


Fig. 4. Absorption spectra of the compounds (a) **2a** and **5a**, (b) **3a** and **6a**, (c) **2b** and **5b**, and (d) **3b** and **6b** in DMSO. Concentration = 1.00×10^{-5} M.

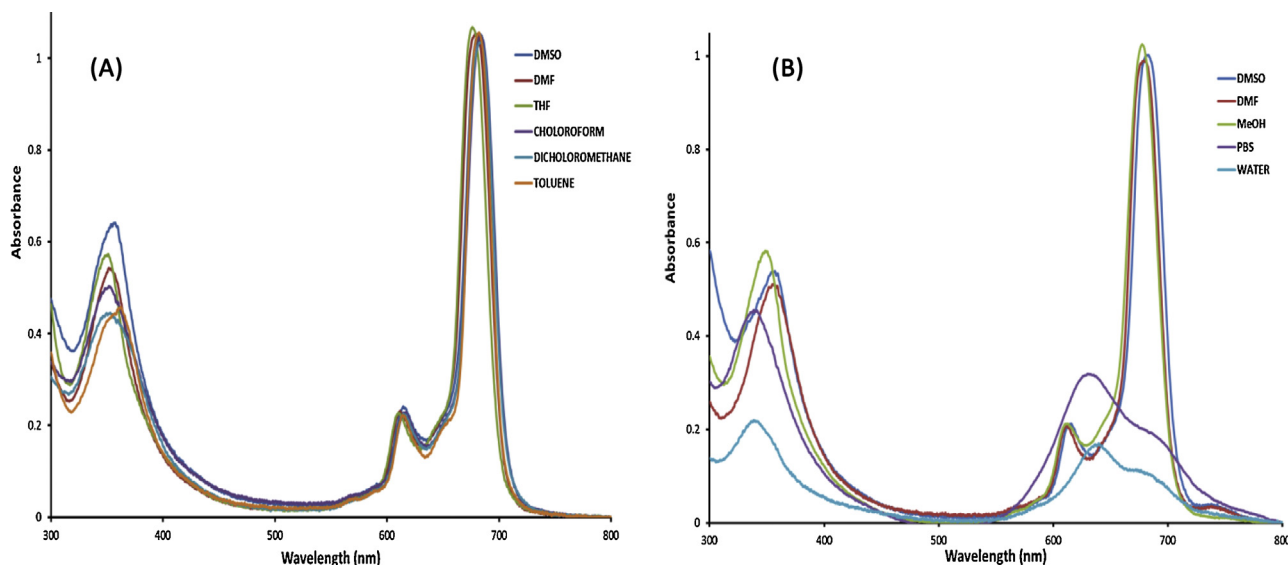


Fig. 5. UV-vis absorption spectra of: (A) **2a** and (B) **2b** in different solvents. Concentration = 1.00×10^{-5} M.

6b) also showed excellent solubility in water. The electronic absorption spectra of studied zinc (II) phthalocyanine complexes were also studied in different solvents (Fig. 5 as an example for compound **2a** and its quaternized derivative **2b**).

3.2.2. Aggregation studies

The UV-vis spectra of non-ionic zinc (II) phthalocyanine derivatives (**2a**, **3a**, **5a**, and **6a**) showed monomeric behavior evidenced by a single (narrow) Q bands in all studied solvents. On the other hand, the quaternized ionic zinc (II) phthalocyanine complexes showed broad peaks at Q band region in aqueous solutions due to aggregation (Fig. 6 as an example for compound **2b** in PBS). The addition of a surfactant, Triton X-100, to the aqueous solution of these complexes gave monomeric peaks at Q band regions as a result of disaggregation.

Phthalocyanine molecules generally form aggregates in solvents. Resulting, phthalocyanine aggregation in a decrease in intensity of Q-band absorption, at the same time a new, broader and blue-shifted band is seen to increase in intensity. This shift to lower wavelengths corresponds to formation of H-type aggregates. Aggregation reduces the photoactivity of photosensitizer compounds as well phthalocyanines through dissipation of energy by aggregates. The aggregation behavior of the studied zinc (II) phthalocyanine complexes substituted with 2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy and 2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy groups (**2a**, **3a**, **5a** and **6a**) and their quaternized derivatives (**2b**, **3b**, **5b** and **6b**) were investigated at different concentrations in DMSO (Fig. 7 as examples for complex **5a**). The Beer-Lambert law was obeyed for all of these compounds at concentrations ranging from 1.2×10^{-5} to 2×10^{-6} M.

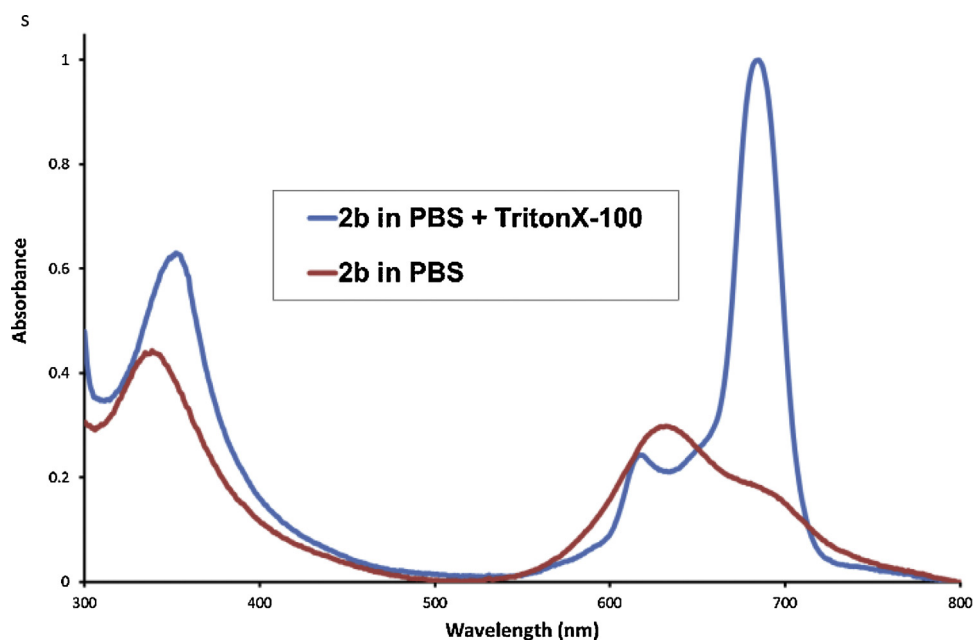


Fig. 6. Absorption spectra of **2b** in PBS and addition of TritonX-100 (1%, v:v) to PBS solution. Concentration = 1.00×10^{-5} M.

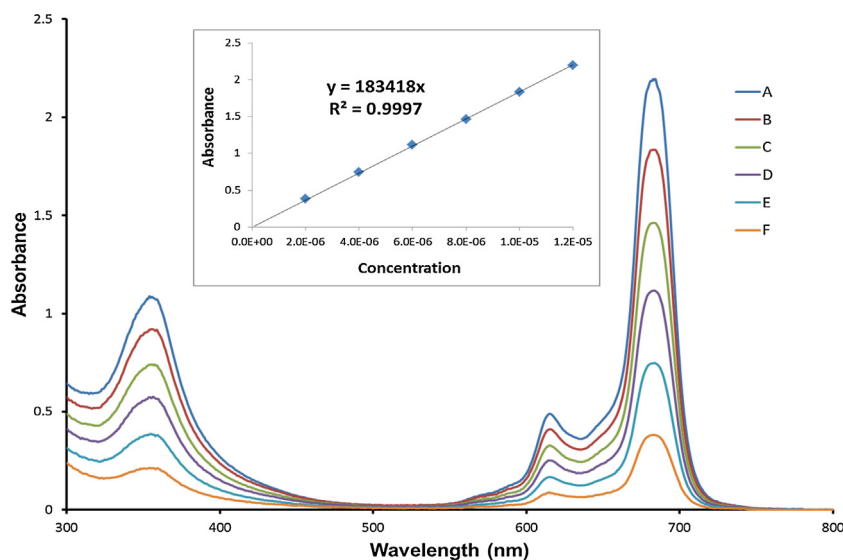


Fig. 7. Absorbance changes of **5a** in DMSO at different concentrations: 12×10^{-6} (A), 10×10^{-6} (B), 8×10^{-6} (C), 6×10^{-6} (D), 4×10^{-6} (E), and 2×10^{-6} (F) M (inset: plot of absorbance versus concentration).

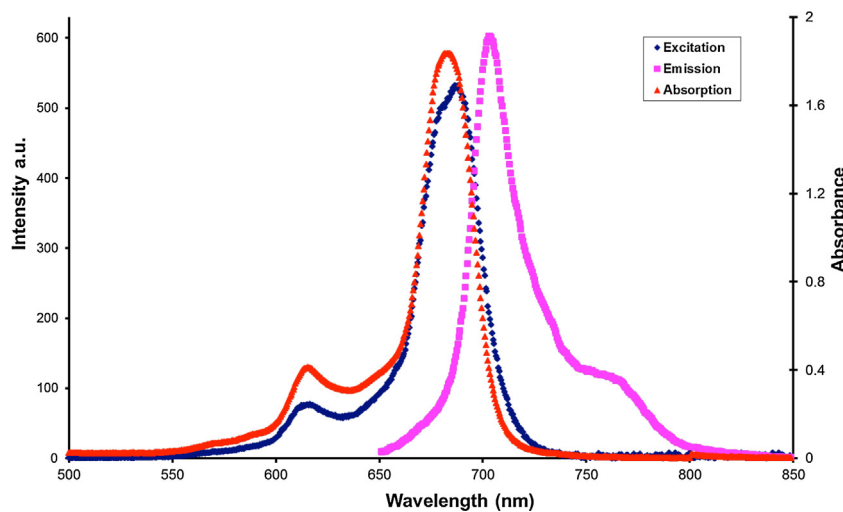


Fig. 8. Absorption, excitation and emission spectra for compound **5a** in DMSO. Excitation wavelength = 640 nm.

All substituted zinc (II) phthalocyanine complexes did not show any aggregation at this concentration range in DMSO.

3.2.3. Fluorescence spectra

The fluorescence emission, absorption and excitation spectra of newly synthesized zinc (II) phthalocyanine complexes were studied in DMSO (Fig. 8 for compound **5a** as an example). All substituted zinc (II) phthalocyanine complexes showed similar fluorescence behavior in DMSO. Fluorescence emission and excitation maxima were listed in Table 1. The observed Stokes' shifts were within the region observed for typical zinc (II) phthalocyanine complexes. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for all studied zinc (II) phthalocyanine complexes suggesting that the molecules did not show any degradation during excitation in DMSO. The fluorescence behaviors of quaternized zinc (II) phthalocyanines were also examined in PBS but, they did not show any fluorescence in PBS solution. It could be due to the formation of aggregates among the zinc phthalocyanine molecules in PBS solution.

Table 2

Photophysical and photochemical data of unsubstituted and substituted zinc (II) phthalocyanine complexes in DMSO.

Compound	Solvent	Φ_F	τ_F (ns)	Φ_d	Φ_Δ
2a	DMSO	0.13	2.13	2.38×10^{-5}	0.47
2b	DMSO	0.19	3.94	5.28×10^{-5}	0.71
	PBS	–	–	3.02×10^{-5}	0.067
3a	DMSO	0.11	1.93	7.04×10^{-5}	0.70
3b	DMSO	0.14	2.69	6.08×10^{-5}	0.85
	PBS	–	–	2.21×10^{-3}	0.30
5a	DMSO	0.03	0.78	1.01×10^{-5}	0.18
5b	DMSO	0.11	3.20	1.04×10^{-4}	0.28
	PBS	–	–	2.00×10^{-5}	0.01
6a	DMSO	0.01	0.64	1.08×10^{-5}	0.43
6b	DMSO	0.10	2.69	2.72×10^{-5}	0.65
	PBS	–	–	6.01×10^{-5}	0.14
Std ZnPc	DMSO	0.20 ^a	3.99	2.61×10^{-5b}	0.67 ^c

^a Data from Ref. [23].

^b Data from Ref. [31].

^c Data from Ref. [32].

3.2.4. Fluorescence quantum yields and lifetimes

Fluorescence consists when an orbital electron of a photosensitizer relaxes to its ground state by emitting a photon of light after being excited to a higher quantum state. The fluorescence quantum yield (Φ_F) gives the efficiency of the fluorescence process. This value defined as the ratio of the number of photons emitted to the number of photons absorbed [21].

The Φ_F values of the studied zinc (II) phthalocyanine compounds (**2a** and **b**, **3a** and **b**, **5a** and **b**, **6a** and **b**) are typical

for MPC compounds. These values ranged from 0.03 to 0.19 in DMSO. The Φ_F values of all 2-[2-[3-(dimethylamino)phenoxy]ethoxy]ethoxy and 2-[2-[3-(diethylamino)phenoxy]ethoxy]ethoxy substituted zinc(II) phthalocyanines were lower than the unsubstituted zinc (II) Pc (Std-ZnPc) in DMSO, Table 2. When compared the studied zinc (II) Pc compounds, the quaternization of the zinc (II) phthalocyanines increased the Φ_F values. It could be suggested that the lone pair electrons of the nitrogen atoms on the substituents in non-quaternized complexes (**2a**, **3a**, **5a** and **6a**)

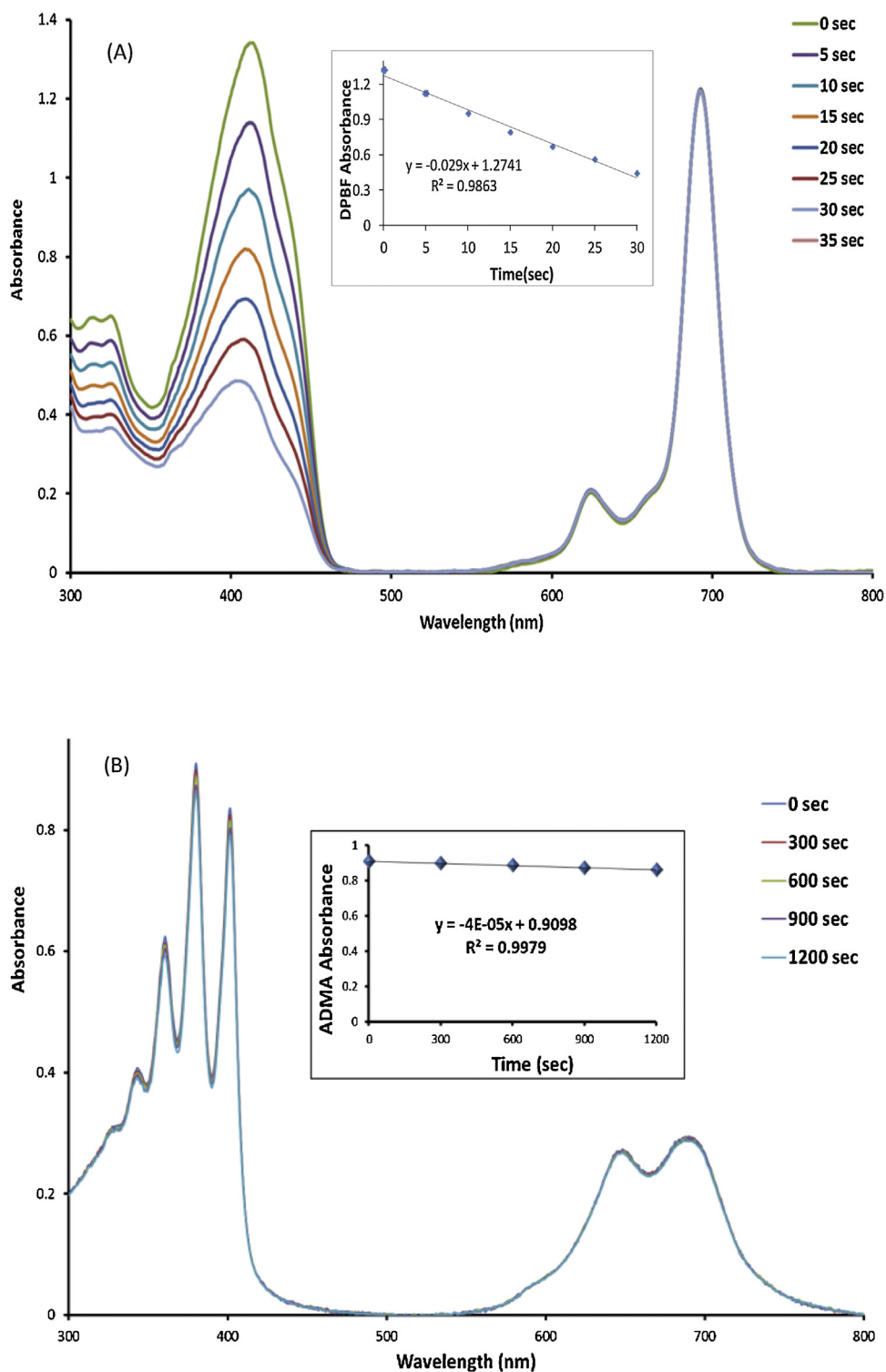


Fig. 9. Absorbance changes during the determination of singlet oxygen quantum yield. This determination was for compound **6b** in (A) DMSO and (B) PBS at a concentration of 1.0×10^{-5} M (inset: plot of DPBF or ADMA absorbances versus irradiation time).

were engaged when they quaternized. In addition, the peripherally substituted zinc (II) phthalocyanine compounds (**2a** and **b**, **5a** and **b**) showed higher Φ_F values than non-peripherally substituted counterparts (**3a** and **b**, **6a** and **b**) suggesting not as much of quenching of the excited singlet state by peripheral substitution compared to the non-peripheral substitution. These results suggest that the substituents position on the phthalocyanine framework and quaternization of the substituents affect on the Φ_F values of these compounds.

Fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before returns to its ground state by emitting [22]. In this study, the fluorescence lifetime values of studied zinc (II) phthalocyanines were determined by using time correlated single photon counting (TCSPC) method. All time-resolved fluorescence studies were carried out in DMSO. The fluorescence decay of studied zinc (II) Pc compounds resulted in monoexponential curves with lifetime range from 0.64 to 3.94 ns. For comparison the value of unsubstituted zinc (II) Pc was measured and lifetime was found as 3.99 ns. The τ_F values of studies zinc (II) Pc complexes were shorter than unsubstituted zinc (II) Pc resulting increasing of the quenching by substitution of 2-[2-[3-(dimethylamino)phenoxy]ethoxy]ethanol or 2-[2-[3-(diethylamino)phenoxy]ethoxy]ethanol groups on the phthalocyanine framework. When the compare of the substituent position, τ_F values of the peripherally substituted zinc (II) phthalocyanine compounds (**2a**, **2b**, **5a** and **b**) were higher compared to non-peripherally substituted zinc (II) Pc compounds (**3a**, **3b**, **6a** and **b**) in DMSO (Table 2), suggesting less quenching of zinc (II) phthalocyanine compounds by peripherally substitution. Moreover, the quaternization of the nitrogen atoms on the substituents affected on the lifetime values of the zinc (II) phthalocyanines. The τ_F values were increased by the quaternization. It also could be suggested that the lone pair electrons of the nitrogen atoms on the substituents in non-quaternized complexes (**2a**, **3a**, **5a** and **6a**) were engaged when they quaternized.

3.2.5. Singlet oxygen quantum yields

Singlet oxygen (1O_2) occurs because of the energy transfer between the triplet state of photosensitizers and ground state molecular oxygen during the photodynamic therapy (PDT) process.

This transfer must be as efficient as possible to generate large amounts of singlet oxygen. The generating amounts of singlet oxygen is quantified by the singlet oxygen quantum yield (Φ_Δ), a parameter giving an indication of the potential of molecules to be used as photosensitizers in applications where singlet oxygen is required such as type II mechanism in the PDT applications. The singlet oxygen quantum yield (Φ_Δ) corresponds to the number of singlet oxygen molecules generated by one photon absorbed by a photosensitizer [21].

In this study, the Φ_Δ values were determined using a chemical method in DMSO and PBS for studied zinc (II) phthalocyanine complexes. 1,3-Diphenylisobenzofuran (DPBF) and 9,10-antracenediyl-bis(methylene)dimalonic acid (ADMA) were used as a singlet oxygen quenchers for the determination of singlet oxygen quantum yields in DMSO and PBS, respectively. The disappearance of DPBF absorbance at 417 nm for all zinc (II) phthalocyanine complexes and ADMA absorbance at 380 nm for ionic zinc (II) phthalocyanines was monitored using UV-vis spectrophotometer (Fig. 9 for compound **6b** as an example). The Q band intensities of studied zinc (II) Pc compounds did not exhibit any changes during the Φ_Δ determinations, supporting that the compounds were not degraded during singlet oxygen studies. The Φ_Δ values of the substituted zinc (II) Pc complexes and unsubstituted zinc (II) Pc complexes in DMSO are given in Table 2. The Φ_Δ values of tetra-substituted zinc (II) Pc compounds (**2b**, **3a** and **3b**) are higher than the Φ_Δ values of unsubstituted zinc (II) Pc compound in DMSO. Especially, the Φ_Δ values of quaternized zinc (II) phthalocyanine derivatives are relatively higher than their non-ionic counterparts in DMSO. It could be due to the increasing of the molecule sizes by the addition of methyl groups on the substituents' nitrogen atoms as well as sulphate anions as counterion.

Table 2 shows that lower Φ_Δ values were observed in PBS solutions compared to in DMSO for all studied quaternized zinc (II) phthalocyanine complexes. It can be explained according to the results given in reference [23]. Singlet oxygen absorbs light at around 1270 nm, water is also absorbs light at around this wavelength and low singlet oxygen lifetime is observed in this medium. On the other hand, the absorption of the DMSO in this wavelength is very limited and longer singlet oxygen lifetime is observed in DMSO solution [23].

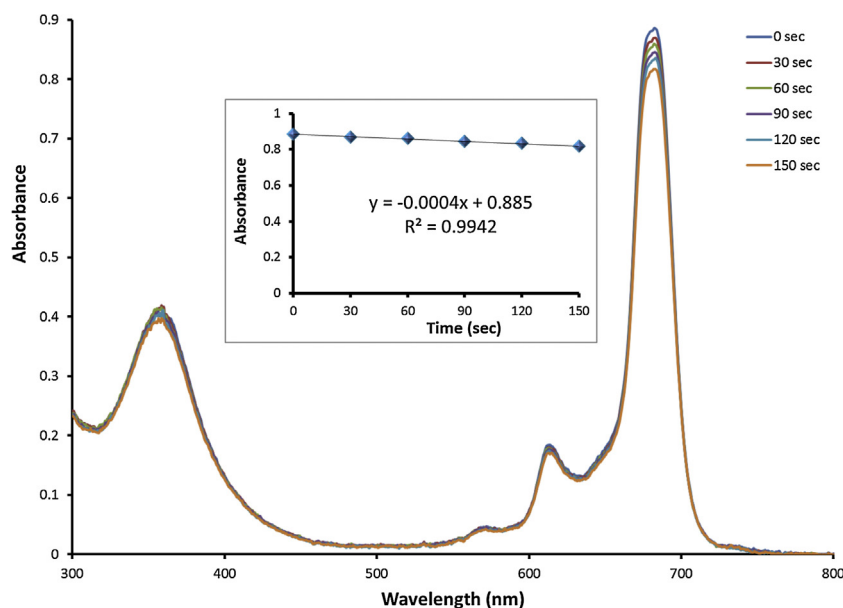


Fig. 10. Absorbance changes during the photodegradation study of **3b** in DMSO showing the decreasing of the Q and B bands at 30 s intervals (inset: plot of Q band absorbance versus time).

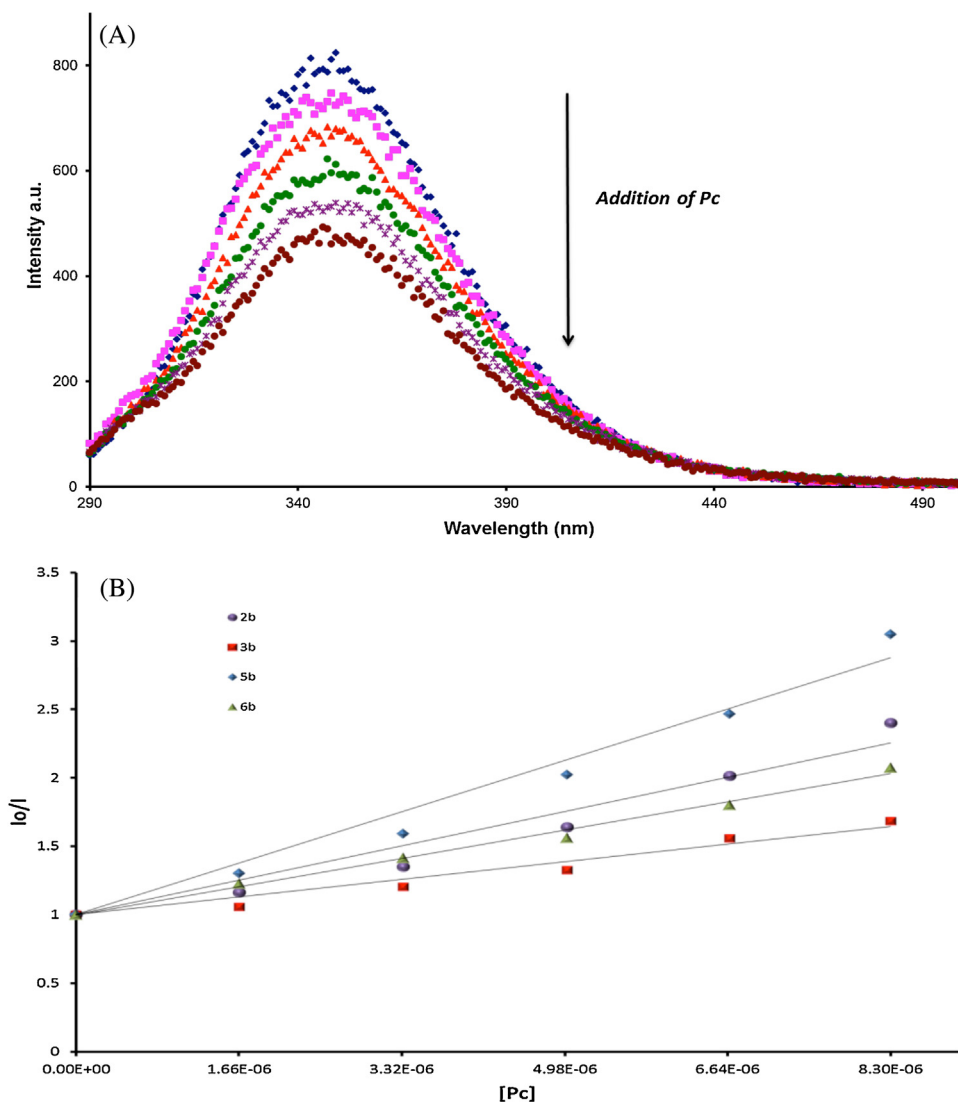


Fig. 11. (A) Fluorescence emission spectral changes of BSA on addition of different concentrations of **6b** in PBS solution and (B) Stern–Volmer plots for quenching of BSA by quaternized complexes (**2b**, **3b**, **5b**, and **6b**) in PBS solution. [BSA] = 3.00×10^{-5} M and [Pc] = 0, 1.66×10^{-6} , 3.33×10^{-6} , 5.00×10^{-6} , 6.66×10^{-6} , 8.33×10^{-6} M.

3.2.6. Photodegradation studies

Light irradiation cause degradation of the molecules. Photodegradation studies can be used to determination of the stability of compounds and this is especially important for those compounds intended for use in photocatalytic applications such as PDT. Photodegradation is the oxidative degradation of a compound under light illumination and the photodegradation degree can be determined by the photodegradation quantum yield (Φ_d). Photodegradation of a compound depends on the structure of the compound, concentration, nature of the solvent and light intensity [21].

The spectral changes for all tetra-substituted zinc (II) phthalocyanine complexes during light irradiation are confirmed photodegradation occurred without phototransformation. The collapse of the absorption spectra without any distortion of the shape confirms photodegradation not associated with phototransformation into different forms of MPc absorbing light in the visible region (Fig. 10 as an example for **3b**). The Φ_d values, found in this study, are order of 10^{-5} and similar phthalocyanine derivatives having different metals and substituents on the phthalocyanine ring in literature [21]. It was reported in literature that stable zinc Pc compounds show Φ_d values as low as 10^{-6} and unstable ones show

Φ_d values of the order of 10^{-3} [24]. Table 2 shows that the Φ_d values of tetra-substituted zinc (II) phthalocyanine compounds (**2a** and **b**, **3a** and **b**, **5a** and **b**, **6a** and **b**) are similar but the Φ_d value of compound **3b** in PBS is higher than other compounds.

3.2.7. Binding of water soluble quaternized zinc (II) phthalocyanine complexes to BSA protein

The binding of quaternized zinc (II) phthalocyanine complexes (**2b**, **3b**, **5b** and **6b**) to BSA were studied by spectrofluorometry at room temperature in PBS solution. An aqueous solution of BSA (fixed concentration) was titrated with varying concentrations of the respective zinc (II) phthalocyanine solutions. For this reason, the investigation of binding properties of photosensitizers with BSA is of interest. The solutions of the ionic quaternized zinc (II) phthalocyanine complexes (**2b**, **3b**, **5b** and **6b**) in five different concentrations (0 , 1.66×10^{-6} , 3.33×10^{-6} , 5.00×10^{-6} , 6.66×10^{-6} , 8.33×10^{-6} M in water) were prepared and added to 3.0×10^{-5} M solution of BSA in PBS. BSA was excited at 280 nm and fluorescence emission spectra were recorded between 290 and 500 nm.

Fig. 11A shows the fluorescence emission spectra of BSA solution by the addition of **6b** in PBS as an example. The

Table 3

Binding and fluorescence quenching data for interaction of BSA with quaternized zinc (II) phthalocyanines in PBS solution.

Compound	$K_{SV}/10^5$ (M^{-1})	$k_q/10^{13}$ ($M^{-1}s^{-1}$)
2b	1.58	1.58
3b	0.96	0.96
5b	2.26	2.26
6b	1.24	1.24

fluorescence emission band at 348 nm was decreased by the addition of zinc (II) phthalocyanine solutions. There was a steady decrease in the intrinsic fluorescence emission intensity of tryptophan residues in BSA with increasing of Pc concentration, which can be attributed to the fluorescence quenching between BSA and zinc (II) phthalocyanine complexes (**2b**, **3b**, **5b** and **6b**). BSA and quaternized zinc (II) phthalocyanines showed reciprocal fluorescence quenching on the other; hence it was possible to determine Stern–Volmer quenching constants (K_{SV}). The slopes of the plots shown in Fig. 11B gave K_{SV} values and listed in Table 3. The K_{SV} values of zinc (II) phthalocyanine complexes (**2b**, **3b**, **5b**, and **6b**) were in the order of 10^5 and these values were similar with phthalocyanine derivatives having different metals and substituents on the phthalocyanine ring [25–27].

The bimolecular quenching constant (k_q) values of quaternized zinc (II) phthalocyanines were determined using Eq. (4) given in the Supplementary information. These values were in the order of $10^{13} M^{-1}s^{-1}$, which exceed the proposed value for diffusion-controlled (dynamic) quenching ($10^{10} M^{-1}s^{-1}$ according to the Einstein–Smoluchowski approximation) at room temperature [28]. This was an additional indication that the mechanism of BSA quenching by quaternized phthalocyanines (**2b**, **3b**, **5b** and **6b**)

was not diffusion-controlled (i.e., not dynamic quenching, but static quenching).

3.2.8. Binding of water soluble quaternized zinc (II) phthalocyanine complexes to DNA

In order to determine the binding properties of positively charged phthalocyanines with DNA, the titration of quaternized zinc (II) phthalocyanines with DNA solution was done by monitoring of changes in optical spectrum. DNA binding experiments were performed by titrating $1.00 \times 10^{-5} M$ of quaternized zinc (II) phthalocyanines in PBS+Triton X-100 (1% to prevent aggregation) solutions (2 mL) with $1.74 \times 10^{-4} M$ of DNA (ϵ :6200) stock solution in PBS (0.005 mL) and the changes in the UV–vis absorption spectra of quaternized zinc (II) phthalocyanines were recorded. The absorption spectra of each quaternized phthalocyanines (**2b**, **3b**, **5b** and **6b**) decreased in intensity without any changes in their shapes by the addition of increasing amount DNA. Fig. 12 demonstrates the changes in the absorption spectrum of **3b** upon titration with DNA solution as an example. The observed decreasing in the absorption intensities of the phthalocyanines could be attributed to the formation precipitates due to existence of non-covalent interaction and external groove binding between positively charged phthalocyanine molecules and negative phosphate backbone of DNA. The Pc–DNA complexes formed insoluble green precipitates in PBS solution but any precipitations were not observed in PBS+Triton X-100 solution because the formed complexes are soluble in PBS solution containing Triton X-100 as described in the literature [29]. The linear decrease in the absorbance at 684 nm with increasing concentrations of DNA indicates a tight binding occurring between quaternized zinc (II) phthalocyanines and DNA (Fig. 12, inset) [29].

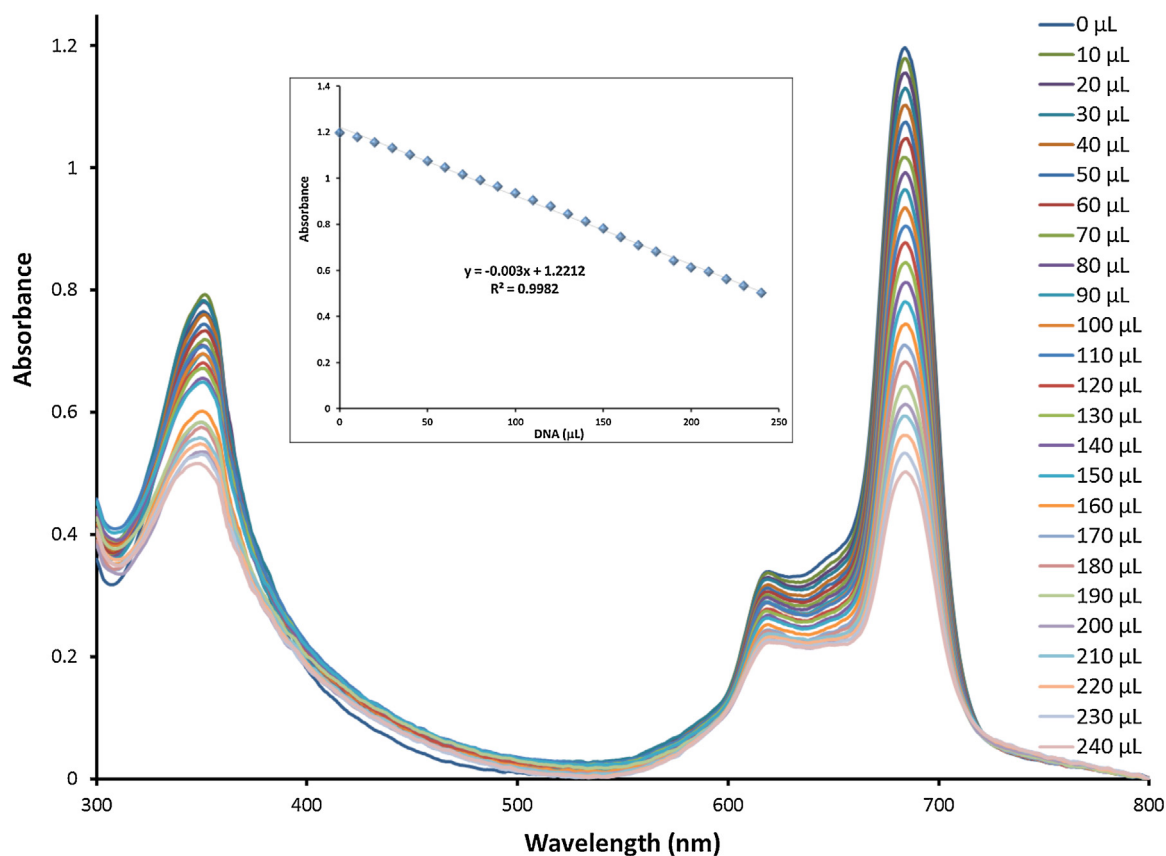


Fig. 12. Electronic titration spectra of $1.00 \times 10^{-5} M$ **3b** with DNA ($1.74 \times 10^{-4} M$) at pH 7.4 in $1 \times$ PBS buffer containing 1% Triton X-100. Inset, the plot of absorbance at 684 nm versus the DNA concentration.

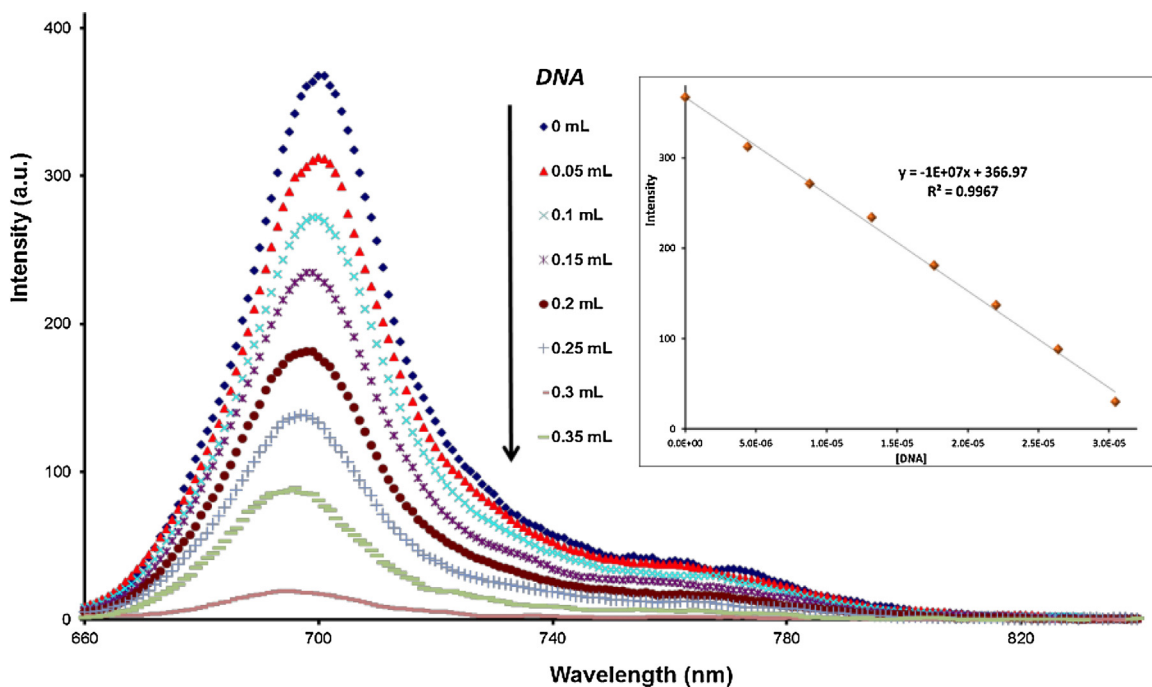


Fig. 13. Emission spectral changes of **[3b]** (1.00×10^{-5} M) by the addition of DNA at pH 7.4 in $1 \times$ PBS buffer containing 1% Triton X-100. Inset, the plot of emission intensities at 700 nm versus the ratio of DNA added at each step to the total **[3b]** concentration.

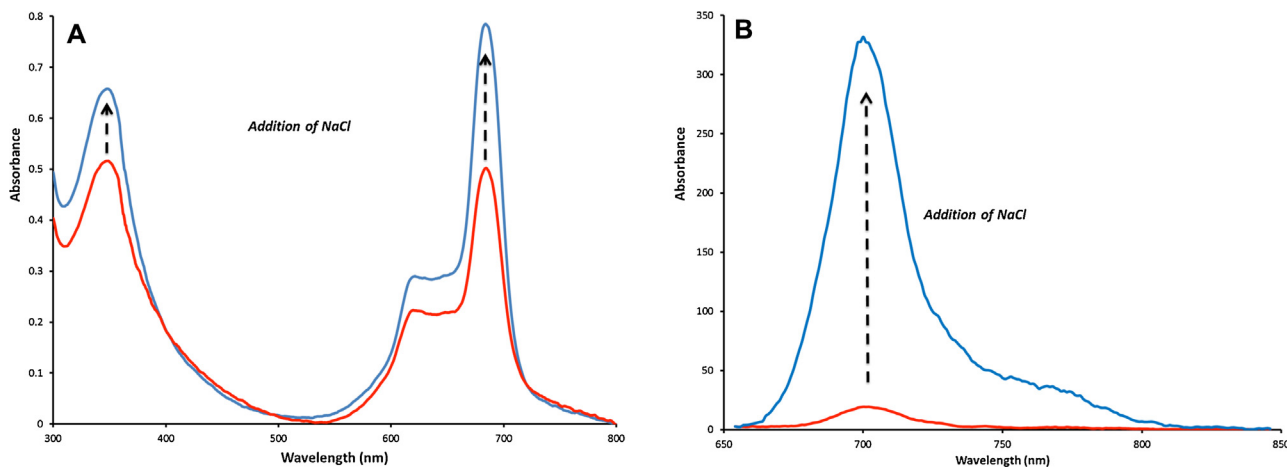


Fig. 14. (A) Electronic absorption and (B) fluorescence emission spectral changes of **3b** in PBS solutions by the addition of NaCl (0.5 M).

Fig. 13 shows that the interaction of quaternized zinc (II) phthalocyanine complexes and DNA is expected to be electrostatic in origin. The emission intensity of the quaternized zinc (II) phthalocyanines is reduced by the addition of DNA to the phthalocyanine solutions which indicates that on interaction occurring between quaternized zinc (II) phthalocyanines and DNA molecules. The inset of **Fig. 13** shows the relationship of the fluorescence intensity of phthalocyanine complex **3b** with the concentration of DNA as an example.

In order to confirm this, the effect of addition of a strong electrolyte such as NaCl [30] was investigated and monitored by both absorption and fluorescence spectroscopy. Both absorption and fluorescence spectral intensities were increased by the addition of NaCl stock solution (0.5 M) (**Fig. 14**) due to dissociation of Pcs-DNA complexes. The changes may be explained as a competition between positively charged quaternized zinc (II)

phthalocyanines and NaCl for nucleic acid sites with sodium ion binding prevailing. The results clearly point to the important role of electrostatic interactions between DNA and Pc molecules.

4. Conclusion

In the presented work, novel tetra peripherally and non-peripherally zinc (II) phthalocyanine complexes substituted with 2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethanol and 2-{2-[3-(diethylamino)phenoxy]ethoxy}ethanol groups (**2a**, **3a**, **5a** and **6a**) and their water soluble quaternized derivatives (**2b**, **3b**, **5b** and **6b**) were synthesized for the first time. Newly synthesized zinc (II) phthalocyanines were characterized by standard spectroscopic methods (UV-vis IR, ^1H NMR, ^{13}C NMR, mass spectroscopy) and elemental analysis results. While the synthesized non-ionic zinc (II) phthalocyanines showed good solubility in most organic

solvents, the quaternized ionic derivatives exhibited excellent solubility in aqueous media as well. However, the quaternized ionic derivatives formed aggregated species in aqueous solutions indicated with the broad peaks at Q band region in the UV–vis spectra of these complexes. The photophysical and photochemical properties of the synthesized zinc (II) phthalocyanines were determined in DMSO for non-ionic complexes and in both DMSO and PBS solutions for quaternized ionic complexes. These properties especially high singlet oxygen generation of the studied zinc (II) phthalocyanines revealed that these newly synthesized zinc (II) phthalocyanines are good candidates for photodynamic therapy applications. The bovine serum albumin (BSA) and DNA binding behavior of the studied water-soluble quaternized zinc (II) phthalocyanines (**2b**, **3b**, **5b** and **6b**) were also investigated by fluorescence and both fluorescence and absorption spectroscopies, respectively. The obtained results indicated that interaction occurred between BSA or DNA molecules and water soluble zinc (II) phthalocyanines. In conclusion, all of these results demonstrated that newly synthesized zinc (II) phthalocyanines especially water-soluble derivatives can be good candidates for photodynamic therapy of cancer treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2014.11.007>.

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