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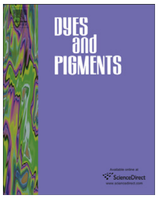

Synthesis and photophysicochemical properties of novel water soluble phthalocyanines

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ABSTRACT

In this study, the peripherally and non-peripherally tetra 2,3-bis[3-(diethylamino)phenoxy]propoxy substituted zinc (II) phthalocyanines (**6** and **7**), axially disubstituted silicon (IV) (**8**) phthalocyanine with some substituent and their quaternized derivatives (**6a**, **7a** and **8a**) were synthesized for the first time as photosensitizers for photodynamic therapy (PDT). The newly synthesized phthalocyanines were characterized by using standard spectroscopic methods such as ^{1}H NMR, ^{13}C NMR, IR, UV–vis, mass and elemental analysis as well. The aggregation, photophysical properties (such as fluorescence quantum yields and lifetimes) and photochemical properties (such as singlet oxygen generation and photostability) were also determined in DMSO for non-ionic phthalocyanines and in both DMSO and aqueous solutions for quaternized ionic phthalocyanines.

1. Introduction

Metal-free and metallophthalocyanines (Pcs) are one of the important types of tetrapyrrole compounds and they show wide range of applications in various areas such as gas and chemical sensors, electrochromic and electroluminescent displays, photovoltaics and semiconductors, electronic devices, liquid crystals, non-linear optics and photodynamic therapy (PDT) [1–7].

Unsubstituted metal-free and metallophthalocyanines show very limited solubility in most of organic solvents and water. This disadvantage is minimized their applications in such area. Whereas peripheral or non-peripheral substitution of phthalocyanine core and axial substitution of central metal ion with different bulky group such as crown ethers, alkyl, alkoxy, alkylthio, tertiary butyl groups improve their solubility in apolar or polar organic solvents [8–17]. On the other hand, the substitution of phthalocyanine ring with substituents such as COOH, SO_3H and quaternized amino groups gave water soluble phthalocyanine derivatives [18–20]. Especially, quaternized ammonium groups are particularly useful to acquire solubility within a wide range of buffers. Furthermore, axially-substituted silicon phthalocyanines (SiPcs) are of marvelous interest to scientists because they are generally not able to aggregate due to their special structural features [21]. Incorporation of closed shell or non-transition metals such as zinc (II) and silicon (IV) in the center of the phthalocyanine ring results in complexes with high triplet state quantum yields and long triplet lifetimes, which are required for efficient photodynamic activity [22].

Photodynamic therapy (PDT) is a newly non-invasive technique for treatment of malignant tumors or macular degeneration. During the photodynamic reaction, the photosensitizer (PS), which is selectively retained by tumor cells, promoted to the excited singlet state with light in the presence of oxygen, decays to the triplet state and generates highly reactive oxygen species (ROS) such as singlet oxygen through intermolecular triplet–triplet energy transfer to oxygen. Basically two types of reactions can occur after photoactivation of a photosensitizer. The produced ROS are toxic to cells and tissues. Therefore cancer cells are destroyed after PDT activity. An essential element of PDT is the photosensitizer that it absorbs the light, produce the ROS and gives the desired therapeutic outcome [23]. Over the past decade, various type of

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photosensitizers were developed to better absorption, greater tumor specificity and less cutaneous photosensitivity in PDT treatment.

Photofrin® (a mixture of hematoporphyrin) is the first-generation photosensitizer currently used in PDT. Compared to porphyrins, chlorins such as meta-tetrahydroxyphenylchlorin (m-THPC, temoporfin, Foscan) offer increased absorption in the farthest-red side band, thus enabling the use of a light with deeper penetration in tissues. These compounds are known as second-generation photosensitizers and they clinically used for the treatment of human mesothelioma and for gynecological, respiratory, and head and neck cancers [24].

Phthalocyanines were also intensely investigated as second generation photosensitizers. They exhibit effective cell penetration because of their chemical stability and proper light absorption behavior at long wavelength. Due to their strong Q band absorption in the red region of spectrum in which the biological tissue are rather transparent and fluorescent, which provides an opportunity for the establishment of their localization in the tissue [7].

In this study, 4-{2,3-bis[3-(diethylamino)phenoxy]propoxy} phthalonitrile (**4**) and 3-{2,3-bis[3-(diethylamino)phenoxy]propoxy}phthalonitrile (**5**) were used for the synthesis of novel peripherally and non-peripherally tetra substituted zinc (II) phthalocyanines (**6** and **7**), respectively. 2,3-Bis[3-(diethylamino) phenoxy]propan-1-ol (**1**) was used for synthesis of novel axially disubstituted silicon phthalocyanine (**8**). Also, their water-soluble ionic derivatives (**6a**, **7a** and **8a**) were also synthesized by quaternization of nitrogen atoms on the substituents. The aim of the present study is to synthesis of novel phthalocyanine compounds as photosensitizers for PDT of cancer treatment. The photophysical properties such as fluorescence quantum yield and lifetimes, and photochemical properties such as singlet oxygen and photodegradation quantum yields were investigated in DMSO for non-ionic phthalocyanine photosensitizers and in both DMSO and aqueous solution for ionic quaternized counterparts.

2. Experimental

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

2.1. Synthesis

2.1.1. 3-{2,3-Bis[3-(diethylamino)phenoxy]propoxy}phthalonitrile (5)

2,3-Bis[3-(diethylamino)phenoxy]propan-1-ol (**1**) (1 g, 2.59 mmol) was dissolved in dry DMF (10 mL) and 3-nitrophthalonitrile (**3**) (0.45 g, 2.59 mmol) was added to the solution. After stirring 10 min, finely ground anhydrous K_2CO_3 (1.07 g, 7.77 mmol) was added to portion wise within 2 h with efficient stirring. The reaction mixture was stirred under a nitrogen atmosphere at 60 °C for 96 h. Then, this mixture was poured into water (100 mL) and the aqueous phase was extracted with chloroform (3 × 50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and then filtered off. Solvent was evaporated and the crude product was purified by passing through an aluminum oxide column using chloroform as eluent. Yield: 0.5 g (38%). IR (KBr pellet) ν (cm^{-1}): 3086 (Ar–H), 2971–2872 (Aliph. C–H), 2230 ($C\equiv N$), 1611 ($C=N$), 1584, 1564, 1502, 1455, 1376, 1355, 1269, 1196, 1138, 1073, 1024, 940, 794. ^1H NMR (400 MHz, $CDCl_3$), (δ: ppm): 7.54 (t, 2H, $J = 6.2$, Ar–H), 7.43 (d, 2H, $J = 7.8$, Ar–H), 7.25–7.21 (m, 2H, Ar–H), 7.15 (d, 2H, $J = 8.1$, Ar–H), 6.58 (s, 1H, Ar–H), 6.38–6.31 (m, 2H, Ar–H), 4.25–4.20 (m, 5H, CH_2–O, CH–O), 3.36 (m, 8H, CH_2–N), 1.18 (m, 12H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), (δ: ppm): 167.80, 161.54, 155.04, 149.83, 134.16, 132.44, 130.91, 130.79, 128.81, 126.41, 122.13, 121.19, 120.39, 116.98, 115.32, 112.93, 109.26, 108.96, 105.48, 103.37, 68.16, 66.26, 44.45, 12.45. MS (ESI), (m/z) calc. 512.64; found: 512.48 $[M]^+$. Elemental Analysis: (Found: C 72.82, H 7.23, N 10.69%, $C_{31}H_{36}N_4O_3$ (512.64) requires C 72.63, H 7.08, N 10.93%).

2.1.2. 2(3),9(10),16(17),23(24)-Tetrakis-{2,3-bis[3-(diethylamino) phenoxy]propoxy}phthalocyaninato zinc (II) (6)

A mixture of compound **4** (0.25 g, 0.48 mmol), anhydrous zinc acetate (0.045 g, 0.24 mmol) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (5 drops) in 2 mL *n*-pentanol was heated to 160 °C and stirred at this temperature for 24 h under a nitrogen atmosphere. A green solution was poured into cold ethanol, left for half an hour and crude product was filtered off. Then, this crude product washed with hot ethanol, diethyl ether and dried in vacuum. The green product was purified by passing through an aluminum oxide column using $CHCl_3$:CH_3OH (100:2) as eluent system. Yield: 0.096 g (38%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3083 (Ar–H), 2966–2867 (Aliph. C–H), 1603 ($C=N$), 1569, 1498, 1466, 1392, 1354, 1268, 1215, 1117, 1087, 1043, 966, 820, 745, 686. ^1H NMR (400 MHz, $CDCl_3$), (δ: ppm): 7.73–7.68 (m, 8H, Ar–H), 7.55–7.50 (m, 8H, Ar–H), 7.12 (m, 4H, Ar–H), 6.59–6.56 (m, 8H, Ar–H), 6.34–6.23 (m, 16H, Ar–H), 4.22–4.11 (m, 20H, –CH_2–O, CH–O), 3.35–3.31 (m, 32H, –CH_2–N), 1.27 (m, 48H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), (δ: ppm): 167.98, 162.76, 159.87, 155.44, 149.62, 149.21, 132.43, 130.94, 130.91, 130.40, 129.96, 128.81, 122.09, 110.28, 108.93, 107.38, 105.47, 100.70, 98.82, 98.11, 69.42, 68.16, 44.50, 12.61. UV–vis (DMSO) λ_{max} nm (log ε): 685 (5.06), 618 (4.44), 356 (4.86). MALDI-TOF-MS m/z calc. 2115.96; found: 2115.74 $[M]^+$. Elemental Analysis: (Found: C 70.56, H 6.60, N 10.32%, $C_{124}H_{144}N_{16}O_{12}Zn$ (2115.96) requires C 70.39, H 6.86, N 10.59%).

2.1.3. 1(4),8(11),15(18),22(25)-Tetrakis-{2,3-bis[3-(diethylamino) phenoxy]propoxy}phthalocyaninato zinc (II) (7)

The synthetic method to that of compound **6** was used to obtain for compound **7** by using a mixture of compound **5** (0.15 g, 0.29 mmol), anhydrous zinc acetate (0.27 g, 0.14 mmol) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (4 drops) in 2 mL *n*-pentanol. The crude product was purified by column chromatography on aluminum oxide by using $CHCl_3$ as eluent. Yield: 0.035 g (23%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3060 (Ar–H), 2965–2865 (Aliph. C–H), 1605 ($C=N$), 1566, 1498, 1471, 1393, 1332, 1233, 1194, 1115, 1076, 1022, 986, 879, 800, 744, 684. ^1H NMR (400 MHz, $CDCl_3$), (δ: ppm): 7.69 (s, 4H, Ar–H), 7.54 (m, 4H, Ar–H), 7.17–7.05 (m, 20H, Ar–H), 6.52–6.43 (m, 16H, Ar–H), 4.24–4.13 (m, 20H, –CH_2–O, CH–O), 3.41–3.32 (m, 32H, –CH_2–N), 1.27 (m, 48H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), (δ: ppm): 167.29, 161.86, 159.54, 156.23, 149.64, 149.12, 136.15, 132.42, 130.90, 130.26, 129.86, 128.80, 123.34, 116.81, 112.42, 111.60, 105.94, 104.92, 104.50, 102.31, 69.48, 68.16, 44.40, 12.53. UV–vis (DMSO) λ_{max} nm (log ε): 703 (5.30), 632 (4.60), 319 (4.81). MALDI-TOF-MS m/z calc. 2115.96; found: 2115.62 $[M]^+$. Elemental Analysis: (Found: C 70.64, H 6.52, N 10.22%, $C_{124}H_{144}N_{16}O_{12}Zn$ (2115.96) requires C 70.39, H 6.86, N 10.59%).

2.1.4. Bis ({2,3-bis[3-(diethylamino)phenoxy]propoxy}) phthalocyaninato silicon (IV) (8)

A mixture of dichloro(phthalocyaninato)silicon (150 mg, 0.24 mmol) and 2,3-bis[3-(diethylamino)phenoxy]propan-1-ol (**1**) (185 mg, 0.48 mmol) in toluene (15 mL) was stirred and then sodium hydride (19.8 mg, 0.48 mmol) was added to this mixture. After refluxing for 24 h under a nitrogen atmosphere, the reaction mixture was cooled to room temperature, and then solvent was evaporated to dryness under reduced pressure. Finally, the crude product was purified by column chromatography on aluminum oxide using $CHCl_3$:CH_3OH (100:2) as eluent system. Yield: 0.122 g

(38%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3060 (Ar–H), 2964–2868 (Aliph. C–H), 1609 (C=N), 1569, 1499, 1470, 1427, 1333, 1289, 1214, 1165, 1120, 1095, 1077, 1021, 910, 870, 732, 686. ^{1}H NMR (400 MHz, CDCl$_3$), (δ: ppm): 9.65–9.62 (m, 8H, Pc-H$_\alpha$), 8.35–8.32 (m, 8H, Pc-H$_\beta$), 7.56 (m, 4H, Ar–H), 6.54 (m, 4H, Ar–H), 5.94 (m, 4H, Ar–H), 5.61 (m, 4H, Ar–H), 3.33 (m, 16H, CH$_2$–N), 1.28 (m, 24H, –CH$_3$), 0.78 (m, 4H, CH$_2$–O), 0.40 (m, 2H, CH–O), −1.00 (m, 4H, Si–O–CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$), (δ: ppm): 159.00, 149.59, 148.39, 135.89, 130.94, 128.92, 123.81, 104.36, 100.67, 98.27, 68.17, 66.93, 43.96, 12.60. UV–vis (DMSO) λ_{max} nm (log ε): 678 (5.17), 642 (4.59), 613 (4.51), 355 (4.86). MALDI-TOF-MS *m/z* calc. 1311.64; found: 1312.50 [M+H]$^+$. Elemental Analysis: (Found: C 71.66, H 6.08, N 13.08%, $C_{78}H_{82}N_{12}O_6Si$ (1311.64) requires C 71.42, H 6.30, N 12.81%).

*2.1.5. 2(3),9(10),16(17),23(24)-Tetrakis-{2,3-bis[3-(diethylmethylamino)phenoxy]propoxy} phthalocyaninato zinc (II) iodide (**6a**)*

Compound **6** (0.035 g, 0.010 mmol) was dissolved in CHCl$_3$ (3 mL) and stirred with 2.5 mL of methyl iodide at room temperature for 2 days. The green precipitate was filtered off, washed with chloroform, acetone and diethyl ether. The precipitate was dried in vacuum. Yield: 0.020 g (62%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3011 (Ar–H), 2921–2865 (Aliph. C–H), 1601 (C=N), 1462, 1392, 1333, 1257, 1217, 1115, 1088, 1043, 963, 871, 745, 688. ^{1}H NMR (400 MHz, DMSO-d$_6$), (δ: ppm): 7.94 (m, 4H, Ar–H), 7.74–7.71 (m, 8H, Ar–H), 7.58–7.54 (m, 16H, Ar–H), 7.30–7.26 (m, 8H, Ar–H), 7.08–7.05 (m, 8H, Ar–H), 4.38–4.34 (m, 20H, –CH$_2$–O, CH–O), 3.78–3.75 (m, 32H, –CH$_2$–N), 3.60–3.56 (m, 24H, N–CH$_3$), 1.04 (m, 48H, –CH$_3$). UV–vis (DMSO) λ_{max} nm (log ε): 682 (5.27), 615 (4.61), 357 (5.00). MALDI-TOF-MS *m/z* calc. 3251.47; found: 2236.30 [M − 8I]$^+$. Elemental Analysis: (Found: C 48.98, H 4.89, N 7.12%, $C_{132}H_{168}I_8N_{16}O_{12}Zn$ (3251.47) requires C 48.76, H 5.21, N 6.89%).

*2.1.6. 1(4),8(11),15(18),22(25)-Tetrakis-{2,3-bis[3-(diethylmethylamino)phenoxy]propoxy}phthalocyaninato zinc (II) iodide (**7a**)*

The synthetic method to that of compound **6a** was used to obtain compound **7a** by using a mixture of compound **7** (0.027 g,

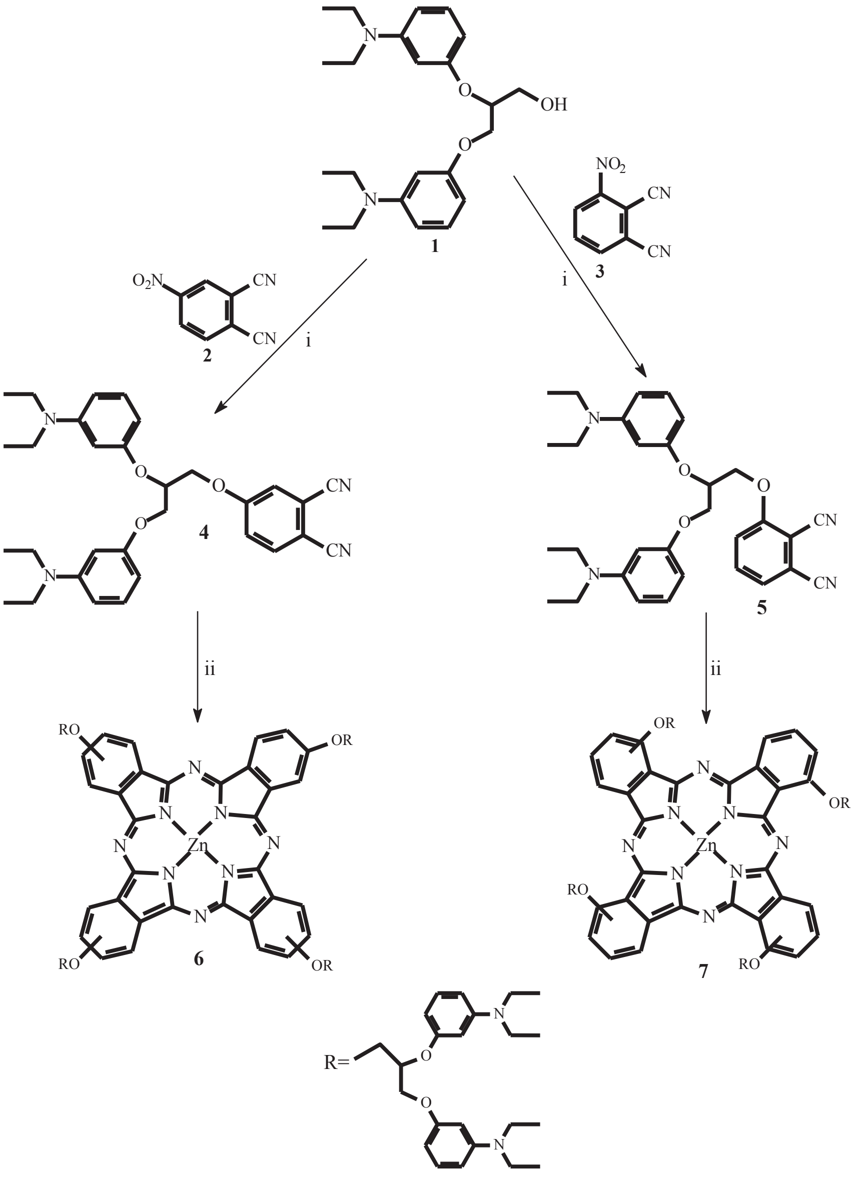

Fig. 1. The synthesis of the zinc (II) phthalocyanines **6** and **7**. (i) K_2CO_3, N_2, DMF. (ii) $Zn(CH_3COO)_2$, *n*-pentanol, DBU, 160 °C.

0.012 mmol), chloroform (3 mL) and methyl iodide (2.5 mL). Yield: 0.015 g (38%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3021 (Ar–H), 2926–2870 (Aliph. C–H), 1604 (C=N), 1574, 1477, 1445, 1393, 1329, 1233, 1114, 1089, 1045, 977, 878, 743, 686. ^{1}H NMR (400 MHz, DMSO-d$_6$), (δ: ppm): 7.86 (m, 4H, Ar–H), 7.72–7.66 (m, 20H, Ar–H), 7.58–7.55 (m, 8H, Ar–H), 7.20–7.17 (m, 12H, Ar–H), 4.42–4.37 (m, 20H, –CH$_2$–O, CH–O), 3.80–3.77 (m, 32H, –CH$_2$–N), 3.65–3.62 (m, 24H, N–CH$_3$), 1.06 (m, 48H, –CH$_3$). UV–vis (DMSO) λ_{max} nm (log ε): 696 (5.28), 628 (4.56), 337 (4.70). MALDI-TOF-MS *m/z* calc. 3251.47; found: 2236.42 [M − 8I]$^+$. Elemental Analysis: (Found: C 49.10, H 4.81, N 7.22%, $C_{132}H_{168}I_8N_{16}O_{12}Zn$ (3251.47) requires C 48.76, H 5.21, N 6.89%).

*2.1.7. Axially bis ({2,3-bis[3-(diethylmethylamino)phenoxy] propoxy})phthalocyaninato silicon (IV) iodide (**8a**)*

The synthetic method to that of compound **6a** was used to obtain compound **8a** by using a mixture of compound **8** (0.050 g, 0.038 mmol), chloroform (4 mL) and methyl iodide (3 mL). Yield: 0.021 g (29%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3009 (Ar–H), 2920–2849 (Aliph. C–H), 1607 (C=N), 1490, 1471, 1427, 1334, 1290, 1257, 1165, 1121, 1078, 988, 910, 875, 736, 690. ^{1}H NMR (400 MHz, DMSO-d$_6$), (δ: ppm): 9.75–9.72 (m, 8H, Pc-H$_\alpha$), 8.41–8.38 (m, 8H, Pc-H$_\beta$), 7.62–7.58 (m, 8H, Ar–H), 7.22–7.18 (m, 8H, Ar–H), 3.79–3.76 (m, 16H, CH$_2$–N), 3.63–3.60 (m, 12H, N–CH$_3$), 1.65 (m, 6H, CH$_2$–O, CH–O), 1.02 (m, 24H, –CH$_3$), –1.04 (m, 4H, Si–O–CH$_2$). UV–vis (DMSO) λ_{max} nm (log ε): 678 (5.20), 613 (4.52), 355 (4.85). MALDI-TOF-MS *m/z* calc. 1879.40; found: 1372.79 [M-4I + H]$^+$. Elemental Analysis: (Found: C 52.61, H 4.79, N 9.22%, $C_{82}H_{94}I_4N_{12}O_6Si$ (1879.40) requires C 52.40, H 5.04, N 8.94%).

3. Results and discussion

3.1. Synthesis and characterization

General synthetic routes for the synthesis of new tetra peripherally and non-peripherally zinc (II) phthalocyanines **6** and **7**, axially disubstituted silicon (IV) phthalocyanine **8** bearing 2,3-bis [3-(diethylamino)phenoxy]propoxy groups and their water soluble quaternized derivatives **6a**, **7a** and **8a** are given in Figs. 1–3, respectively. Reaction of phthalonitrile compounds **4** or **5** with Zn(CH$_3$COO)$_2$ salt in the presence of DBU as a N-donor base in *n*-pentanol led to formation of zinc (II) phthalocyanines **6** and **7**, respectively. Silicon (IV) phthalocyanine complex **8** was synthesized by heating silicon phthalocyanine dichloride with 2,3-bis[3-(diethylamino)phenoxy]propan-1-ol (**1**) in the presence of NaH in toluene at 115 °C for 24 h. Quaternization of the phthalocyanines **6**, **7** and **8** was achieved by the reaction of these phthalocyanines with excess methyl iodide as a quaternization agent in CHCl$_3$ at room temperature. The structures of novel compounds were characterized by a combination of ^{1}H NMR, ^{13}C NMR, IR, UV–vis, mass spectroscopic data and elemental analysis as well.

In the IR spectrum of compound **5**, stretching vibrations of C≡N (2230 cm^{-1}) and aliphatic CH (2971–2872 cm^{-1}) appeared at the expected frequencies. In the ^{1}H NMR spectrum of this compound, the OH group belonging to compound **1** disappeared as expected

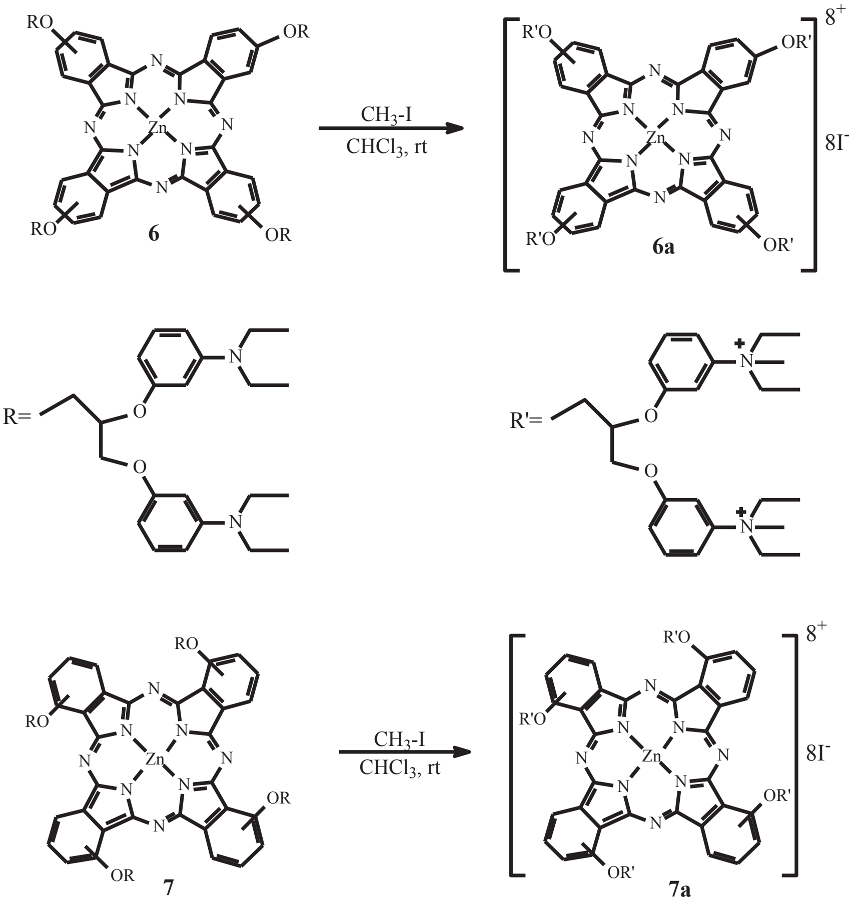

Fig. 2. The synthesis of the water soluble zinc (II) phthalocyanines **6a** and **7a**.

after formation of phthalonitrile compound **5**. In the ^{13}C NMR spectrum of this compound, the presence of nitrile carbon atoms was observed at 116.98 and 112.93 ppm. The presence of a molecular ion peak at $m/z = 512$ $[M]^+$ confirmed the proposed structure of compound **5**.

The IR spectra of the zinc (II) phthalocyanines **6** and **7** clearly indicate the formation of phthalocyanines by the cyclotetramerization of the phthalonitrile derivatives **4** and **5** due to disappearance of the C≡N peaks at 2231 and 2230 cm^{-1}, respectively. The IR spectra of zinc (II) phthalocyanines **6** and **7** showed very similar behavior. No major changes in the IR spectra of were observed after quaternization (for **6a** and **7a**) of these phthalocyanines. The formation of silicon phthalocyanine complex **8** was clearly confirmed by the disappearance of the OH band at 3330 cm^{-1} for compound **1** in the IR spectrum of phthalocyanine **8**. No major change in the IR spectra was also observed after quaternization (for **8a**) of silicon (IV) phthalocyanine **8**.

The ^{1}H NMR spectra of peripherally and non-peripherally tetrasubstituted zinc (II) phthalocyanines **6** and **7** showed peaks belonging to aromatic protons at between 7.73 and 6.23 ppm for complex **6** and between 7.69 and 6.43 ppm for complex **7**. Examining the ^{1}H NMR spectra of zinc (II) phthalocyanine complexes **6** and **7** in $CDCl_3$ exhibited the expected chemical shifts. The ^{1}H NMR spectrum of axially disubstituted silicon phthalocyanine **8** showed peaks belonging to H_α and H_β protons at between 9.65–9.62 and 8.35–8.32 ppm, respectively. Also, in ^{1}H NMR spectrum of SiPc **8**, the peaks belonging to aliphatic CH_2 protons in Si–O–CH_2 bond were shifted negative region (−1.00 ppm) because of magnetic anisotropy of phthalocyanine ring [25]. The NMR spectra of quaternized compounds **6a**, **7a**, and **8a** showed more unresolved patterns compared to non-quaternized derivatives.

In the MALDI-TOF-MS of compounds **6**, **7** and **8**, the molecular ion peaks were observed at $m/z = 2115.74$ as $[M]^+$, 2115.62 as $[M]^+$ and 1312.50 as $[M+H]^+$, respectively, and the observation of these peaks were clearly indicates the formation of desired products. In the MALDI-TOF mass spectra of water soluble complexes **6a**, **7a** and **8a**, the molecular ion peaks were observed at $m/z = 2236.30$ $[M-8I]^+$, 2236.42 $[M-8I]^+$ and 1372.79 $[M\text{-}4I+H]^+$, respectively. These observed molecular ion peaks in mass spectra support the proposed formula for these compounds.

3.2. Photophysical and photochemical studies

3.2.1. Ground state electronic absorption spectra

UV–vis spectroscopy is one of the best spectroscopic technique for determination of the formation of phthalocyanines. This spectroscopy is a quite useful method for characterization of phthalocyanine compounds. Generally, two absorption bands are observed for phthalocyanine compounds in their electronic absorption spectra. One of them is observed 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

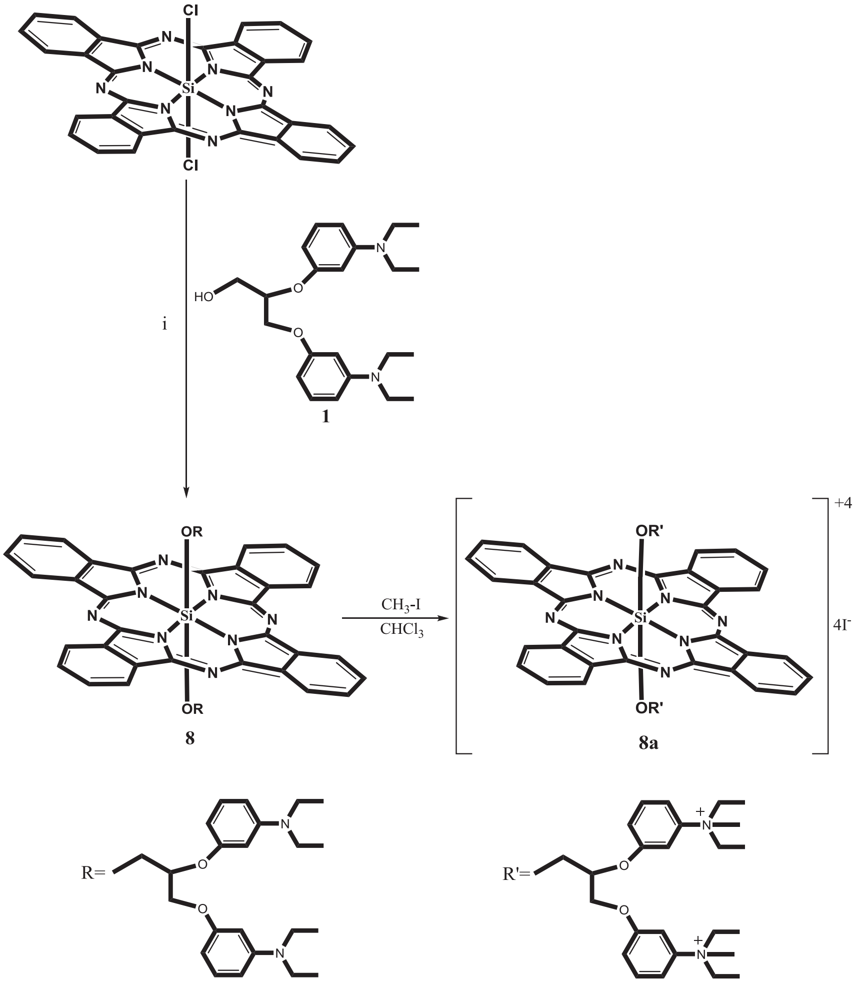

Fig. 3. The synthesis of axially disubstituted silicon phthalocyanine **8** and its water soluble derivative **8a**. (i) Toluene, NaH, reflux.

phthalocyanine ring and known as Q and the other one is observed in the ultraviolet region of spectrum at around 300–450 nm arising from deeper π levels → LUMO and known as B or Soret band [26].

In this study, the UV–vis spectra of the studied phthalocyanine compounds showed characteristic absorptions in the Q band region at 685 nm for compound **6**, 703 nm for compound **7**, 678 nm for **8**, 682 nm for compound **6a**, 696 nm for compound **7a**, 678 nm for compound **8a**, in DMSO. The B band absorptions of these phthalocyanines (**6**, **7**, **8**, **6a**, **7a** and **8a**) were observed at around 320–355 nm. While the quaternized silicon (IV) phthalocyanine (**8a**) showed single narrow Q band at 684 nm, the quaternized ionic zinc (II) phthalocyanines showed broad Q bands at 640 and 682 nm for **6a**, and 650 and 693 nm for **7a** in aqueous solution.

3.2.2. *Aggregation studies*

The electronic absorption spectra of studied non-ionic phthalocyanine complexes (**6**, **7** and **8**) and also their quaternized ionic derivatives (**6a**, **7a** and **8a**) showed monomeric behavior in DMSO evidenced by a single (narrow) Q band (Fig. 4). The electronic absorption spectra of studied phthalocyanines were also measured in DMSO at different concentrations for the determination of the aggregation behavior of these phthalocyanines. The Lambert–Beer law was obeyed for all of these compounds at concentrations ranging from 1.2 × 10^{-5} to 2 × 10^{-6} M. All substituted phthalocyanine complexes did not show any aggregation at this concentration range in DMSO.

In this study, the newly synthesized zinc (II) and silicon (IV) phthalocyanines (**6**, **7**, **8**, **6a**, **7a** and **8a**) showed good solubility in many organic solvents. Their quaternized ionic derivatives (**6a**, **7a** and **8a**) showed excellent solubility in water as well. The electronic absorption spectra were measured in different solvents such as DMSO, DMF, THF, chloroform, dichloromethane and toluene for studied non-ionic phthalocyanines (Fig. 5a as an example for compound **6**) and DMSO, DMF, water and phosphate buffer solution (PBS) for quaternized ionic phthalocyanines (Fig. 5b as an example for compound **6a**) for the investigation of aggregation behavior of these phthalocyanines in different solvents. The UV–vis spectra of non-ionic phthalocyanine derivatives (**6**, **7** and **8**) showed monomeric behavior evidenced by a single (narrow) Q bands in all studied solvents. While the peripheral and non-peripheral quaternized ionic zinc (II) phthalocyanine derivatives showed single narrow Q bands in DMSO and DMF, they showed broad peaks at Q band region in aqueous solutions (Fig. 5b as examples for compound **6a**) due to aggregation of these phthalocyanines in aqueous solution. The addition of a surfactant, Triton X-100, to the aggregated aqueous solution of these complexes gave monomeric peaks at Q band regions as a result of disaggregation (Fig. 5b as example for compound **6a**). Otherwise, the quaternized ionic silicon (IV) phthalocyanine (**8a**) showed non-aggregated species in aqueous solution compared to zinc (II) phthalocyanine counterparts due to the substitution of 2,3-bis[3-(diethylamino)phenoxy]propoxy groups on the axially positions of this compound (Fig. 6).

3.2.3. *Fluorescence spectra*

The fluorescence emission, absorption and excitation spectra of newly synthesized peripherally or non-peripherally tetra substituted zinc (II) phthalocyanine complexes (**6** and **7**), axially disubstituted silicon (IV) phthalocyanine (**8**) and their quaternized

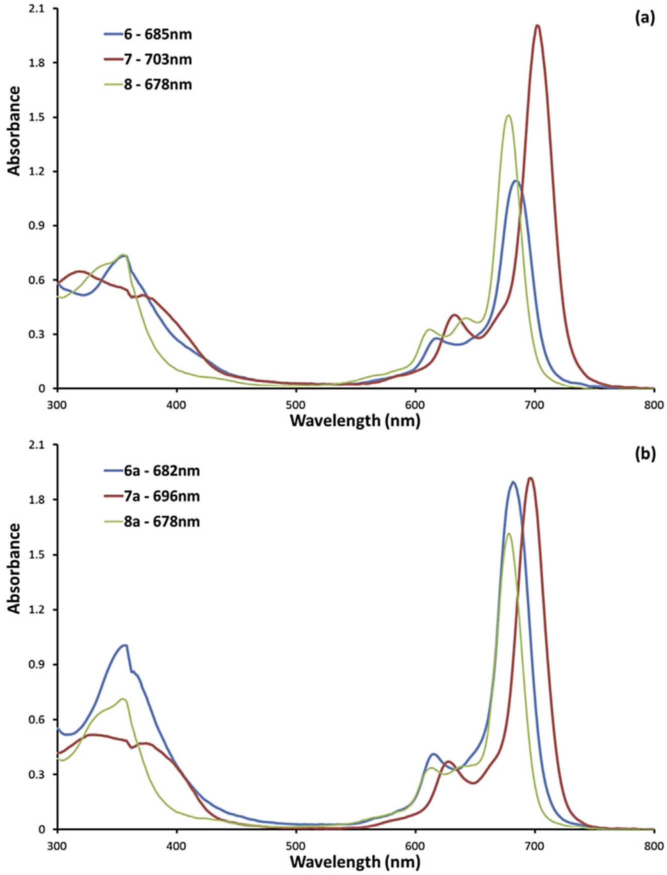

Fig. 4. Electronic absorption spectra of the compounds (a) **6**, **7** and **8**, (b) **6a**, 7**a** and **8a** in DMSO. Concentration = 1.00 × 10^{-5} M.

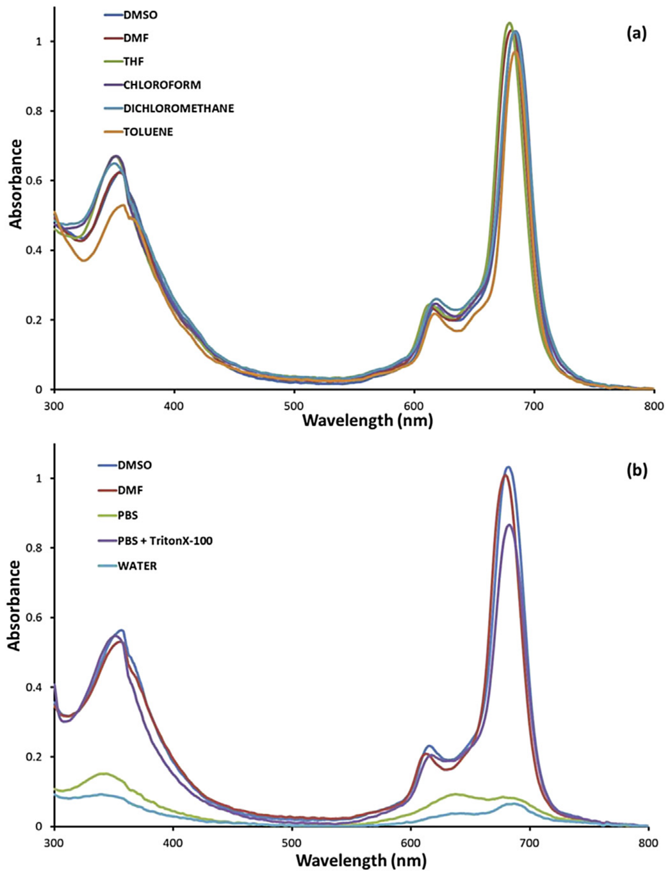

Fig. 5. Electronic absorption spectra of: (a) **6** and (b) **6a** in different solvents. Concentration = 1.00 × 10^{-5} M.

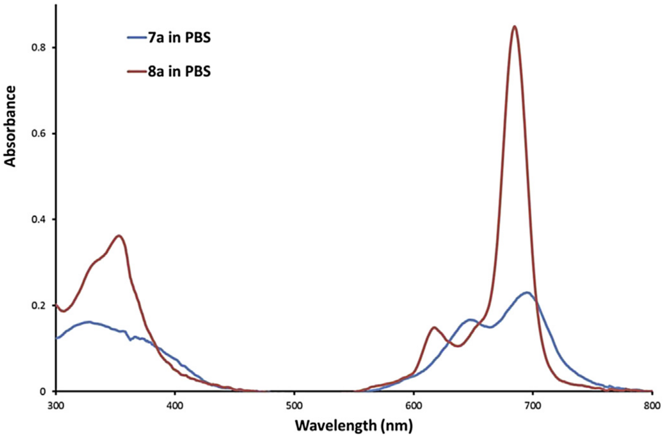

Fig. 6. Electronic absorption spectra of **7a** and **8a** in PBS solution. Concentration = 1.00 × 10^{-5} M.

water soluble derivatives (**6a**, **7a** and **8a**) showed similar fluorescence behavior in DMSO (Fig. 7 for compound **7a** as an example). Fluorescence emission maxima were observed at 692 nm for compound **6**, 693 nm for compound **6a**, 710 nm for compound **7**, 705 nm for compound **7a**, 678 nm for compound **8** and 691 nm for compound **8a** in DMSO. The observed Stokes' shifts were within the region observed for typical phthalocyanine complexes. The excitation spectra were similar with absorption spectra and both were mirror images of the emission spectra for all studied phthalocyanine complexes suggesting that the molecules did not show any degradation during excitation of these phthalocyanines in DMSO. However the fluorescence behaviors of ionic phthalocyanine derivatives were also examined in PBS solutions. While the ionic quaternized zinc (II) phthalocyanines did not show any fluorescence in this media due to the aggregation of these phthalocyanines, the quaternized ionic silicon (IV) phthalocyanine (**8a**) showed fluorescence emission in PBS solution because this phthalocyanine did not show any aggregation in this media.

3.2.4. Fluorescence quantum yields and lifetimes

When an orbital electron exciting to a higher quantum state in the photosensitizer, it relaxes to the ground state by emitting a photon of light consists of fluorescent. The fluorescence quantum yield (Φ_F) allows the efficiency of the fluorescence process. This value defined as the ratio of the number of photons emitted to the number of photons absorbed [27].

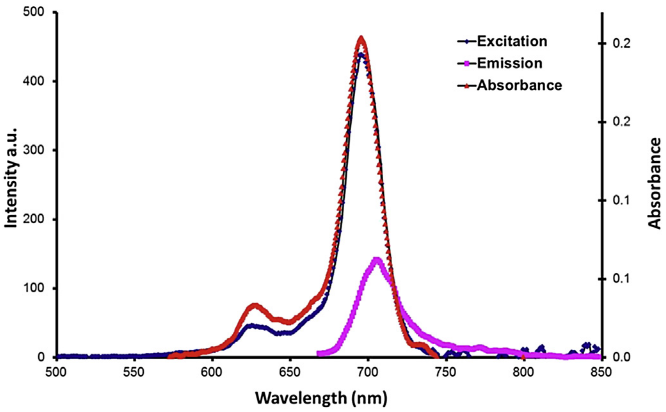

Fig. 7. Absorption, excitation and emission spectra for compound **7a** in DMSO. Excitation wavelength = 655 nm.

The fluorescence quantum yield (Φ_F) and fluorescence lifetime values of the studied phthalocyanine complexes were measured in DMSO for non-ionic phthalocyanines and for ionic quaternized phthalocyanines in both DMSO and PBS solutions. The Φ_F values of the studied phthalocyanine complexes (**6**, **7**, **8**, **6a**, **7a** and **8a**) were found ranged from 0.027 to 0.307 in DMSO, Table 1. However, Φ_F values of ionic quaternized phthalocyanines did not calculate due to their non-fluorescence behavior in PBS solution but Φ_F value of ionic quaternized silicon (IV) phthalocyanine (**8a**) was calculated as 0.267 in this solution because this compound gave monomeric solution in PBS. When compared to the studied phthalocyanine complexes, the non-ionic phthalocyanines showed very low Φ_F values than quaternized ionic counterparts in DMSO. This may be due to enhanced fluorescence quenching of diethylamino groups on the substituents because of the intramolecular photoinduced electron transfer (PET) effect. The quaternization of the studied phthalocyanines efficiently inhibits the intramolecular PET process, resulting in a stronger fluorescence emission because lone pair electrons of nitrogen atoms on the substituents were engaged and the molecules were charged as positively. In addition, Φ_F value of non-peripherally ionic zinc (II) phthalocyanine (**7a**) was found to be higher than other studied phthalocyanine complexes. It could be due to less fluorescence quenching of non-peripheral substitution of the substituents than peripheral positions.

On the other hand, fluorescence lifetime (τ_F) refers to the average time of a molecule stays in its excited state before returns to its ground state by emitting. Many factors such as internal conversion, intersystem crossing, aggregation and used solvent effects the fluorescence lifetime of a photosensitizer [28]. Fluorescence lifetime values (τ_F) of the synthesized phthalocyanine complexes were measured by a time correlated single photon counting (TCSPC) method in DMSO solutions. Fluorescence lifetime spectra were given in Fig. 8 for compound **8a** as an example in both DMSO and PBS solution. Only the τ_F value of quaternized silicon phthalocyanine (**8a**) could be calculated among the studied ionic phthalocyanine because of their non-fluorescence behavior of zinc (II) derivatives in PBS. While the quaternization of the studied zinc (II) phthalocyanines decreased the τ_F values for zinc (II) phthalocyanines (**6a** and **7a**), this value increased after quaternization for silicon (IV) phthalocyanine (**8a**) in DMSO (Table 1).

3.2.5. Singlet oxygen quantum yields

PDT process relies on the energy transfer between the triplet state of a photosensitizer and ground state molecular oxygen thus formed the singlet oxygen ($^1O_2$). The generating amount of singlet

Table 1
Photophysical and photochemical data of unsubstituted and substituted phthalocyanine complexes in DMSO and PBS solutions.

Compound	Solvent	Φ_F	τ_F (ns)	Φ_d (10^{-5})	Φ_Δ
6	DMSO	0.080	3.79	2.14	0.077
6a	DMSO	0.249	2.82	1.46	0.458
	PBS	–	–	4.12	0.202
7	DMSO	0.027	4.46	1.02	0.063
7a	DMSO	0.307	2.75	3.98	0.670
	PBS	–	–	1.11	0.174
8	DMSO	0.029	4.75	1.76	0.018
8a	DMSO	0.140	5.49	1.78	0.365
	PBS	0.267	4.78	2.20	0.210
Std ZnPc	DMSO	0.20[a]	3.99	2.61[b]	0.67[c]

[a] Data from Ref. [29].
[b] Data from Ref. [33].
[c] Data from Ref. [34].

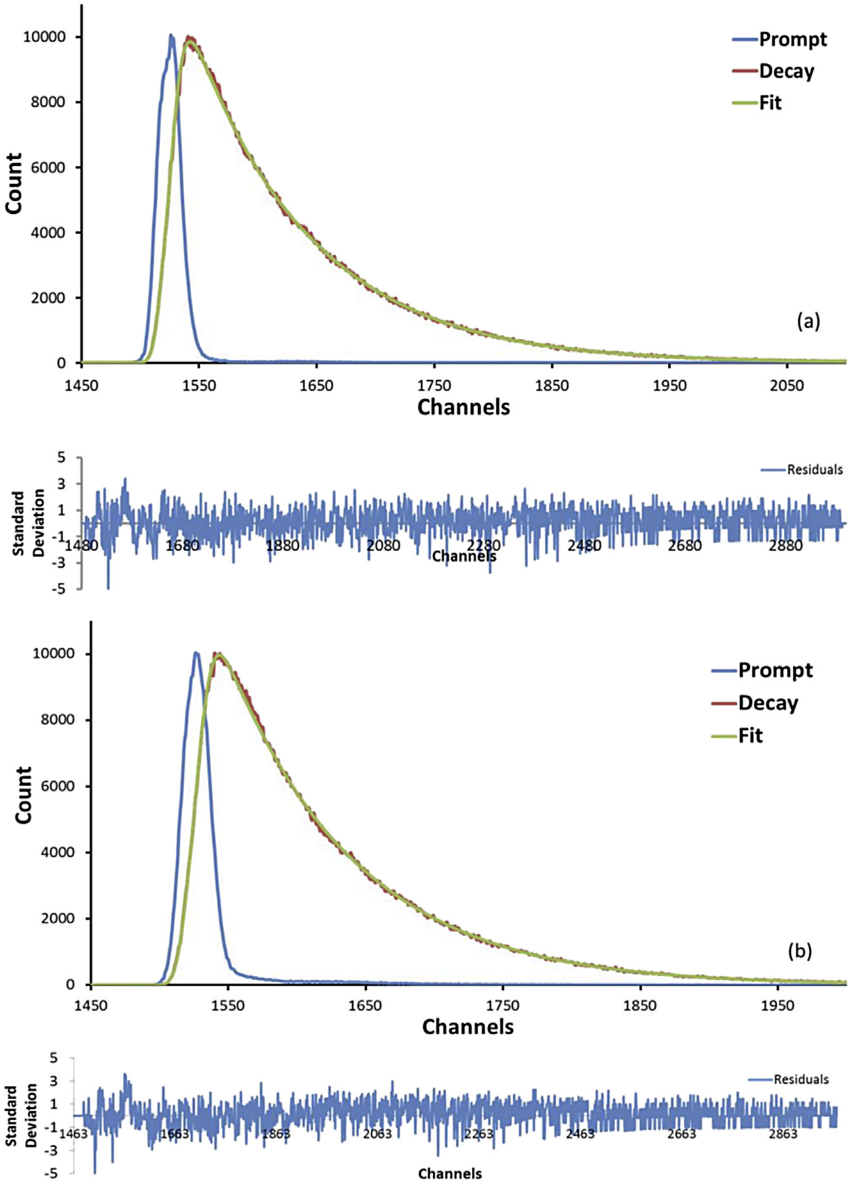

Fig. 8. Time correlated single photon counting (TCSPC) fluorescence decay curve of compound **8a** (a) in DMSO (b) in PBS.

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 PDT. The singlet oxygen quantum yield (Φ_Δ) is correspond the number of singlet oxygen molecules generated by one photon absorbed by a photosensitizer [28]. Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO for studied non-ionic phthalocyanines and in both DMSO and PBS solutions for ionic quaternized derivatives. The chemical method was used for determination of Φ_Δ values using 1,3-diphenylisobenzofuran (DPBF) and 9,10-antracenediyl-bis(methylene)dimalonoic acid (ADMA) as singlet oxygen quenchers in organic and aqueous media, respectively. The decreasing of DPBF absorbance at 417 nm or ADMA absorbance at 380 nm was monitored using UV–vis spectrophotometer (Fig. 9 for compound **7a** as an example). There was no change in the Q band intensity during the Φ_Δ determinations because of complexes are not degraded during singlet oxygen studies.

The Φ_Δ values of the substituted phthalocyanine derivatives in DMSO for both non-ionic or ionic phthalocyanines and PBS for only ionic phthalocyanines were given in Table 1. The studied non-ionic phthalocyanines showed very low Φ_Δ values in DMSO. It is believed that the photoinduced electron transfer(PET) process of diethylamino groups on the substituents quench singlet oxygen excited state of non-ionic phthalocyanines, resulting in the reduced singlet oxygen production. The studied phthalocyanines showed higher singlet oxygen generation after quaternization because engaging of lone pair electrons of nitrogen atoms efficiently inhibits the intramolecular PET process, resulting in higher singlet oxygen generation. Compound **7a** showed the highest Φ_Δ value in all the studied phthalocyanine compounds in DMSO. The low Φ_Δ values were observed in PBS compared to in DMSO. It was explained by the fact that singlet oxygen absorbs light at 1270 nm and water also absorbs light at around this wavelength while DMSO exhibits little absorption in this region [29] resulting in higher Φ_Δ values were observed in DMSO compare to PBS solution.

3.2.6. *Photodegradation studies*

Light irradiation is degraded of the molecule. Photodegradation is used to specify the stability of compounds which is useful for

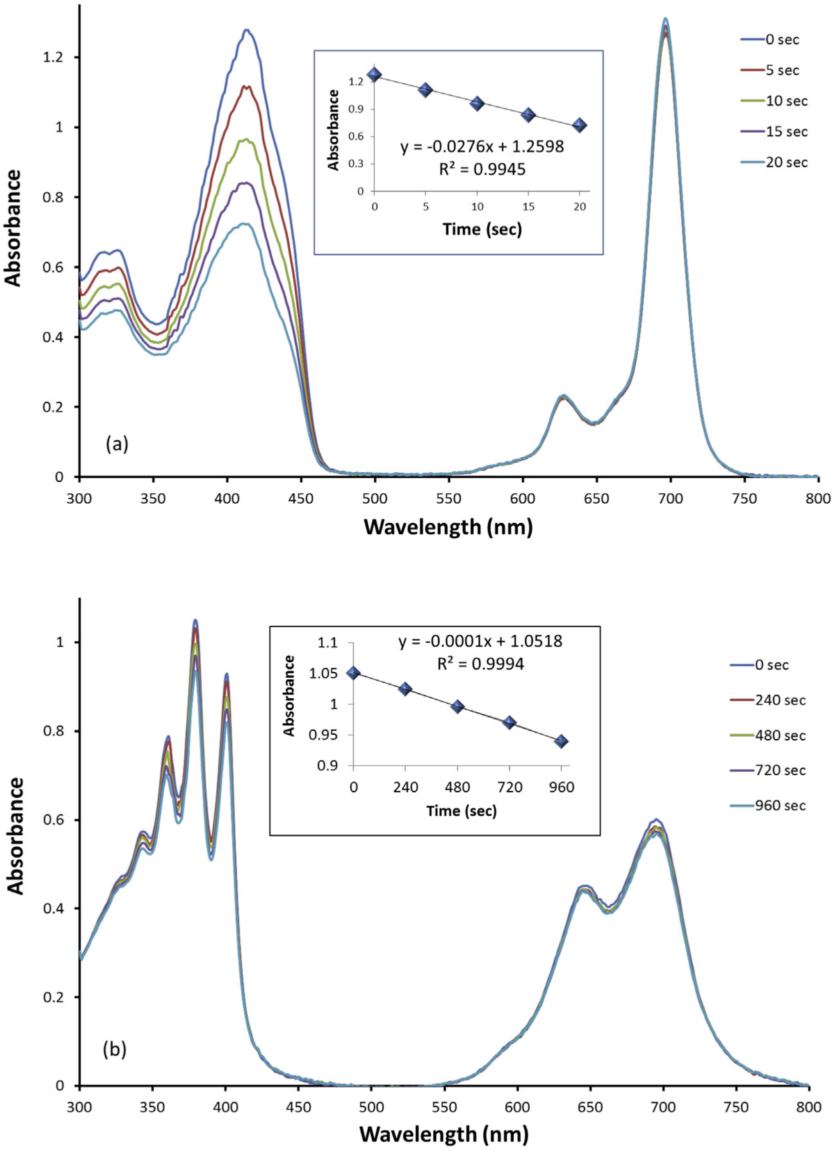

Fig. 9. Absorbance changes during the determination of singlet oxygen quantum yield. This determination was recorded for compound **7a** (a) in DMSO and (b) in PBS at a concentration of 1.0 × 10^{-5} M (inset: plot of DPBF or ADMA absorbances versus irradiation time).

determination of the photosensitizing ability of the compounds as PDT agents. Photodegradation degree can be detected by photodegradation quantum yield (Φ_d) and it depends on the structure, light intensity, used solvent and the concentration [30].

The spectral changes for all studied phthalocyanines during light irradiation are confirmed photodegradation occurred without phototransformation (Fig. 10 as an example for **7a** in both DMSO and PBS) because only Q and B bands were decreased and any new band formation did not observed. The Φ_d values were found the order of 10^{-5} and similar with phthalocyanine derivatives having different metals and substituents [28]. Table 1 shows that the Φ_d values of all studied phthalocyanine compounds (**6**, **7**, **8**, **6a**, **7a** and **8a**) are similar with unsubstituted zinc (II) phthalocyanine.

3.2.7. Binding of water soluble quaternized ionic phthalocyanine derivatives to BSA protein

BSA is one of certain plasma protein in the blood, which contribute significantly to physiological functions and effective in drug delivery. For this reason, the investigation of binding properties of a photosensitizers with BSA is of interest. The binding of quaternized phthalocyanine derivatives (**6a**, **7a** and **8a**) to BSA were studied by spectrofluorometry at room temperature in PBS solution. BSA solution was titrated with varying concentrations of the relative phthalocyanine solutions. BSA was excited at 280 nm and fluorescence emission spectra were recorded between 290 nm and 500 nm.

Fig. 11a shows the fluorescence emission spectra of BSA solution by the addition of **6a** in PBS as an example. The fluorescence emission band for BSA at 348 nm was reduced by the addition of quaternized ionic phthalocyanine solutions due to the interaction of the phthalocyanine molecules with tryptophan residues on BSA protein. BSA and quaternized ionic phthalocyanines showed reciprocated 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 2. The K_{SV} values of **6a**, **7a** and **8a** were in the order of 10^5

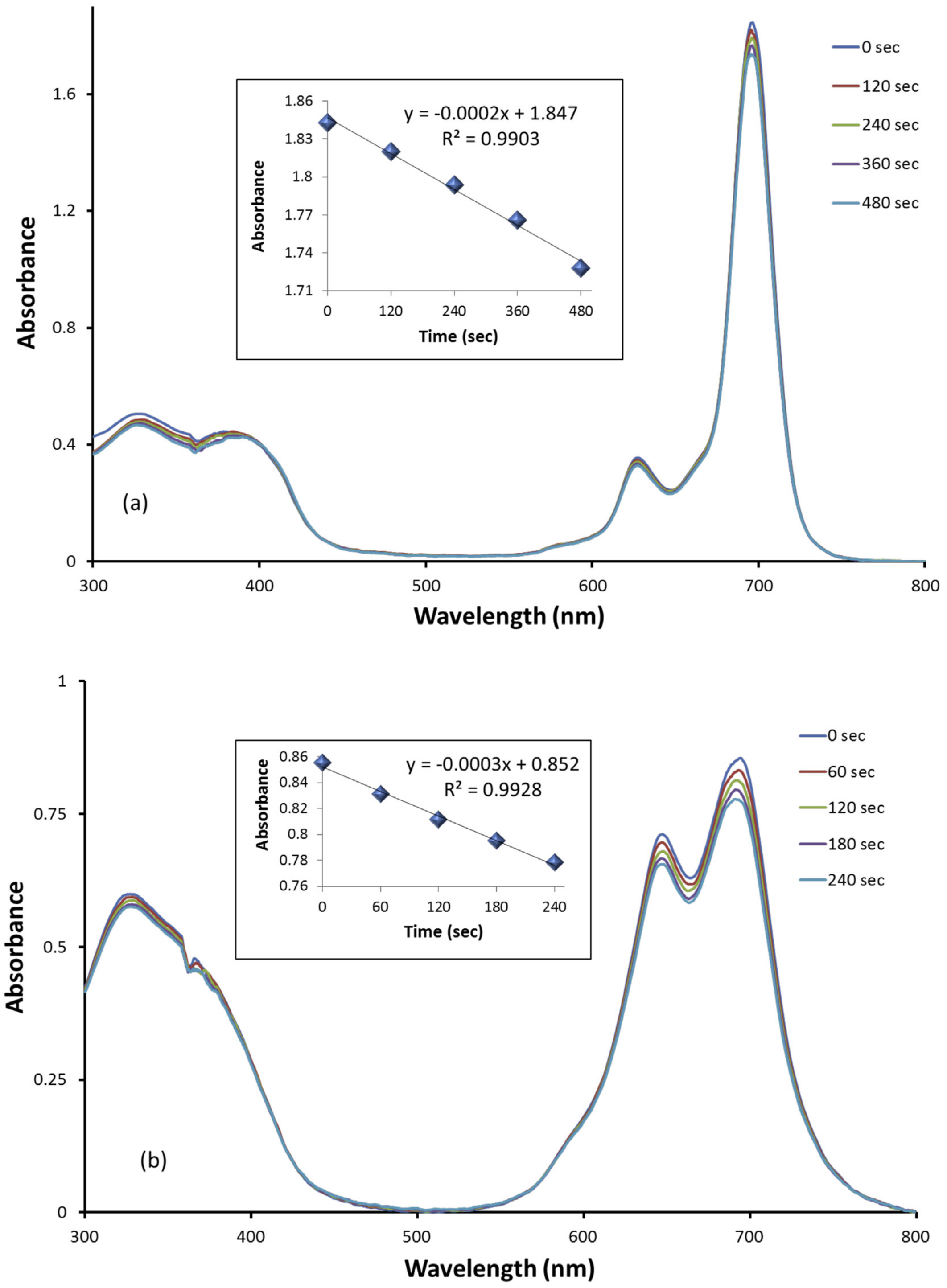

Fig. 10. Absorbance changes during the photodegradation study of **7a** (a) in DMSO and (b) in PBS showing the decreasing of the Q at 120 s and 60 s intervals respectively (inset: plot of Q band absorbance versus time).

and these values were similar with phthalocyanine derivatives having different metals and substituents on the phthalocyanine ring [22,31].

The bimolecular quenching constant (k_q) values of quaternized phthalocyanine derivatives were determined using equation 6 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 [32]. This is an indication that the mechanism of BSA quenching by quaternized zinc (II) phthalocyanines is not diffusion controlled.

4. Conclusion

In this study, the peripherally and non-peripherally tetra substituted zinc (II) (**6** and **7**) and axially disubstituted silicon (IV) phthalocyanine (**8**) compounds containing {2,3-bis

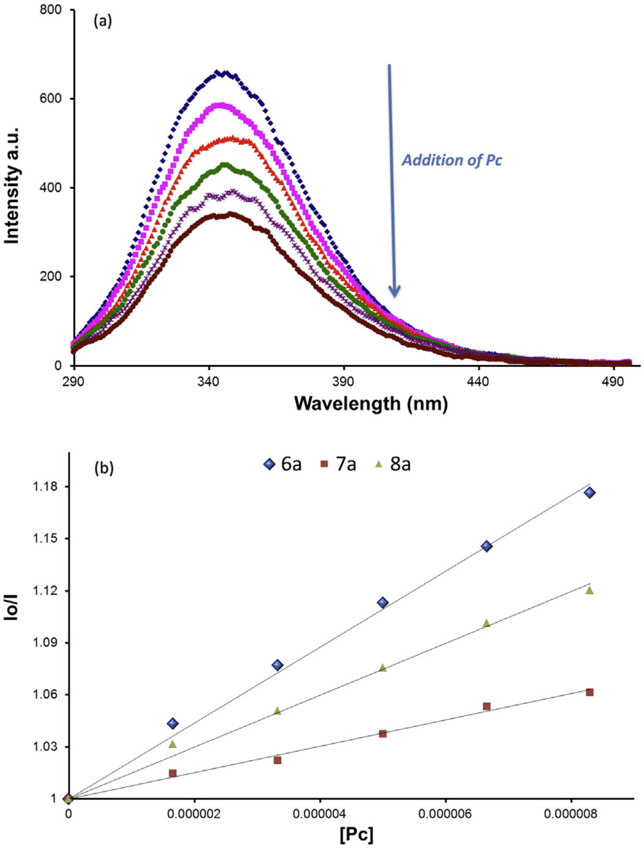

Fig. 11. (a) Fluorescence emission spectral changes of BSA by addition of different concentrations of **6a** in PBS solution. (b) Stern–Volmer plots for quenching of BSA by quaternized complexes (**6a**, **7a** and **8a**) in PBS solution. [BSA] = 3.00 × 10^{-5} M and [Pc] = 0, 1.66 × 10^{-6}, 3.33 × 10^{-6}, 5.00 × 10^{-6}, 6.66 × 10^{-6}, 8.33 × 10^{-6} M.

Table 2
Binding and fluorescence quenching data for interaction of BSA with quaternized phthalocyanine complexes in PBS solution.

Compound	$K_{SV}/10^5$ (M^{-1})	$k_q/10^{13}$ (M^{-1} s^{-1})
6a	0.712	2.53
7a	1.084	3.94
8a	0.846	1.54

[3-(diethylamino)phenoxy]propoxy} groups and their quaternized ionic derivatives (**6a**, **7a** and **8a**) were synthesized for the first time. The newly synthesized phthalocyanines were characterized by a combination of spectroscopic data such as IR, ^{1}H NMR, ^{13}C NMR, UV–vis and mass, and elemental analysis as well. While all non-ionic phthalocyanines were soluble in most of organic solvents, the quaternized ionic derivatives were also soluble in aqueous media. The photophysical and photochemical properties of the studied phthalocyanines were also investigated in DMSO for non-ionic phthalocyanines and in both DMSO and PBS for ionic counterparts. The studied phthalocyanines showed better photophysical and photochemical behavior especially high singlet oxygen generation after quaternization due to the inhibition of intramolecular photoinduced electron transfer (PET) effect between substituents and phthalocyanine core. As a result, these phthalocyanines offer potential as candidate photosensitizers for treatment of cancer by photodynamic therapy.

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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.dyepig.2015.10.035.

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