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Highly soluble 3,4-(dimethoxyphenylthio) substituted phthalocyanines: Synthesis, photophysical and photochemical studies

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ABSTRACT

The synthesis of a new 3,4-(dimethoxyphenylthio) substituted phthalonitrile (**1**) and its soluble metal free (**2**), zinc (II) (**3**), oxo-titanium (IV) (**4**) and nickel (II) (**5**) phthalocyanine derivatives are reported for the first time. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H NMR, UV–Vis, fluorescence spectroscopies and mass spectra. General trends are described for fluorescence, photodegradation and singlet oxygen quantum yields and fluorescence lifetimes of oxo-titanium (IV) and zinc (II) phthalocyanine compounds in dimethylsulfoxide (DMSO). The effects of the metal ion on the photophysical and photochemical parameters for these phthalocyanines (**3** and **4**) are also reported.

1. Introduction

Phthalocyanines (Pcs), a family of aromatic macrocycles based on an extensive delocalized 18π electron system, have been extensively studied due to their unique optical, electronic, catalytic and structural properties. The phthalocyanine (Pc) structure has been considerably scrutinized for improved chemical and physical properties. It is the smart modification of the phthalocyanine structure that has been shown to effectively improve its photochemical and photophysical properties [1]. Phthalocyanine derivatives have been used in a number of applications which include Langmuir–Blodgett films [2], chemical sensors [3], semiconductors [4] and liquid crystals [5] due to their unique properties. PDT is an effective single modality treatment for several medical indications, including cancer, age-related maculopathy, periodontitis, malignant and premalignant skin disorders [6–8]. PDT involves the uptake of the photosensitizing compound (photosensitizer) by cancerous tissues or other sites of therapeutic interest (e.g., neovascular regions), followed by selective irradiation with visible or IR light of an appropriate wavelength that is absorbed by the photosensitizer [9–11]. Three fundamental requirements for PDT are oxygen, light source, and photosensitizer. Each factor is harmless by itself, but their combination can produce cytotoxic agents such as singlet oxygen. Phthalocyanines have played a vital role in the field of photodynamic therapy (PDT) owing to their admirable photosensitizing ability [12] and as a result, they are being utilized in clinical photo diagnosis [13]. Also they can be used in jet printing inks, catalysts, display devices, data storage, solar cells and photonic devices [14–16]. The PDT properties of the phthalocyanine dyes are strongly influenced by the presence and nature of central metal ion and substituents introduced on the periphery of the phthalocyanines. Complexation of phthalocyanines with transition metals gives dyes with short lifetimes. Closed shell, diamagnetic ions, such as Zn (II) give metallophthalocyanines with both high triplet quantum yield and long triplet life time [17].

A major disadvantage of Pcs is their low solubility in common organic solvents or in water. Their insolubility causes difficulties for many applications rendering the synthesis of soluble derivatives. The solubility of phthalocyanines in apolar solvents can be improved by introducing different kinds of bulky substituents, such as alkyl, alkoxy, alkylthio and crown ether groups on the phthalocyanine framework [18–22].

Thiol substituted metallophthalocyanine (MPc) complexes show rich spectroscopic and photochemical properties. For example, they are known to absorb at longer wavelengths (>700 nm) [23,24] than other MPc complexes. Therefore, these complexes have a very feature for applications in optoelectronics, near-IR devices and PDT [25]. Our previous papers have described

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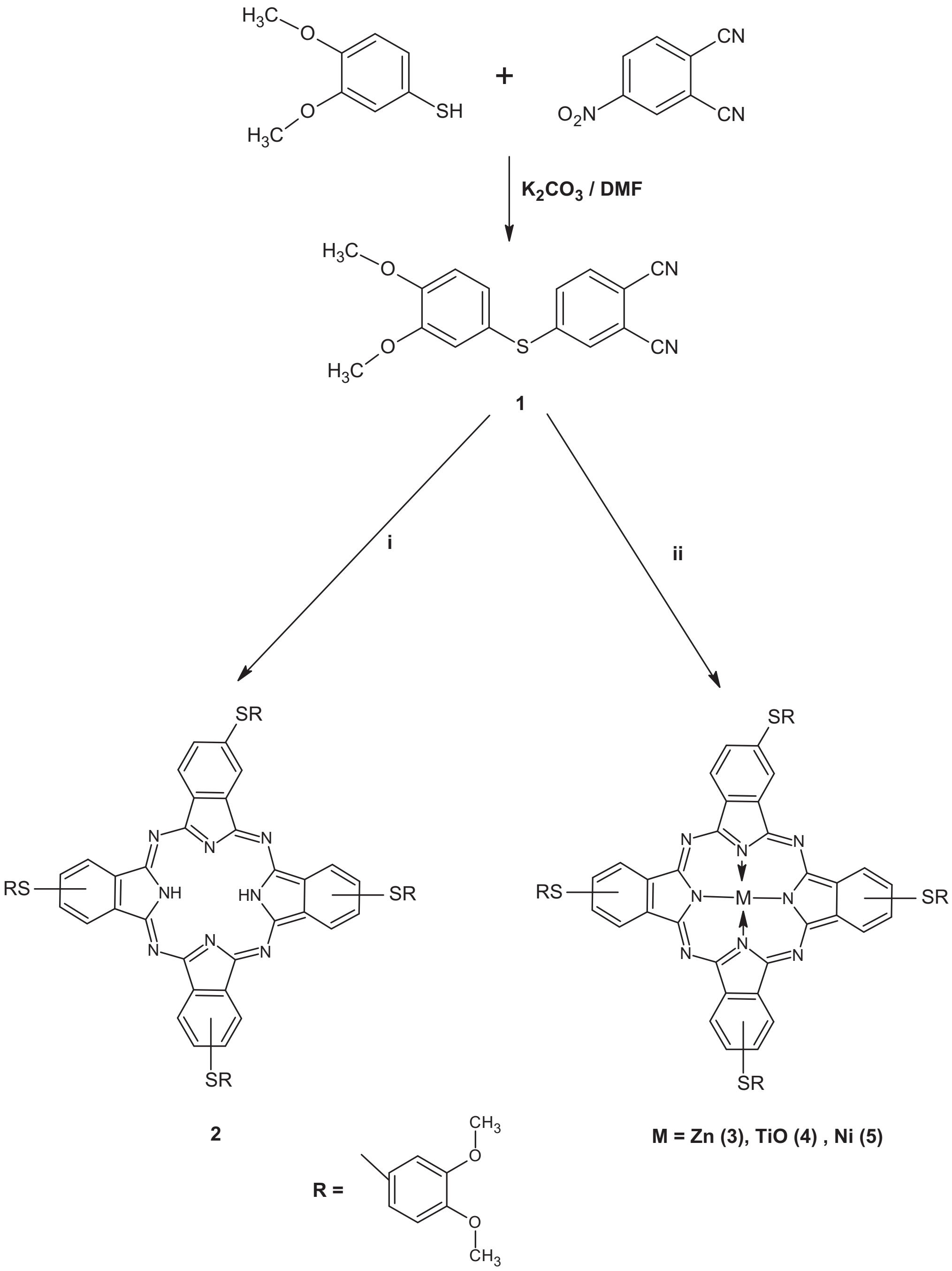

Scheme 1. Synthetic route of tetra (3,4-dimethoxyphenylthio) substituted metal free, zinc (II), oxo-titanium (IV) and nickel (II) phthalocyanine derivatives (i) (for **2**) DBU, 1-pentanol, 12 h, argon atm, (ii) zinc (II) acetate (for **3**), titanium (IV) butoxide (for **4**), nickel (II) acetate (for **5**), DBU, 1-pentanol, 10 h, argon atm.

synthesis, photophysical and photochemical properties of zinc and titanium phthalocyanines carrying various substituents [26–32]. However, these studies on MPc complexes are still very limited. The using of 3,4-dimethoxyphenylthio groups as a substituent on the phthalocyanine is reported for the first time. In this study, this group was substituted at peripheral position of phthalocyanine framework for improve the solubility and prevent aggregation of phthalocyanines [30]. Tetra-3,4-dimethoxyphenylthio substituted metal free (**2**) and metallophthalocyanines (**3–5**) exhibit good solubility in the common organic solvents without aggregation and the using of sulfur as linker atoms in the complexes is expected to red shift of the Q band [33], which is also important for photophysicochemical properties. This work have also been investigated the photosensitizing tendencies of tetra 3,4-dimethoxyphenylthio substituted Zn (II) and TiO (IV) phthalocyanines (Scheme 1). The effect of the nature of central metal atom on the photophysical and photochemical properties of the new zinc (II) and titanium (IV) phthalocyanine complexes have been discussed in DMSO.

2. Experimental

2.1. Materials

Dimethylsulfoxide (DMSO), 1-pentanol, methanol (CH_3OH), n-hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone, K_2CO_3, ethanol and dimethylformamide

(DMF) were purchased from Merck, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), zinc (II) acetate ($Zn(CH_3COO)_2$), titanium (IV) butoxide ($Ti(OCH_2CH_2CH_2CH_3)_4$), nickel (II) acetate ($Ni(CH_3COO)_2$), 1,3-diphenylisobenzofuran (DPBF), 4-nitrophthalonitrile and 3,4-dimethoxythiophenol were purchased from Sigma Aldrich. Column chromatography was performed on silica gel 60 (0.04–0.063).

2.2. Equipment

Absorption spectra in the UV–Visible region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. FT-IR spectra (KBr pellets) were recorded on a Perkin Elmer Spectrum One Spectrometer. The mass spectra were acquired on a Bruker Daltonics (Bremen, Germany) MicroTOF mass spectrometer equipped with an electronspray ionization (ESI) source. The instrument was operated in positive ion mode using an m/z range of 50–3000. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 1 bar and drying gas flow 8 ml/min. ^1H NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. Elemental analyses were obtained with a Thermo Flash EA 1112 Series.

Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Intor) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 700 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. (1) [34],

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**2**, **3** and **5**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [35] was employed as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program which uses the Strickler–Berg equation [36]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

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

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in the literature [37–39]. Typically, a 3 ml portion of the phthalocyanine derivatives (absorbance ~1.5 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in Refs. [37–39]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with ZnPc (in DMSO) as a reference. DPBF was used as chemical quencher for singlet oxygen in DMSO. Eq. (3) was employed for the calculations:

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

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc $\Phi_\Delta^{Std} = 0.67$ in DMSO [40], R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**3** and **4**) and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples (**3** and **4**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [41], the concentration of quencher (DPBF) was lowered to $\sim 3 \times 10^{-5}$ mol dm^{-3}. Solutions of sensitizer (containing DPBF) were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. The light intensity of 7.05×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in the literature [37–39]. Photodegradation quantum yields were determined using Eq. (4),

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

where C_0 and C_t are the samples (**3** and **4**) concentrations before and after irradiation, respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area and t is the irradiation time, I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**3** and **4**). A light intensity of 2.35×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.5. Synthesis

2.5.1. 3,4-(Dimethoxyphenylthio) phthalonitrile (*1*)

Mixture of 3,4-dimethoxythiophenol (1.00 g, 5.90 mmol) and 4-nitrophthalonitrile (0.99 g, 5.90 mmol) in DMF (10 ml) was stirred under argon atmosphere at room temperature. K_2CO_3 (2.07 g, 15 mmol) was added three times and the reaction mixture was stirred at room temperature for 24 h. Then reaction mixture was dropped into ice water, and the precipitate was filtered off, washed with water and methanol and then dried. The crude product was recrystallized from ethanol. Finally the pure product was dried in vacuum. Yield: 1.46 g (72%). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3078 (Ar–CH), 2961, 2834 (CH), 2230 (C≡N), 1579 (C=C), 1475, 1456, 1442, 1383, 1325, 1277 (C–O–C), 740 (C–S–C). ^1H NMR ($CDCl_3$): δ = 7.59 (1H, m, Ar–H), 7.33–7.27 (2H, m, Ar–H), 7.18–7.16 (1H, m, Ar–H), 7.08–6.98 (2H, m, Ar–H), 3.97 (3H, s, C–H), 3.89 (3H, s, C–H). Calc. for $C_{16}H_{12}N_2O_2S$: C, 64.90; H, 4.10; N, 9.45; S, 10.80; Found. C, 64.96; H, 4.12; N, 9.39; S, 10.83. MS (GC–MS) m/z: Calc.: 296.35, Found: 296 $[M]^+$.

2.5.2. 2(3),9(10),16(17),23(24)-Tetrakis-[3,4-(dimethoxyphenylthio)] phthalocyanine (*2*)

Compound (**1**) (0.20 g, 0.67 mmol) and 2 ml of dry 1-pentanol were placed in a standard Schlenk tube in the presence of DBU (0.20 ml, 0.132 mmol) under an argon atmosphere and this mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was precipitated by addition of into n-hexane. The crude product was precipitated, collected by filtration and washed with hot hexane, ethanol and methanol. The crude green product was further purified by chromatography over a silica gel column using THF and then a mixture of $CHCl_3$: MeOH (20/1 by volume) as eluents. Yield = 0.035 g (18%). UV–Vis (DMSO): λ_{max} nm (log ε) 346 (4.46), 648 (4.05), 716 (4.71); (toluene): λ_{max} nm (log ε) 340 (4.41), 642 (4.00), 709 (4.62). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3289 (N–H), 3060 (Ar–CH), 2933, 2838 (CH), 1606 (C=C), 1582, 1501, 14761, 1349, 1252 (C–O–C), 1017, 740 (C–S–C). ^1H NMR ($CDCl_3$): δ = 8.62–6.81 (24H, m, Ar–H), 4.12–3.68 (24H, m, CH_3). Calc. for $C_{64}H_{50}N_8O_8S_4$: C, 64.74; H, 4.24; N, 9.44; S, 10.80%. Found: C, 64.12; H, 4.17; N, 9.89; S, 10.46%. MS (ESI-MS) *m*/*z*: Calc.: 1187.3; Found: 1187.2 $[M]^+$.

2.5.3. 2(3),9(10),16(17),23(24)-Tetrakis-[3,4-(dimethoxyphenylthio)]phthalocyaninato zinc (II) (3)

A mixture of compound (**1**) (0.20 g, 0.67 mmol), DBU (0.20 ml, 0.132 mmol) and $Zn(OAc)_2$ (0.13 g, 0.67 mmol) in 2 ml 1-pentanol was stirred and refluxed under argon atmosphere for 12 h. The resulting green suspension was cooled and crude product was precipitated by addition of n-hexane. This product was purified with column chromatography using THF and then $CHCl_3$:MeOH (10/1 by volume) as eluents. Yield: 0.075 g (35%). UV–Vis (DMSO): λ_{max} nm (log ε) 365 (4.97), 626 (4.74), 696 (5.39); (toluene): λ_{max} nm (log ε) 355 (4.90), 619 (4.69), 688 (5.21). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3062 (Ar–CH), 2933, 2838 (CH), 1582 (C=C), 1606 (C=C), 1501, 1460, 1436, 1394, 1348, 1311, 1229 (C–O–C), 929, 847, 815, 741 (C–S–C). ^1H NMR ($CDCl_3$): δ = 8.12–6.79 (24H, m, Ar–H), 3.85–374 (24H, m, CH_3). Calc. for $C_{64}H_{48}N_8O_8S_4Zn$: C: 61.45, H: 3.85, N: 8.95, S: 10.25, Found C: 61.75, H: 3.91, N: 8.86, S: 10.31. MS (ESI-MS) *m*/*z*: Calc.: 1250.80, Found: 1250.20 $[M]^+$.

2.5.4. 2(3),9(10),16(17),23(24)-Tetrakis-[3,4-(dimethoxyphenylthio)]phthalocyaninato oxotitanium (IV) (4)

The synthesis and purification of **4** was as outlined for **3**, except titanium (IV) butoxide (0.115 ml, 0.34 mmol) was employed instead of zinc acetate. The amounts of the other reagents were: compound **1** (0.2 g, 0.67 mmol) and DBU (0.10 ml) in 2 ml 1-pentanol. Yield: 0.078 g (37%). UV–Vis (DMSO): λ_{max} nm (log ε) 350 (4.73), 647 (4.53), 718 (5.39); (toluene): λ_{max} nm (log ε) 352 (4.79), 643 (4.61), 714 (5.44). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3083 (Ar–CH), 2944, 2865 (CH), 1581 (C=C), 1506, 1462, 1261 (C–O–C), 1019 (Ti=O), 748 (C–S–C). ^1H NMR ($CDCl_3$): δ = 9.01–7.36 (24H, m, Ar–H), 3.99–3.82 (24H, m, CH_3). Calc. for $C_{64}H_{48}N_8TiO_9S_4$: C, 61.53; H, 3.87; N, 8.97; S, 10.27%, Found: C, 62.39; H, 4.01; N, 9.06; S, 10.15%. MS (ESI-MS) *m*/*z*: Calc.: 1250.8, Found: 1250.8 $[M]^+$.

2.5.5. 2(3),9(10),16(17),23(24)-Tetrakis-[3,4-(dimethoxyphenylthio)]phthalocyaninato nickel (II) (5)

The synthesis and purification of **5** was as outlined for **3**, except $Ni(OAc)_2$ (0.11 g, 0.67 mmol) was employed instead of zinc acetate. The amounts of the other reagents were compound **1** (0.2 g, 0.67 mmol) and DBU (0.10 ml) in 2 ml 1-pentanol. Yield: 0.045 g (20%). UV–Vis (DMSO): λ_{max} nm (log ε) 296 (4.94), 625 (4.66), 687 (4.37); (toluene): λ_{max} nm (log ε) 303 (4.73), 619 (4.36), 687 (5.03). FT-IR ν_{max}/cm^{-1} (KBr pellet): 3071 (Ar–CH), 2942, 2838 (CH), 1589 (C=C), 1510, 1478, 1430, 1387, 1338, 1265 (C–O–C), 929, 847, 815, 751 (C–S–C). ^1H NMR ($CDCl_3$): δ = 9.15–7.28 (24H, m, Ar–H), 4.03–3.89 (24H, m, CH_3). Calc. for $C_{64}H_{48}N_8NiO_8S_4$: C, 61.79; H, 3.89; N, 9.01; S, 10.31%, Found: C, 62.39; H, 3.81; N, 9.17; S, 10.41%. MS (ESI-MS) *m*/*z*: Calc.: 1244.06, Found: 1244.5 $[M]^+$.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route of novel phthalocyanines (**2–5**) is shown in Scheme 1. Peripherally tetra-substituted metal free (**2**), zinc (II) (**3**), oxo-titanium (IV) (**4**) and nickel (II) (**5**) phthalocyanines are prepared by template cyclotetramerization of newly synthesized 3,4-dimethoxyphenylthio substituted phthalonitrile (**1**). 2(3),9(10),16(17),23(24)-Tetra-substituted (peripheral position) phthalocyanines can be synthesized from 4-substituted phthalonitriles [10]. The preparation of metallophthalocyanine derivatives from the aromatic nitrile occurs under same reaction conditions. The syntheses of complexes (**3–5**) were achieved by treatment of 3,4-dimethoxyphenylthio substituted phthalonitrile (**1**) with zinc (II) acetate, titanium (IV) butoxide or nickel (II) acetate in dry 1-pentanol (Scheme 1). In this study, synthesized tetrakis-3,4-dimethoxyphenylthio substituted phthalocyanine compounds were obtained as isomer mixtures as expected. No attempt was made to separate the isomers of complexes (**2–5**).

All of these new phthalocyanines (**2–5**) were purified by column chromatography. They were obtained in a moderate yield (18% for **2**, 35% for **3**, 37% for **4** and 20% for **5**) and were characterized by elemental analysis together with the spectral data (^1H NMR, FT-IR, mass and UV–Vis spectroscopies). The characterization data of the new compounds are consistent with the assigned formula as shown in Section 2.

Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All studied phthalocyanine complexes (**2–5**) exhibited excellent solubility in organic solvents such as DCM, $CHCl_3$, THF, toluene, DMF and DMSO.

The characteristic vibrations corresponding to C≡N were observed at 2230 cm^{-1} for compound **1** in the FT-IR spectrum. The C–O–C vibrations and the thio ether (C–S–C) vibrations for compound **1** were observed at 1277 cm^{-1} and 740 cm^{-1}, respectively. Aromatic C–H and aliphatic C–H vibrations occurred at 3078 cm^{-1} and between 2961 and 2834 cm^{-1} for the phthalonitrile (**1**), respectively. The ^1H NMR spectrum of the compound **1** showed signals with δ ranging from 7.59 to 6.98 belonging to aromatic protons and 3.89 to 3.97 ppm belonging to aliphatic protons for compound **1**. In the mass spectrum of phthalonitrile compound (**1**) obtained by the relatively soft GC–MS technique, the molecular ion peak was observed at *m*/*z* 296 $[M]^+$.

After conversion into phthalocyanines (**2**, **3**, **4** and **5**) the characteristic sharp C≡N stretch at 2230 cm^{-1} for phthalonitrile **1** disappeared in the FT-IR spectra of phthalocyanine derivatives. The FT-IR spectra of metal-free (**2**) and metallophthalocyanines (**3**, **4** and **5**) are very similar. The significant difference is the presence of N–H vibrations of the inner phthalocyanine core which are assigned to a weak vibration at 3289 cm^{-1} for the metal-free compound. The characteristic vibrations corresponding to the thioether groups (C–S–C) were observed at 740 (for **2**), 741 (for **3**), 748 (for **4**), and 751 cm^{-1} (for **5**). The synthesized phthalocyanine complexes (**2–5**) showed characteristic vibrations belong to ether groups (C–O–C) at ca. ~1250 cm^{-1}, aromatic CH stretching at ca. 3062 cm^{-1} and aliphatic CH stretching at ca. 2844–2950 cm^{-1}. FT-IR bands at 1019 cm^{-1} correspond to Ti=O vibration from the bond between Ti and the axial oxygen ligand confirmed titanium phthalocyanine (**4**) formation.

The ^1H NMR spectra of tetra-substituted phthalocyanine complexes (**2–5**) showed broad peaks when compared with that of corresponding phthalonitrile derivative (**1**). It is likely that broadness is due to both chemical exchange caused by aggregation–disaggregation equilibrium in $CDCl_3$ and the fact that the product obtained in this reaction is a mixture of four positional isomers which are expected to show chemical shifts which slightly differ from each other for tetra substituted complexes (**2–5**). The 3,4-dimethoxyphenylthio substituted phthalocyanines were found to be pure by ^1H NMR with all the substituents and ring protons observed in their respective regions. The tetra substituted phthalocyanines (**2** to **5**) showed the phthalocyanine ring protons

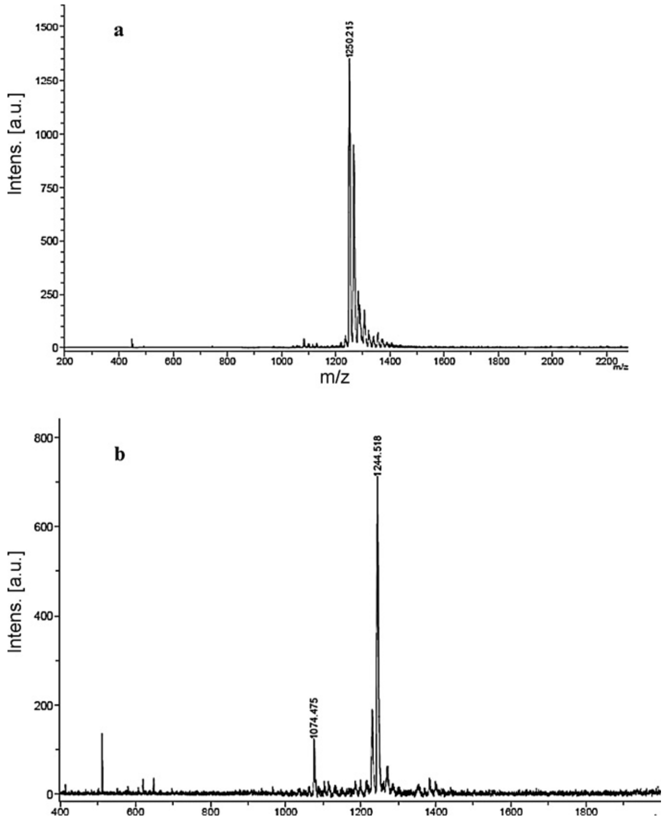

Fig. 1. The mass spectra of the compounds **3** (a) and **5** (b).

as unresolved multiplets (most likely due to the presence of isomers). The NH-protons of compound **2** could not be observed in the ^{1}H NMR spectrum owing to the probable strong aggregation of the molecules [42]. The phthalocyanine ring and aromatic protons for peripherally tetra substituted complexes were observed in the range 8.62–6.81 ppm for **2** integrating for 24 protons, 8.12–6.79 for **3** integrating for 24 protons, 9.01–7.36 for **4** integrating for 24 protons and 9.15–7.28 ppm for **5** integrating for 24 protons as expected. The CH_3 protons for complexes (**2–5**) were observed at 4.12–3.68 for **2**, 3.85–3.74 ppm for **3**, 3.99–3.82 ppm for **4** and 4.03–3.89 ppm for **5** integrating totally for 24 protons for all studied phthalocyanine complexes, as expected. Although the presence of isomers as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals, the observed spectra of all studied complexes were relatively well-resolved.

In the mass spectra of phthalocyanines obtained by the relatively soft ESI-MS technique, the molecular ion peaks were observed at m/z 1187.2 for **2**, 1250.2 for **3**, 1250.8 for **4** and 1244.5 for **5** (Fig. 1, using complexes **3** (a) and **5** (b) as examples). Elemental analysis results were also consistent with the proposed structures of **1** to **5** as expected.

3.2. Ground state electronic absorption and fluorescence spectra

The ground state electronic spectra are especially useful to identify the structure of the phthalocyanines. Generally, UV–Vis spectra of phthalocyanines show typical electronic spectra with two strong absorption bands known as Q and B bands. The Q-band in the visible region at ca. 600–750 nm is attributed to the π–π^* transition from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) of the Pc (−2) ring and the B band in the UV region at ca. 300–400 nm arises from the deeper π–π^* transitions [43], but contains a small contribution from n–π^*transition.

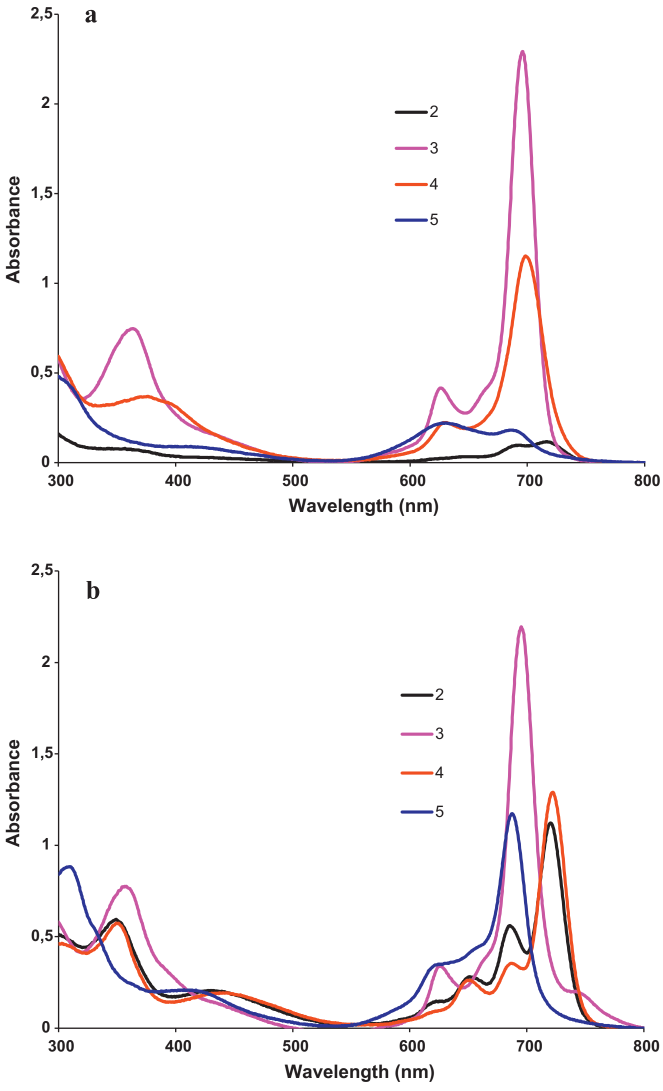

Fig. 2. Absorption spectra of: (a) **2–5** in DMSO and (b) **2–5** in chloroform. Concentration ~1×10^{-5} mol dm^{-3}.

The ground state electronic absorption spectra of the peripherally tetra-substituted phthalocyanine complexes (**3–5**) showed monomeric behavior evidenced by a single (narrow) Q band, typical of non-aggregated metallo phthalocyanine complexes in chloroform and DMSO. The electronic spectra of phthalocyanine compounds (**2**, **3**, **4** and **5**) are given in Fig. 2. In the UV–Vis spectrum of metal-free phthalocyanine (**2**), the characteristic split Q band was observed at 686 and 719 nm in chloroform which can be attributed $a_{1u} \rightarrow$ eg transition [44]. A typical spectrum of the metal-free phthalocyanine (**2**) showed B band at 347 in chloroform Fig. 2b. The UV–Vis absorption spectra of metallophthalocyanines **3**, **4** and **5** in $CHCl_3$ were observed the intense Q absorption at 696, 721 and 690 nm, respectively. The Q band absorptions were also observed at 696 nm for **3**, 718 nm for **4** and 687 nm for **5** in DMSO. In addition, the intense B band absorptions were observed at 357 nm for **3**, 348 nm for **4** and 307 nm for **5** in $CHCl_3$ and 365 nm for **3**, 350 nm for **4** and 296 nm for **5** in DMSO, respectively (Fig. 2) The Q band of the titanium phthalocyanine complex (**4**) was red-shifted when compared to the corresponding other studied phthalocyanine complexes (**2**, **3** and **5**) in all studied solvents due to the central metal effect. The Q-band absorption maxima of the TiOPcs are about

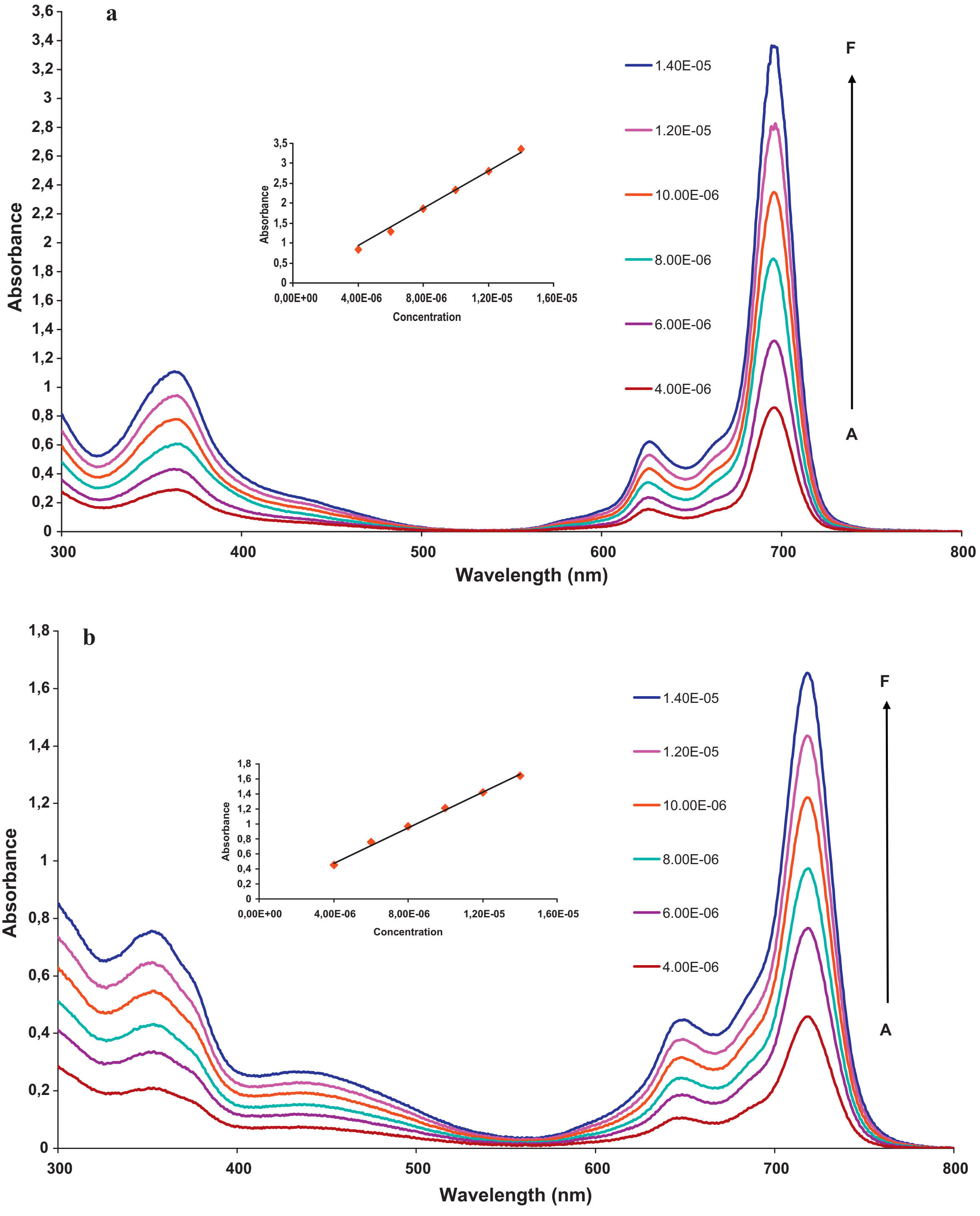

Fig. 3. Absorption spectral changes of **3** (a) and **4** (b) in DMSO at different concentrations: 4×10^{-6} (A), 6×10^{-6} (B), 8×10^{-6} (C), 10×10^{-6} (D), 12×10^{-6} (E) and 14×10^{-6} (F) mol dm^{-3}. (Inset: plot of absorbance versus concentration.)

20 nm longer than other common metal Pcs, such as Mg, Al, Zn, and Ga, which are more suitable for PDT.

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, central metal ions and temperature. In this study, the aggregation behavior of the phthalocyanine complexes (**2–5**) was investigated in different solvents (DMSO, DMF, $CHCl_3$, toluene and THF). For complexes, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) were observed in DMSO. However, Beer–Lambert law was obeyed for all of the compounds in the concentrations ranging from 4×10^{-6} to 14×10^{-6} mol dm^{-3} (Fig. 3 as examples for complexes **3** (a) and **4** (b)).

The fluorescence behavior of the metal free (**2**), zinc (**3**) and oxo-titanium (**4**) phthalocyanine complexes were studied in DMSO. Fig. 4 shows the absorption, fluorescence emission and excitation spectra for complex **3** as an example in DMSO. Fluorescence emission intensities were observed at 707 nm for **2**, 707 nm for **3** and

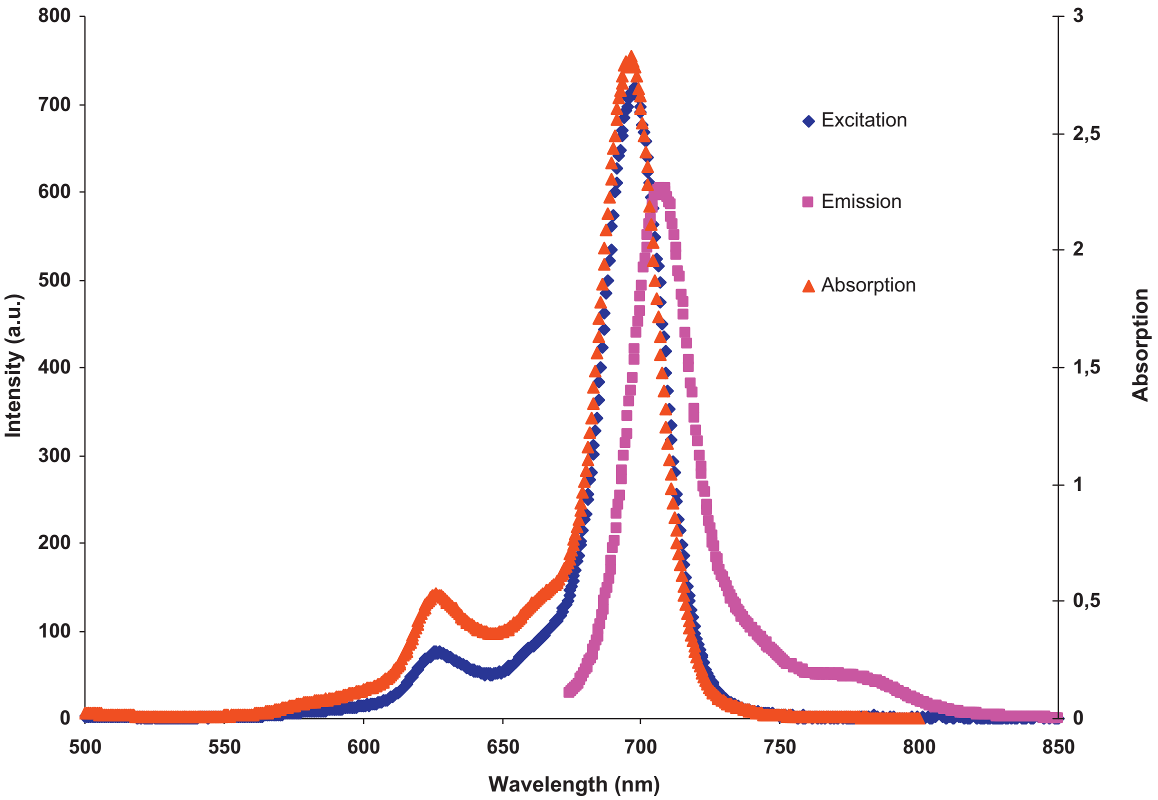

Fig. 4. Absorption, excitation and emission spectra for compound **3** (Excitation wavelength = 665 nm) in DMSO.

710 nm for **4**. The shape of the excitation spectra (λ_{Ex} = 705 nm for **2**, 697 nm for **3** and 700 nm for **4**) of studied compounds was similar to their absorption spectra. This proximity of the wavelength of the Q band absorption to the Q band maxima of the excitation spectrum for phthalocyanine compounds suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation. The observed Stokes shifts are 2 nm for **2**, and 10 nm for **3** and **4** in DMSO. The nickel (II) phthalocyanine compound (**5**) did not show fluorescence in DMSO.

3.3. Photophysical and photochemical properties

3.3.1. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of metal free (**2**), zinc (II) (**3**) and oxo-titanium (IV) (**4**) phthalocyanines were studied in DMSO. While the Φ_F values of metal free (**2**), and oxo-titanium (IV) phthalocyanine (**4**) complexes are lower than typical of phthalocyanine complexes, the Φ_F value of zinc (II) phthalocyanine complex (**3**) ($\Phi_F = 0.15$) is typical of MPc complexes in DMSO [45]. But the Φ_F value of the substituted zinc phthalocyanine complex (**3**) is lower than for unsubstituted ZnPc ($\Phi_F = 0.20$) [35] in DMSO. The value of Φ_F was lower for substituted oxotitanium (IV) phthalocyanine complex (**4**) ($\Phi_F = 0.013$) when compared to respective unsubstituted TiO (IV) phthalocyanine complex ($\Phi_F = 0.13$) [46]. It is possible that photo induced electron transfer from the donor moiety (dimethoxy benzene) to the acceptor (Pc moiety) is responsible for this, similar to the case in Refs. [47,48].

Fluorescence lifetime (τ_F) is the average time a molecule stays in its excited state before fluorescence, and this value is directly related to that of Φ_F. Lifetimes of fluorescence (τ_F) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been found between experimentally and theoretically determined lifetimes for the unaggregated molecules [49]. Thus we suggest that the τ_F values obtained using this equation is an appropriate measure of fluorescence lifetimes. While the τ_F value of the studied zinc phthalocyanine compound (**3**) is within the range ($\tau_F = 0.95$ ns), the τ_F values of the studied metal-free (**2**) ($\tau_F = 0.41$ ns) and oxo-titanium (IV) (**4**) ($\tau_F = 0.13$ ns) phthalocyanine compounds are lower than reported for Pc compounds [45]. All studied phthalocyanine compounds showed lower τ_F values than unsubstituted ZnPc ($\tau_F = 3.0$ ns) in DMSO. The short fluorescence lifetime is likely due to the electron transfer as mentioned above. For the substituted complexes, longer τ_F value is obtained for the zinc phthalocyanine compound (**3**) compared to other studied phthalocyanine compounds (**2** and **4**).

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also investigated in this study. The τ_0 values of the studied metal-free (**2**) ($\tau_0 = 19.52$ ns) and oxo-titanium (IV) phthalocyanine (**4**) ($\tau_0 = 10.04$ ns) compounds are longer than unsubstituted ZnPc ($\tau_0 = 6.80$ ns) in DMSO. The τ_0 value of the studied zinc (II) phthalocyanine (**3**) ($\tau_0 = 6.20$ ns) compound is slightly lower than unsubstituted ZnPc ($\tau_0 = 6.80$ ns) in DMSO. The substituted metal-free phthalocyanine compound (**2**) showed the longest τ_0 values when compared to other substituted complexes (**3** and **4**) in DMSO. The rate constants for fluorescence (k_F) values of studied metal-free (**2**) ($k_F = 0.51 \times 10^8\ s^{-1}$) and oxo-titanium phthalocyanine (**4**) ($k_F = 1.00 \times 10^8\ s^{-1}$) are lower than unsubstituted ZnPc ($k_F = 1.47 \times 10^8\ s^{-1}$) in DMSO. The k_F value of studied zinc phthalocyanine complex (**3**) ($k_F = 1.61 \times 10^8\ s^{-1}$) is slightly higher than unsubstituted ZnPc in DMSO.

3.3.2. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) is a measure of singlet oxygen generation and the Φ_Δ values were obtained using Eq. (3). Singlet oxygen quantum yields were studied using a chemical method (DPBF) in DMSO. Fig. 5 shows spectral changes observed during photolysis of complex **3** in DMSO in the presence of DPBF as an example. The disappearance of DPBF was monitored using

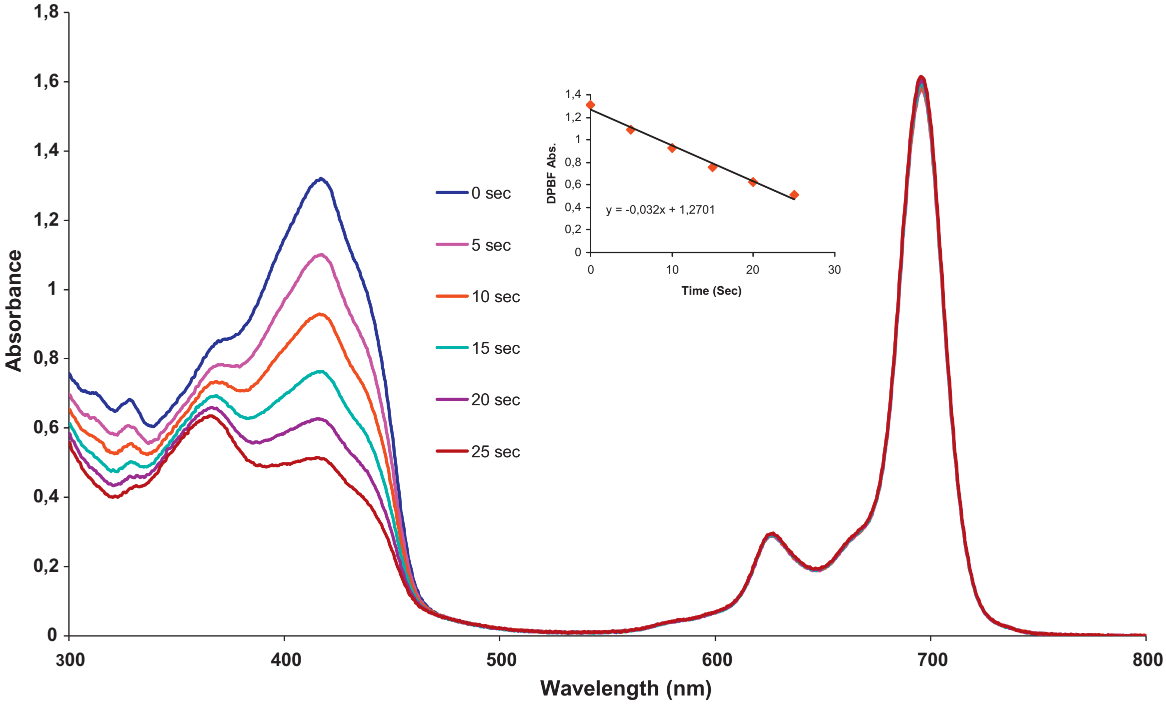

Fig. 5. Absorption changes during the determination of singlet oxygen quantum yield. This determination was for compound **3** in DMSO at a concentration of 1×10^{-5} mol dm^{-3}. (Inset: plot of DPBF absorbance versus time.)

UV–Vis spectral changes. There were no changes in the Q band intensities during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies. The Φ_Δ values are: 0.49 for compound **3** and 0.10 for compound **4** in DMSO. The values of Φ_Δ were lower for substituted complexes (**3** and **4**) when compared to respective unsubstituted ZnPc ($\Phi_\Delta = 0.67$) [40] and TiO (IV) ($\Phi_\Delta = 0.79$) [46] phthalocyanine complexes in DMSO, but still enough for photocatalytic applications such as PDT. Oxotitanium (IV) phthalocyanine complex has lower Φ_Δ values than the Zn (II) phthalocyanine complex due to central atom effect.

3.3.3. Photodegradation studies

Photodegradation is a process where a phthalocyanine is degraded under light irradiation. It can be used to determinate Pcs stability and this is especially important for those molecules intended for use as photocatalysts. The photobleaching stabilities

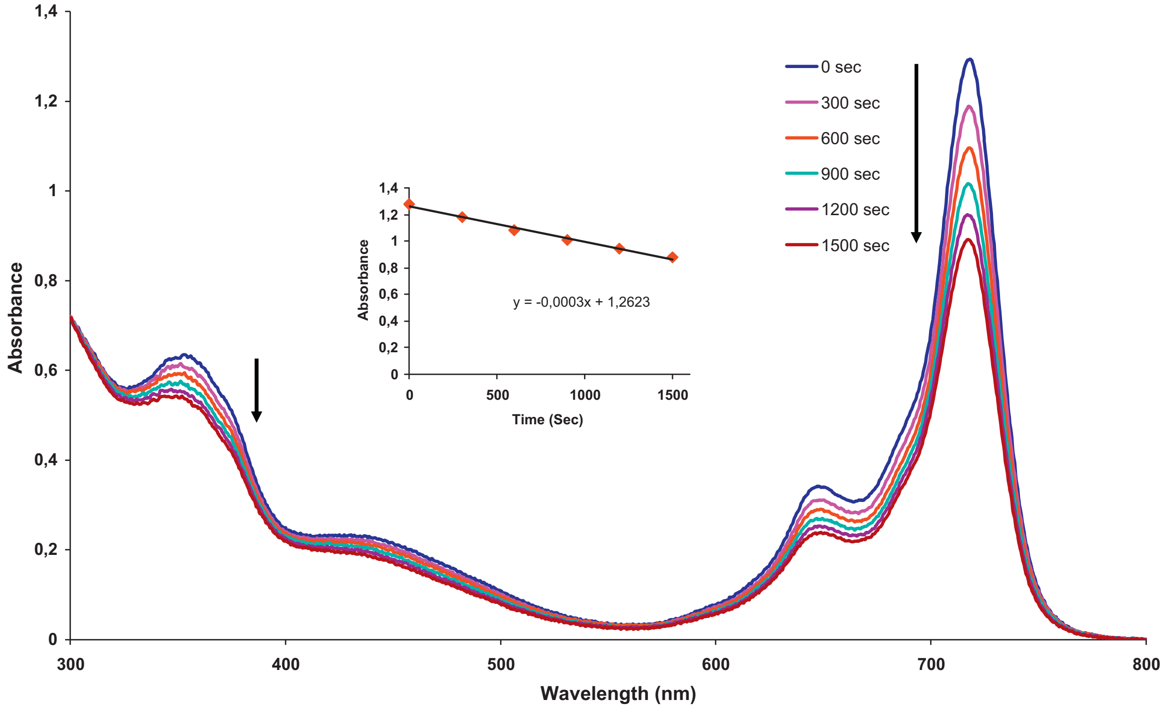

Fig. 6. Absorption changes during the photodegradation studies of compound **4** in DMSO showing the disappearance of the Q-band at 5 min intervals. (Inset: plot of absorbance versus time.)

of studied phthalocyanine complexes (**3** and **4**) were determined in DMSO by monitoring the decrease in the intensity of the Q band under irradiation with increasing time. The complexes showed about the same stability with Φ_d of the order of 10^{-5}. These values show that the molecules are of moderate stability in DMSO. Stable ZnPc molecules show values as low as 10^{-6} and for unstable molecules, values of the order 10^{-3} have been reported [45]. The spectral changes observed for all the complexes (**3** and **4**) during irradiation confirmed that photodegradation occurred without phototransformation (Fig. 6 as an example for complex **4**). The photodegradation value of the complex **3** is 1.18×10^{-5} and it is more stable to degradation compared to unsubstituted ZnPc ($\Phi_d = 2.61 \times 10^{-5}$) [50] in DMSO. Complex **4** is ($\Phi_d = 7.18 \times 10^{-5}$) less stable than complex **3** in DMSO.

4. Conclusion

This work has been described the synthesis, spectral and photophysicochemical properties of *tetrakis*-(3,4-dimethoxyphenylthio) phthalocyanines. The structure of the novel compounds were confirmed by FT-IR, UV–Vis, mass and NMR spectroscopies, as well as elemental analysis. All studied phthalocyanine compounds (**2**, **3**, **4** and **5**) have good solubility in common organic solvents such as DMSO, DMF, toluene, $CHCl_3$, THF and DCM without aggregation. The photophysical and photochemical properties of the phthalocyanines (**2**, **3** and **4**) were investigated in DMSO. The effect of the nature of the central metal atom on the photophysical and photochemical parameters of the phthalocyanine complexes (**3** and **4**) are also reported in this study. These properties give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (such as Type II mechanism), especially complex **3** may be good candidate as a photosensitizer for PDT application.

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