New soluble methylendioxy-phenoxy-substituted zinc phthalocyanine derivatives: Synthesis, photophysical and photochemical studies

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Abstract

The syntheses of new three phthalonitriles (1, 2 and 3), together with photophysical and photochemical properties of the resulting peripherally and non-peripherally tetrakis- and octakis 3,4-(methylendioxy)-phenoxy-substituted zinc phthalocyanines (4, 5 and 6) are described for the first time. Complexes 4, 5 and 6 have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR spectroscopy, electronic spectroscopy and mass spectra. Complexes 4, 5 and 6 have good solubility in organic solvents such as $CHCl_3$, DCM, DMSO, DMF, THF and toluene and are mainly not aggregated (except for complex 6 in DMSO) within a wide concentration range. General trends are described for singlet oxygen, photodegradation, fluorescence quantum yields, triplet quantum yields and triplet life times of these complexes in DMSO and toluene. Complex 4 has higher singlet oxygen quantum yields, fluorescence quantum yields, triplet quantum yields and triplet life times than complexes 5 and 6. The effect of the solvents on the photophysical and photochemical parameters of the zinc(II) phthalocyanines (4, 5 and 6) are also reported.

Graphical abstract

Photophysical and photochemical studies of the peripherally tetrakis- (4) and octakis- (6) and non-peripherally (5) tetrakis-3,4-(methylendioxy)-phenoxy-substituted zinc phthalocyanines show complex 4 to have higher singlet oxygen quantum yields, fluorescence quantum yields, triplet quantum yields and triplet life times than complexes 5 and 6.
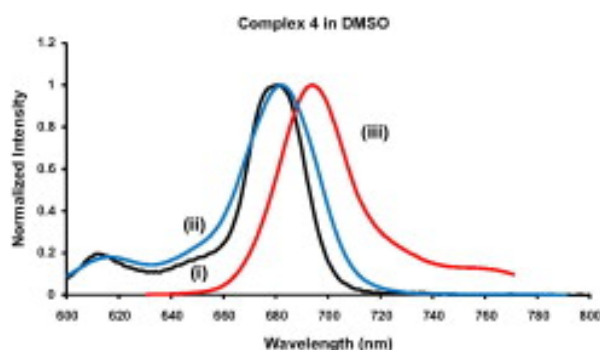
1. Introduction

Phthalocyanines (Pcs) display interesting chemical and physical properties [1] and [2]. Phthalocyanines are very stable and versatile aromatic macrocyclic compounds, capable of incorporating more than 70 metallic and non-metallic ions in the ring cavity. The optical and electronic properties of the phthalocyanine (Pc) macrocycle make it suitable for a wide range of applications. Pcs may be developed for new applications by facile substitution on the periphery (α and β positions) [3], [4], [5] and [6]. Some technological applications of these macrocycles have been intensively investigated, such as electrophotography, photovoltaic and solar cells, semiconductor devices, molecular electronics, Langmuir Blodgett films, electrochromic display devices, low-dimensional conductors and synthetic metals, gas sensors, liquid crystals, nonlinear optics, optical disks, electrocatalytic agents and photodynamic therapy of cancer (PDT) [7], [8] and [9]. In recent years, the study of the potential use of Pcs as photosensitizers for photodynamic cancer therapy [10], [11], [12], [13], [14], [15] and [16] has intensified. PDT employs the combination of light and photosensitizer. Photosensitizer (e.g. Pc) gets excited after the absorption of light of proper wavelength. This is followed by singlet oxygen production by energy transfer from triplet state of the photosensitizer. Metallophthalocyanines (MPcs) have proved to be highly promising as photosensitizers due to their intense absorption in the red region of visible light. High triplet state lifetimes and quantum yields are required for efficient sensitization and these criteria may be fulfilled by the incorporation of diamagnetic metal. Zinc, aluminium and silicon phthalocyanines, in particular, have good photosensitizing properties for PDT [17], [18], [19] and [20]. The general synthesis of organic solvent soluble substituted phthalocyanines is now well established. Pc complexes containing S, N or O containing substituents are known [21], [22] and [23]. However the study of the photochemical and photophysical properties of such complexes is still very limited. In this work the photophysical and photochemical properties of the new oxygen containing tetra-substituted (peripherally and non-peripherally) and octa-substituted zinc-phtalocyanines (Scheme 1), which show good solubility in common organic solvents are reported. The effect of tetra and octa-substitution of zinc Pcs on their photophysical and photochemical properties will be evaluated in dimethylsulfoxide (DMSO) and toluene.
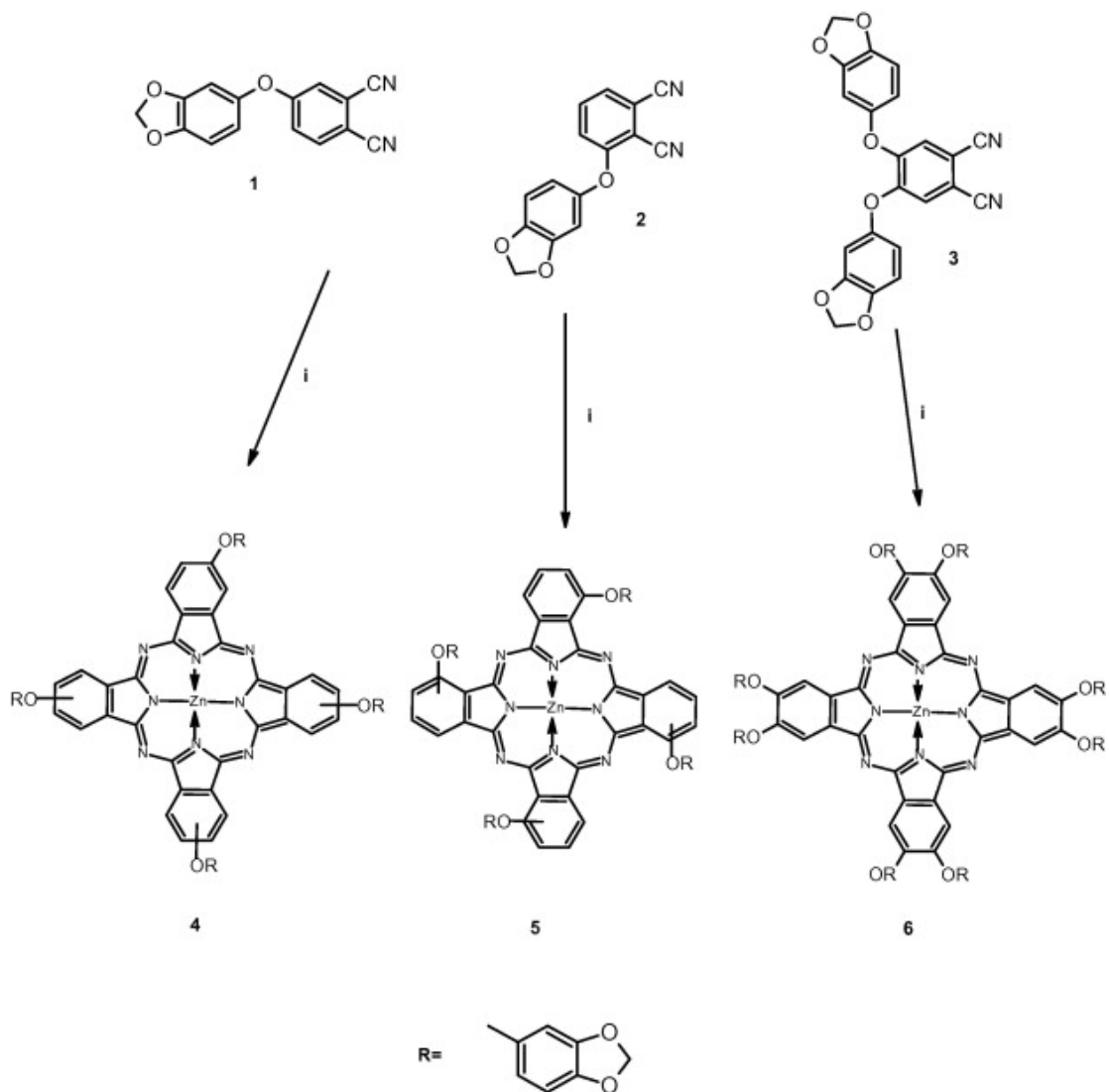
Scheme 1. Synthetic route of three phthalonitriles (1, 2 and 3), and their zinc phthalocyanines derivatives (i) anhydrous $Zn(Ac)_2$, 1-pentanol, 15 h, argon atm.

2. Experimental

2.1. Materials and equipment

Dimethyl sulfoxide (DMSO), *N,N′*-dimethylformamide (DMF), chloroform (CHCl$_3$), tetrahydrofuran (THF), methanol (MeOH), dichloromethane (DCM), 1-pentanol, *n*-hexane, acetone and toluene were purchased from SAARCHEM; zinc phthalocyanine (ZnPc) 1,2-dipheny*iso*benzofuran (DPBF), 4-phthalonitrile, 3-phthalonitrile, 4,5-dichloro-phthalonitrile, 3,4-(methylendioxy)-phenol, 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), potassium carbonate, and zinc acetate were purchased from Aldrich.

FT-IR spectra (KBr pellets) were recorded on a Perkin–Elmer spectrum 2000 FT-IR spectrometer. UV–Vis spectra were recorded on a Cary 500 UV–Vis/NIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained in CDCl$_3$ using a Bruker EMX 400 NMR spectrometer. Elemental analyses were done on Vario Elementar EL III. Fluorescence spectra were recorded on the Varian Eclipse spectrofluoremeter. Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Nd: YAG laser (Quanta-Ray, 1.5 J/90 ns) pumping a dye laser (Lambda Physic FL 3002, Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses. Photo-irradiations were done using a General Electric Quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 20 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter. Mass spectras were obtained using a ABI Voyager DE-STR Maldi TOF instrument at University of Stellenbosch.

2.2. Synthesis

2.2.1. 4-[3,4-(Methylendioxy)-phenoxy]-phthalonitrile (1)

The 4-nitrophthalonitrile (4.40 g, 25.35 mmol) was dissolved in DMF (35 ml) under argon and 3,4-(methylendioxy)-phenol (3.50 g, 25.35 mmol) was added. After stirring for 30 min at room temperature, finely ground anhydrous potassium carbonate (8.65 g, 63.40 mmol) was added in portions during 4 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 24 h. Then

the mixture was poured into 400 ml ice water, and the precipitate was filtered off, washed with water and methanol and then dried. The crude product was recrystallized from methanol. Finally the pure product was dried in vacuum. Thin layer chromatography with silica gel was employed to confirm the absence of the starting phthalonitrile.

Yield: 4.50 g (67%). IR spectrum (cm^{-1}): 3084 (Ar–CH), 2226 (C≡N), 1599 (C=C), 1564, 1486, 1417, 1306, 1249, 1096 (C–O–C), 1037, 966, 778, 664. ^{1}H NMR (CDCl$_3$): δ = 7.75 (d, J = 8.41 Hz, 1H, Ar–H), 7.32 (2H, broad s, Ar–H), 6.89 (d, J = 8.16 Hz, 1H, Ar–H), 6.59 (2H, s, Ar–H), 6.08 (2H, s, CH$_2$). ^{13}C NMR (CDCl$_3$): δ = 162.69 (Ar–CO), 149.55 (Ar–CO), 148.19 (Ar–CO), 146.31 (Ar–CH), 135.75 (Ar–C), 121.46 (Ar–CH), 118.46 (Ar–CH), 115.76 (Ar–CN), 113.74 (Ar–CH), 109.30 (Ar–CH), 109.21 (Ar–CH), 102.54 (O–CH). *Anal.* Calc. for C$_{15}$H$_8$N$_2$O$_3$: C, 68.18; H, 3.05; N, 10.06. Found: C, 68.23; H, 3.01; N, 10.01%.

2.2.2. 3-[3,4-(Methylendioxy)-phenoxy]-phthalonitrile (2)

The synthesis of 2 was similar to that of 1, except 3-nitrophthalonitrile (1.25 g, 7.25 mmol) instead of 4-nitrophthalonitrile was employed. The amounts of the other reagents were: 3,4-(methylendioxy)-phenol, 1.00 g (7.25 mmol) and anhydrous potassium carbonate, 2.50 g (18.12 mmol).

Yield: 1.34 g (70%). IR spectrum (cm^{-1}): 3087, 3073 (Ar–CH), 2228 (C≡N), 1576 (C=C), 1438, 1389, 1243, 1097 (C–O–C), 1034, 990, 866, 799, 719. ^{1}H NMR (CDCl$_3$): δ = 7.58 (d, J = 8.42 Hz, 1H, Ar–H), 7.47 (d, J = 7.53 Hz, 1H, Ar–H), 7.13 (d, J = 8.46 Hz, 1H, Ar–H), 6.87 (d, J = 8.33 Hz, 1H, Ar–H), 6.65 (2H, s, Ar–H), 6.07 (2H, s, CH$_2$). (CDCl$_3$): δ = 161.83 (Ar–CO), 150.03 (Ar–CO), 148.45 (Ar–CO), 146.30 (Ar–CH), 134.71 (Ar–C), 120.37 (Ar–CH), 117.72 (Ar–CH), 115.49 (Ar–CN), 113.01 (Ar–CH), 109.15 (Ar–CH), 106.16 (Ar–CH), 102.50 (O–CH). *Anal.* Calc. for C$_{15}$H$_8$N$_2$O$_3$: C, 68.18; H, 3.05; N, 10.06. Found: C, 68.15; H, 3.08; N, 10.11%.

2.2.3. 4,5-[3,4-(Methylendioxy)-phenoxy-phthalonitrile (3)

The synthesis of 3 was similar to that of 1, except 4,5-dichloro-phthalonitrile (0.71 g, 3.62 mmol) instead of 4-nitrophthalonitrile was employed. The amounts of the other reagents were: 3,4-(methylendioxy)-phenol, 1.02 g (7.25 mmol) and anhydrous potassium carbonate, 2.50 g (18.12 mmol).

Yield: 1.00 g (69%). IR spectrum (cm^{-1}): 3084, 3050 (Ar–CH), 2230 (C≡N), 1599 (C=C), 1486, 1444, 1249, 1096 (C–O–C), 1037, 966, 884, 778, 664. ^{1}H NMR (CDCl$_3$): δ = 7.16 (2H, s, Ar–H), 6.88 (d, J = 8.35 Hz, 2H, Ar–H), 6.65 (d, J = 2.38 Hz, 2H, s, Ar–H), 6.59 (dd, J = 8.36, 2.42 Hz, 2H, Ar–H), 6.08 (4H, s, CH$_2$). ^{13}C NMR (CDCl$_3$): δ = 152.72 (Ar–CO), 149.50 (Ar–CO), 148.37 (Ar–CO), 135.46 (Ar–C), 121.40 (Ar–CH), 115.55 (Ar–CN), 113.23 (Ar–CH), 110.52 (Ar–CH), 109.21 (Ar–CH), 102.91 (O–CH). *Anal.* Calc. for C$_{22}$H$_{12}$N$_2$O$_6$: C, 66.00; H, 3.02; N, 7.00. Found: C, 65.94; H, 2.99; N, 7.05%.

2.2.4. (4)-Tetra[3,4-(methylendioxy)-phenoxy]phthalocyaninato zinc(II) (4)

Compound 1 (0.50 g, 1.89 mmol), anhydrous zinc acetate (0.41 g, 1.89 mmol) and 3 ml of dry 1-pentanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.45 ml, 0.29 mmol) under a nitrogen atmosphere and held at reflux temperature for 15 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise 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, CHCl$_3$ and a mixture of THF and CH$_2$Cl$_2$ (1:15 by volume), as eluents, respectively.

Yield: 0.25 g (47%). UV–Vis (DMSO): λ_{max} nm (log ε) 358 (4.95), 613 (4.74), 680 (5.43), (toluene): λ_{max} nm (log ε) 351 (4.84), 612 (4.70), 680 (5.40), (DCM): λ_{max} nm (log ε) 357 (4.97), 612 (4.72), 681 (5.45). IR spectrum (cm^{-1}): 3073 (Ar–CH), 2945, 2892 (CH), 1608 (C=C), 1482, 1396, 1335, 1218, 1093 (C–O–C), 952, 815, 745, 731 (Pc skeletal). ^{1}H NMR (CDCl$_3$): δ = 8.11–6.43 (24H, m, Ar–H), 5.99 (8H, s, CH$_2$). *Anal.* Calc. for C$_{60}$H$_{32}$N$_8$O$_{12}$Zn: C, 64.21; H, 2.87; N, 9.98. Found: C, 64.35; H, 3.03; N, 9.73%. MS (ES$^+$), (*m/z*): Calc. 1122.4. Found: 1123.6 [M$^+$].

2.2.5. (3)-Tetra[3,4-(methylendioxy)-phenoxy]phthalocyaninato zinc(II) (5)

The synthesis and purification of 5 was as outlined for 4, except compound 2 (0.50 g, 1.89 mmol) instead of complex 1 was employed. The amounts of the other reagents were anhydrous zinc acetate (0.41 g, 1.89 mmol), dry 1-pentanol (3 ml) and DBU (0.45 ml, 0.29 mmol).

Yield: 0.20 g (38%). UV–Vis (DMSO): λ_{max} nm (log ε) 365 (4.75), 626 (4.72), 697 (5.40), (Toluene): λ_{max} nm (log ε) 352 (4.82), 626 (4.83), 696 (5.53), (DCM): λ_{max} nm (log ε) 358 (4.70), 627 (4.61), 694 (5.39). IR spectrum (cm^{-1}): 3077 (Ar–CH), 2955, 2885 (–CH), 1607 (C=C), 1477, 1395, 1333, 1236, 1090 (C–O–C),

1038, 968, 928, 878, 815, 744 (Pc skeletal). ^{1}H NMR (CDCl$_3$): δ = 8.43–6.49 (24H, m, Ar–H), 5.98 (8H, s, CH$_2$). *Anal*. Calc. for C$_{60}$H$_{32}$N$_8$O$_{12}$Zn: C, 64.21; H, 2.87; N, 9.98. Found: C, 64.15; H, 3.01; N, 9.77%. MS (ES$^+$), (*m/z*): Calc. 1122.4. Found: 1123.6 [M$^+$].

2.2.6. 2,3-Octakis-[3,4-(methylendioxy)-phenol]phthalocyaninato zinc(II) (6)

The synthesis and purification of 6 was as outlined for 4, except compound 3 (0.50 g, 1.25 mmol) instead of complex 1 was employed. The amounts of the other reagents were anhydrous zinc acetate (0.27 g, 1.25 mmol), dry 1-pentanol (3 ml) and DBU (0.45 ml, 0.29 mmol).

Yield: 0.13 g (25%). UV–Vis (DMSO): λ_{max} nm (log ε) 359 (5.01), 629 (4.78), 679 (5.24), (Toluene): λ_{max} nm (log ε) 363 (4.63), 614 (4.49), 680 (5.11), (DCM): λ_{max} nm (log ε) 359 (4.99), 612 (4.74), 680 (5.350). IR spectrum (cm^{-1}): 3074 (Ar–CH), 2957, 2890 (–CH), 1605 (C$=$C), 1482, 1391, 1334, 1237, 1097 (C–O–C), 1038, 993, 930, 865, 814, 744 (Pc skeletal). ^{1}H NMR (CDCl$_3$): δ = 7.16–6.39 (32H, m, Ar–H), 5.56 (16H, s, CH$_2$). *Anal*. Calc. for C$_{88}$H$_8$N$_8$O$_{24}$Zn: C, 63.41; H, 2.90; N, 6.72. Found: C, 63.01; H, 3.12; N, 6.97%. MS (ES$^+$), (*m/z*): Calc. 1666.7; Found: 1667.6 [M$^+$].

2.3. Photophysical studies

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method) [24] and [25], (Eq. (1)):

(1)

$$\Phi_F = \Phi_{F(Std)} \frac{F \cdot A_{Std} \cdot n^2}{F_{Std} \cdot A \cdot n_{Std}^2}$$

where F and F_{Std} are the areas under the fluorescence curves of 4–6 and the standard, respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation wavelengths (which was $\sim$0.05 in all solvents used), and n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc in DMSO (Φ_F = 0.20) [26], was employed as the standard.

2.3.2. Triplet quantum yields and lifetimes

The solutions for triplet quantum yields and lifetimes were introduced into a 1.0 mm pathlength UV–Vis spectrophotometric cell, deaerated using nitrogen and irradiated at the Q-band maxima. Triplet state quantum yields (Φ_T) of 4–6 were determined by the triplet absorption method [27], using zinc phthalocyanine (ZnPc) as a standard; Eq. (2):

(2)

$$\Phi_T = \Phi_T^{Std} \cdot \frac{\Delta A_T \cdot \varepsilon_T^{Std}}{\Delta A_T^{Std} \cdot \varepsilon_T}$$

where ΔA_T and ΔA_T^{Std} are the changes in the triplet state absorbances of 4–6 and the standard, respectively. ε_T and ε_T^{Std} are the triplet state molar exctinction coefficients for 4–6 and the standard, respectively. Φ_T^{Std} is the triplet quantum yield for the standard, ZnPc (Φ_T = 0.65 in DMSO [28] and 0.65 in toluene [29]). ε_T and ε_T^{Std} were determined from the molar extinction coefficients of their respective ground singlet state (ε_s and ε_s^{Std}) and the changes in absorbances of the ground singlet states (ΔA_S and ΔA_S^{Std}), according to Eq. (3):

(3)

$$\varepsilon_T = \varepsilon_S \cdot \frac{\Delta A_T}{\Delta A_S}$$

Quantum yields of internal conversion (Φ_{IC}) were obtained from Eq. (4), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of the 4–6 molecules.

(4)

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T).$$

2.4. Photochemical studies

2.4.1. Singlet oxygen quantum yields

Quantum yields of singlet oxygen photogeneration were determined as previously explained in detail [30], [31] and [32] in air (no oxygen bubbled) using the relative method with ZnPc as reference and DPBF as chemical quencher for singlet oxygen, using Eq. (5):

(5)

$$\Phi_\Delta = \Phi_\Delta^{Std} \cdot \frac{R_{DPBF} I_{abs}^{Std}}{R_{DPBF}^{Std} I_{abs}}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard, ZnPc ($\Phi_\Delta = 0.67$ in DMSO [33] and 0.58 in toluene [32]). R_{DPBF} and R_{DPBF}^{Std} are the DPBF photobleaching rates in the presence of 4–6 and the standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by 4–6 and the standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [34], the concentration of DPBF was ~ 3×10^{-5} mol l^{-1}. Solutions of sensitizer (absorbance = 0.2 at the irradiation wavelength) 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 for singlet oxygen studies was 2×10^{15} photons s^{-1} cm^{-2}. The error in the determination of Φ_Δ was ~10% (determined from several Φ_Δ values).

2.4.2. Photodegradation quantum yields

For determination of photodegradation quantum yields, the usual Eq. (6) was employed [30], [31] and [32]:

(6)

$$\Phi_{Pd} = \frac{(C_0 - C_t) V N_A}{I_{abs} S t}$$

where C_0 and C_t in mol dm^{-3} are the concentrations of 4–6 before and after irradiation, respectively; V is the reaction volume; S is the irradiated cell area (2.0 cm^2); t is the irradiation time; N_A is the Avogadro's number and I_{abs} is the overlap integral of the radiation source intensity and the absorption of 4–6 (the action spectrum) in the region of the interference filter transmittance. The light intensity for photodegradation studies was 5×10^{16} photons s^{-1} cm^{-2}.

3. Results and discussion

3.1. Syntheses and characterization

The synthetic routes to novel phthalocyanines (4–6) are shown in Scheme 1. These complexes were prepared by the template cyclotetramerization of 4-[3,4-(methylendioxy)-phenoxy]-phthalonitrile (1), 3-[3,4-(methylendioxy)-phenol]-phthalonitrile (2), 4,5-[3,4-(methylendioxy)-phenol]-phthalonitrile (3) and anhydrous Zn(OAc)$_2$ in the presence of 1-pentanol at reflux temperature under argon atmosphere and in the

presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a strong base. All of these new zinc phthalocyanines were purified by column chromatography and were obtained in a moderate yield (47% for 4, 38% for 5, and 25% for 6) and were also characterized by elemental analysis together with the spectral data (^{1}H NMR, FT-IR, mass and UV–Vis spectra).

The characterization data of the new compounds are consistent with the assigned formula. The tetra-substituted complexes (4 and 5) were isolated as a mixture of isomers, as expected. The presence of isomers might be verified by the slight broadening encountered in the UV–Vis absorption bands and broadening in the ^{1}H NMR spectra as compared with the spectra of octa-substituted phthalocyanines which are composed of a single isomer [35], [36], [37] and [38]. No attempt was made to separate the isomers of 4 and 5.

The characteristic vibrations corresponding to CN and ethers groups (C–O–C) at 2226, 2228 and 2230 cm^{-1} and 1096, 1097, 1096 cm^{-1} were observed for 1, 2 and 3 in the FT-IR spectra, respectively. Aromatic C–H peaks occurred above 3050 cm^{-1} for all the phthalonitriles. The ^{1}H NMR spectrum of the compounds 1, 2 and 3 showed signals with δ ranging from 7.75 to 6.59, belonging to aromatic protons and 6.07 and 6.08 ppm belonging to aliphatic H integrating for a total of 8 protons for 1 and 2, and 12 protons for 3 as expected. ^{13}C NMR spectral data were in good agreement with the proposed structure. The characteristic signals related to aromatic carbon atoms and dicyano carbon atoms about $\delta = 135$ and 115 ppm, respectively for 1–3 supported the structures.

After conversion into zinc phthalocyanine derivations, the characteristic CN stretch at ~2230 cm^{-1} of phthalonitriles 1, 2 and 3 disappeared in the FT-IR spectra, indicative of metallophthalocyanine formation. The characteristic vibrations corresponding to ether groups (C–O–C) were observed at 1093 (for 4), 1090 cm^{-1} (for 5) and 1097 cm^{-1} (for 6) and aromatic C–H peaks were above 3000 cm^{-1} for the complexes.

The compounds were found to be pure by ^{1}H NMR with both the substituents and ring protons observed in their respective regions. The ^{1}H NMR spectra of tetra-substituted phthalocyanine derivatives (4 and 5) and octa-substituted derivative (6) were almost identical with that of the starting compounds 1, 2 and 3 except for broadening and small shift. Complexes 4 and 5 showed complex patterns due to the mixed isomer character of these compounds. In the ^{1}H NMR spectrum of 4 and 5 the aromatic and Pc protons appear between 6.43 and 8.11 ppm (for 4, integrating for 24H), 6.49 and 8.43 ppm (for 5, integrating for 24H), and 6.39 and 7.16 ppm (for 6, integrating for 32H). For all complexes aliphatic protons, were observed at about at 6 ppm, integrating

for a total of 8 protons for 4 and 5 and 16 protons for complex 6. In the mass spectrum of Zn phthalocyanines (4–6), the presence of molecular ion peaks at m/z 1123.6 $[M]^+$, 1123.6 $[M]^+$ and 1667.6 $[M]^+$, respectively, confirmed the proposed structures. Elemental analysis results also were consistent with the proposed structures of all compounds 1–6.

3.2. Ground state electronic absorption spectra

The UV–Vis spectra of the phthalocyanine complexes exhibit characteristic Q- and B-bands. Two principle π–π^* transitions are seen for phthalocyanines: a Q-band (~700 nm, a π–π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the complexes) and a B-band (~300–350 nm, a deeper π–π^* transition from the HOMO's (a_{1u} and a_{2u}) to the LUMO (e_g)) [39] and [40]. The Q-band absorptions in the UV–Vis absorption spectra of the phthalocyanines (4, 5 and 6) were observed as a single high intensity band due to a π–π^* transition at 681, 697 and 680 nm in DMSO, 681, 694 and 680 nm in DCM and 677, 693 and 679 nm in toluene, respectively, Table 1 and Fig. 1.

Table 1.

Spectral parameters of 4, 5 and 6 in DMSO and toluene.

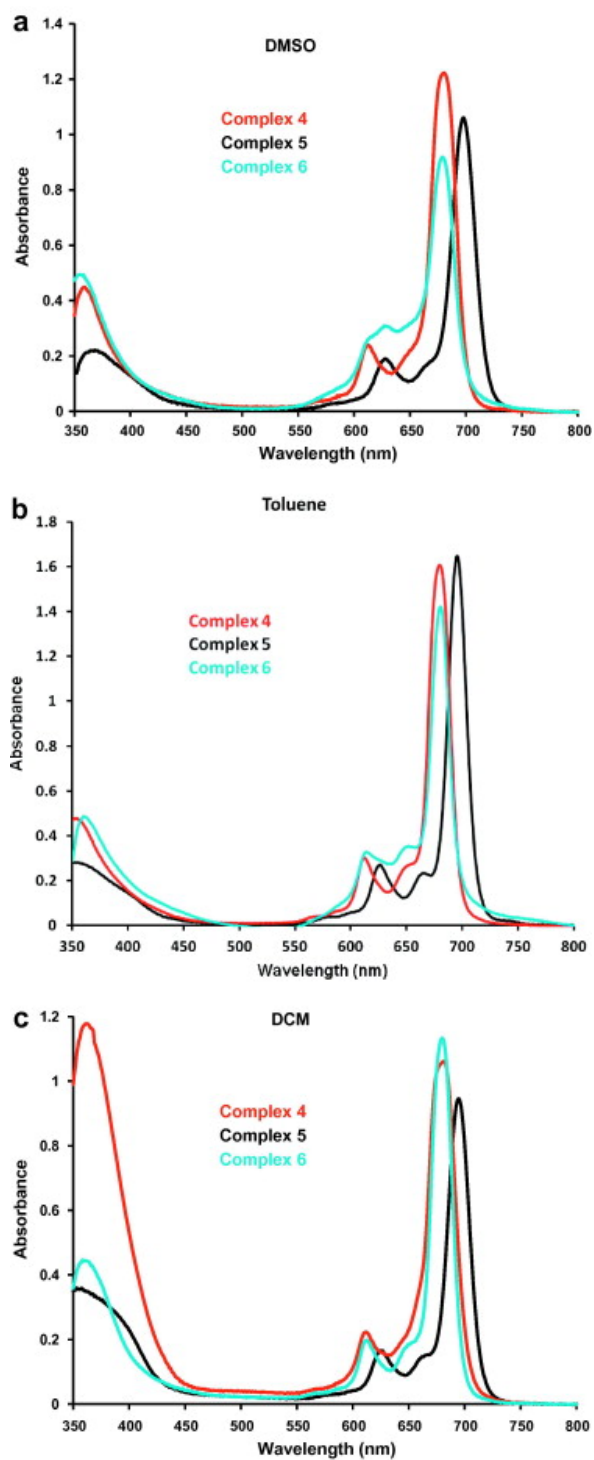| Compound	Solvent	Q-band, λ_{max} (nm)	(log ε)	Excitation, λ_{Ex} (nm)	Emission, λ_{Em} (nm)	Stokes shift, Δ_{Stokes} (nm)
4	DMSO	681	5.43	682	693	12
	toluene	677	5.40	679	689	12
5	DMSO	697	5.40	699	712	15
	toluene	693	5.53	695	705	10
6	DMSO	680	5.24	682	692	12
	toluene	679	5.11	681	689	10

Fig. 1. UV–Vis absorption spectra of 4, 5 and 6 in DMSO (a), concentration $= 4 \times 10^{-6}$ mol dm^{-3}; toluene (b), concentration $= 4 \times 10^{-6}$ mol dm^{-3} for 4 and 5, 10×10^{-6} mol dm^{-3} for 6; DCM (c), concentration $= 4 \times 10^{-6}$ mol dm^{-3}.

In DMSO, toluene and DCM, the Q-band positions of 5 are red-shifted relative to those of 4 and 6, with the greatest red-shifting being observed in DMSO. Non-peripheral substitution greatly influences the energy levels of molecular orbitals and hence the absorption spectrum, whereas peripheral substitution has a smaller effect on the Q-band position. In 5, the (methylendioxy)-phenoxy substituents are closer to the ring, hence they bring about greater destabilization of the a_{1u} orbital (HOMO), and result in larger bathochromic shifts.

The consequence of the substitution with four [3,4-(methylendioxy)-phenoxy] is clearly observed by the high solubility of the Pcs 4, 5 and 6 in organic solvents such as DCM, CHCl$_3$, THF, DMF, DMSO, toluene and acetone. Aggregation behavior of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, nature of solvent and substituents, metal ions and temperature [41]. In this study, the aggregation behavior of the Pcs derivatives (4, 5 and 6) were investigated in DMSO, DCM and toluene at different concentrations. As the concentration was increased, the intensity of absorption of the Q-band also increased and there was no new bands due to the aggregated species [42], Fig. 2. Complexes 4, 5 and 6 did not show aggregation in these solvents. Though complex 6 did not show aggregation in toluene, chloroform, THF and DCM, it showed broad band around 627 nm because of aggregation just in DMSO (Fig 1). DMSO is known to prevent aggregation since it is strong coordinating solvent. However, it has been observed [43] before that aggregation occurs in DMSO and in less coordinating solvents for some MPc derivatives. Except for 6 in DMSO, Lambert–Beer law was obeyed for these compounds in the concentrations ranging from 2.0×10^{-6} to 1.0×10^{-5} mol dm^{-3} as given an example for 5 in toluene in Fig. 2.
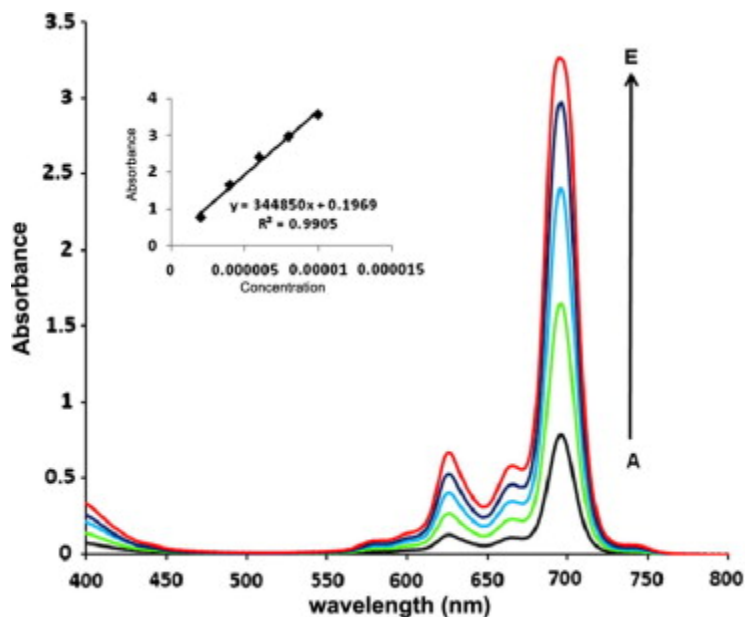
Fig. 2. Absorption spectra of 5 in toluene at different concentration: (A) 2×10^{-6}, (B) 4×10^{-6}, (C) 6×10^{-6}, (D) 8×10^{-6}, (E) 10×10^{-6} mol dm^{-3}.

3.3. Fluorescence spectra, and quantum yields

Fig. 3 shows the absorption, fluorescence excitation and emission spectra of 4, 5 and 6 in DMSO. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for 4 and 5. For complex 6 the emission spectrum shows little less broadening when compared to excitation and absorption spectra, confirming that the aggregates do not fluoresce. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for both complexes suggest that the nuclear configurations of the ground and excited states are similar and not affected by excitation [44]. Fluorescence emission peaks were observed at: 693 nm for 4, 712 nm for 5, 692 nm for 6 in DMSO (Table 1). The Stokes' shifts range from 10 to 15 nm, which is usual for ZnPc derivatives [45].
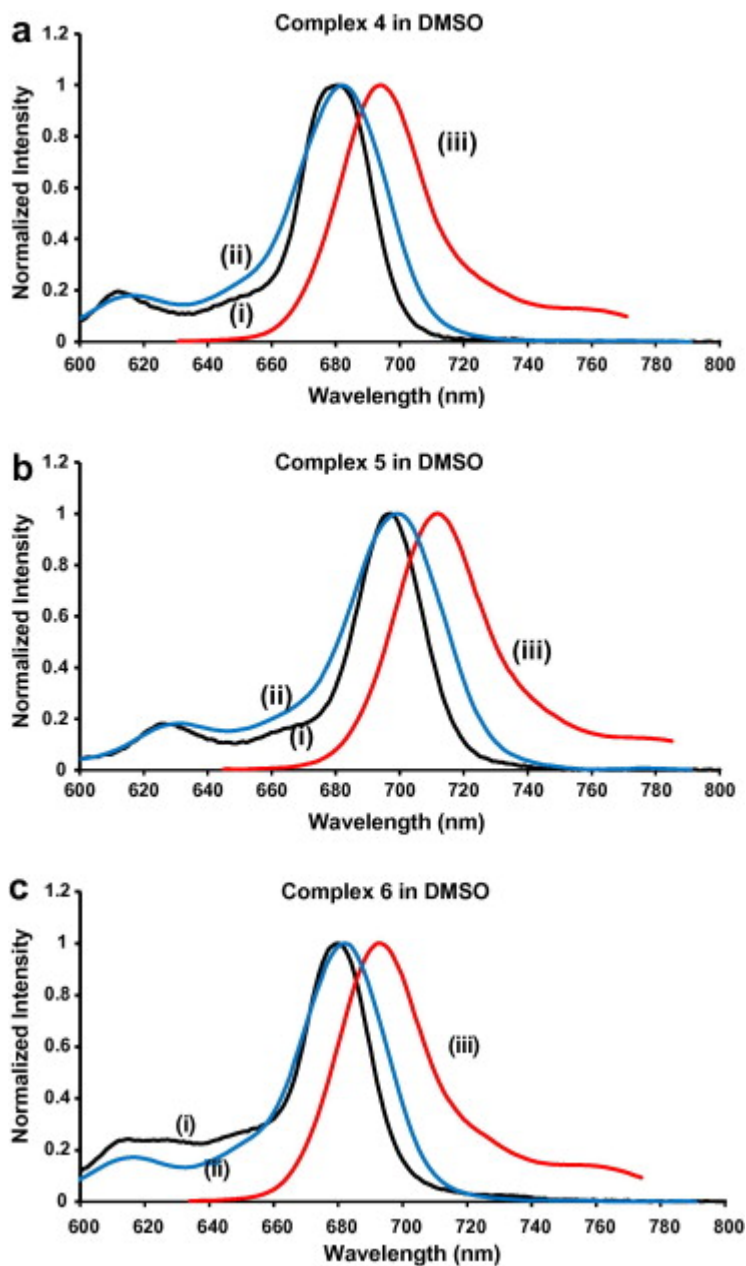
Fig. 3. Absorption (i), excitation (ii) and emission (iii) spectra of the compounds 4 (a), 5 (b), and 6 (c) in DMSO. Excitation wavelength = 682 nm for (4) 699 nm for (5) and 682 nm for (6) in DMSO.

The fluorescence quantum yield (Φ_F) values are different for 4, 5 and 6 in DMSO, but the values are similar for the three complexes in toluene, with 4 showing larger values in both solvents, Table 2. Φ_F values in the two solvents demonstrate that fluorescence is influenced by the environment of the fluorescing molecule, e.g.,

solvent parameters. Solvent effects on Φ_F are usually interpreted in terms of the Förster–Hoffman equation [46] (Eq. (7)), which predicts a direct dependence of Φ_F on solvent viscosity.

(7)

$$\log\Phi_F=C+x\log\eta$$

Table 2.

Photophysical and photochemical properties of 4, 5 and 6 in DMSO and toluene.

Compound	Solvent	Φ_F	τ_T	Φ_T	Φ_{IC}	Φ_d (10^6)	Φ_Δ	S_Δ
4	DMSO	0.18	210	0.66	0.16	1.20	0.48	0.80
	toluene	0.06	150	0.85	0.09	0.83	0.80	0.94
5	DMSO	0.13	210	0.59	0.28	2.00	0.43	0.73
	toluene	0.05	140	0.79	0.16	0.72	0.74	0.89
6	DMSO	0.10	190	0.55	0.35	8.53	0.22	0.26
	toluene	0.05	180	0.73	0.22	0.98	0.65	0.78

The values of Φ_F in the two solvents are in conformity with the Förster–Hoffman equation for the complexes. The viscosities of DMSO and toluene are 1.99 and 0.59 cP, respectively.

Peripherally tetra-substituted complex (4) shows the largest (Φ_F) value in DMSO compared to the other complexes. The octa-substituted complex (6) shows lowest Φ_F value in DMSO. The very low Φ_F value for 6 in DMSO can be explained by the aggregation tendencies of the molecules in this solvent. Aggregation reduces the likelihood of radiative deactivation (fluorescence) through dissipation of energy by the aggregates. Complex 6 showed larger quantum yield for internal conversion (Φ_{IC}, Table 2) in DMSO when compared to complexes 4 and 5, most likely due to aggregation.

3.4. Triplet quantum, yields and lifetimes

Triplet quantum yield (Φ_T) represents the fraction of absorbing molecules that undergo intersystem crossing to the metastable triplet excited state. Therefore, factors which induce spin–orbit coupling will certainly populate the triplet excited state. Transient spectrum for complex 4 in DMSO as shown in Fig. 4, and shows a maximum at 490 nm, hence triplet lifetimes and yields were determined at this wavelength. Fig. 5 displays the triplet decay curves of the complexes (using complex 6 in toluene as an example). The triplet life time for 4 (210 μs), 5 (210 μs) and 6 (190 μs) in DMSO and of 150 (4), 140 (5) and 180 μs (6) in toluene are lower than for unsubstituted ZnPc (350 μs) in DMSO and (330 μs) in toluene [47] respectively. This suggests that the [3,4-(methylendioxy)-phenoxy] substituents quench the triplet state. The τ_T values are higher in DMSO for all complexes. The reason for the large difference in value (going from DMSO to toluene) is not clear, but could partly be ascribed to the higher viscosity of DMSO (1.99 cP) than toluene (0.58 cP). In high viscocity solvents, translational and rotational motions are reduced, thereby reducing the likelihood of non-radiative deactivation of the excited singlet state via internal conversion.
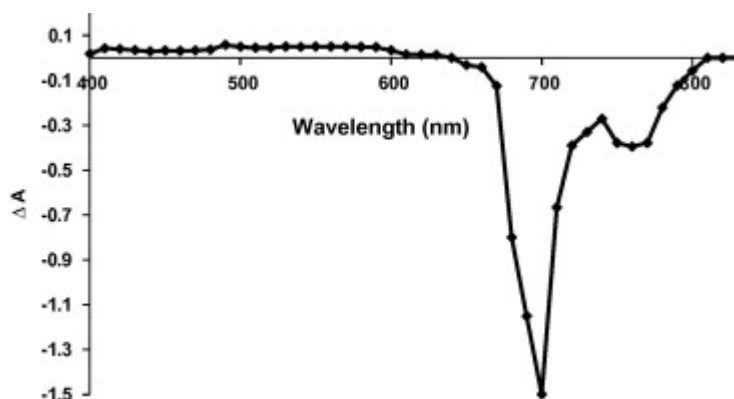

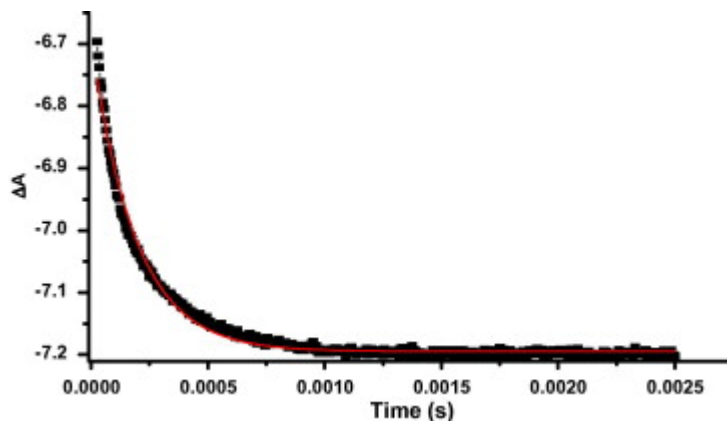Fig. 4. Transient difference spectrum of complex 4 in DMSO.

Fig. 5. Mono-exponential triplet decay profile for complex 6 in toluene.

The triplet quantum yields (Φ_T) for substituted complexes (4, 5 and 6) in toluene are high compared to ZnPc standard in toluene ($\Phi_T = 0.65$ for ZnPc). The high values of Φ_T in toluene suggest efficient intersystem crossing (ISC) in the presence of the substituents for substituted complexes (4, 5 and 6). Complex 6 showed low Φ_T value in DMSO due to the aggregation in this solvent.

3.5. Photochemical properties

3.5.1. 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. (5). Singlet oxygen quantum yields were studied in DMSO and toluene using a chemical method (1,3-diphenylisobenzofuran, DPBF). Fig. 6 shows spectral changes observed during photolysis of complex 4 in toluene in the presence of DPBF. The disappearance of DPBF was monitored using UV–Vis spectroscopy. There were no changes in the Q-band intensities during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies [48]. The Φ_Δ values of three complexes were higher in toluene than in DMSO, corresponding to high Φ_T values in this solvent. The Φ_Δ values for 4, 5 and 6 (0.80, 0.74 and 0.65 in toluene and 0.48, 0.43 and 0.22 in DMSO, respectively) are lower when compared to unsubtituted ZnPc in DMSO (0.67 [33]) and higher in toluene (0.58 [32]). Complex 6 has the lowest the value of Φ_Δ in DMSO (0.22) due to aggregation.
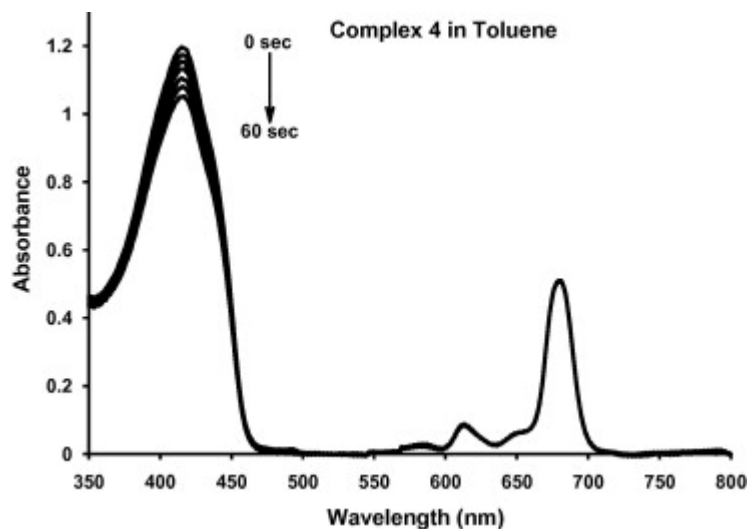
Fig. 6. A typical spectrum for the determination of singlet oxygen quantum yield. This figure was for complex 4 in toluene at a concentration 4×10^{-6} mol dm^{-3}.

The magnitude of the S_Δ ($=\Phi_\Delta/\Phi_T$) represents the efficiency of quenching of the triplet excited state by singlet oxygen. Compound 4, 5 and 6 displayed S_Δ of near unity in toluene and DMSO. However, complex 6 showed very low value in DMSO due to aggregation.

3.5.2. Photodegradation quantum yields

Photodegradation is a process where a phthalocyanine is degraded under light irradiation. It can be used to determinate MPcs stability and this is especially important for those molecules intented for use as photocatalysts. The photobleaching stabilities of complexes 4, 5 and 6 were determined in DMSO and toluene by monitoring the decrease in the intensity of the Q-band under irradiation with increasing time. The photodegradation quantum yield (Φ_d) values for the complexes are listed in Table 2 and are of the order of 10^{-6}. These values show that the molecules are of high stability in two solvents used. Stable ZnPc molecules show values as low as 10^{-6} and for unstable molecules, values of the order 10^{-3} have been reported [49]. Photobleaching quantum yields for the complexes were smaller in toluene than in DMSO, indicating that they are more stable in toluene than in DMSO. This could be due to the high singlet oxygen quantum yields in toluene. Since photobleaching is initiated by singlet oxygen attack. The order of stability among the substituted complexes was 4 > 5 > 6 in DMSO and 5 > 4 > 6 in toluene.

4. Conclusion

In this study, the syntheses, spectral and photophysicochemical properties of soluble peripheral and non-peripheral tetrakis- and octakis [3,4-(methylendioxy)-phenoxy]-substituted zinc phthalocyanines (4, 5 and 6), respectively are discussed. The complexes have good solubility and are mainly monomeric in solution. The introduction of [3,4-(methylendioxy)-phenoxy] on the ring results in high triplet quantum yields (ranging from 0.55 to 0.85 in DMSO and toluene). All complexes showed similar and typical fluorescence quantum yields for MPcs in DMSO. Complex 6 has a low triplet quantum yield (0.65) and singlet quantum yield values (0.22) in DMSO due to aggregation. Triplet lifetimes are higher in DMSO than in toluene for substituted complexes (4, 5 and 6). The tetra-substituted complexes (4 and 5) have good singlet oxygen quantum yields especially complex 4 which has the highest value in both solvents. The Pcs reported in this study can be applied as efficient candidates for solution studies requiring monomeric form of this material. The singlet oxygen quantum yields, which give indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.22 to 0.80. Thus, these complexes show potential as Type II photosensitizers and can be used in photodynamic therapy.

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