Solvent and central metal effects on the photophysical and photochemical properties of 4-benzyloxybenzoxy substituted phthalocyanines

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ARTICLE INFO

ABSTRACT

The synthesis and characterization of new peripherally tetra-4-benzyloxybenzoxy substituted metal-free, zinc and lead phthalocyanines are described for the first time in this study. The influence of various organic solvents and the nature of the central metal ion on the spectroscopic, photophysical and photochemical properties has been investigated. General trends are described for photodegradation, singlet oxygen and fluorescence quantum yields, and fluorescence lifetimes of these compounds in different solvents. Photophysical and photochemical properties of phthalocyanine compounds are very useful for photodynamic therapy applications. Especially high singlet oxygen quantum yields are very important for Type II mechanism. The studied phthalocyanine compounds showed good singlet oxygen generation and these compounds show potential as Type II photosensitizers. The fluorescences of the studied compounds are effectively quenched by 1,4-benzoquinone in different solvents.

1. Introduction

Phthalocyanines (Pcs) have great interest due to their scientific and technological importance in many fields. In recent years, metallophthalocyanines (MPcs) have been extensively studied in non-linear optic applications, chemical sensors, catalysis, liquid crystals, photovoltaic cells, semiconductive materials and photo-dynamic therapy (PDT) [1–4]. The chemical and physical characteristics of these compounds vary with the central metal ion, peripheral substitution and ligands attached to the central metal atom [5].

The wide planar organic surface of the phthalocyanine molecule causes aggregation of the complexes both in solution and in solid state due to the $\pi-\pi^*$ stacking interactions [6,7]. Because aggregation of the molecules affects solubility of the phthalocyanines, many phthalocyanines are poorly soluble in common organic solvents and water. The solubility of these molecules increases by changing peripheral substituents since the substituents increase the distance between the stacked phthalocyanines and enable their solvation [8,9].

Solvents also affect aggregation in phthalocyanine complexes. Organic solvents are known to reduce aggregation whereas aqueous medium results in highly aggregated complexes. However, many phthalocyanine complexes remain aggregated even in non-aqueous solutions [10–12]. Aromatic solvents such as benzene or toluene are known to give narrow Q bands in the absorption spectra for phthalocyanine complexes whereas broadening is observed in non-aromatic solvents [13].

PDT is the novel treatment in cancer therapies and this technique is based on a photochemical reaction, which is initiated by light activation of a photosensitizing drug causing tumor cell death. Light is mainly applied by superficial illumination of the tumor and the surrounding tissue causing drug activation followed by tumor cell death. Pcs and MPcs are useful photosensitizers due to their intense absorption in red region of the visible light [14,15]. Especially zinc phthalocyanine complexes are often used due to their long triplet lifetimes [16]. Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplet excited state and ground state molecular oxygen increases with the lifetime of the excited state [17].

The aim of our research is to synthesize new peripherally substituted metal-free (H_2Pc), zinc ($ZnPc$) and lead ($PbPc$) phthalocyanines as potential PDT agents. Our previous studies have already reported synthesis, photophysical and photochemical properties of various substituted phthalocyanines [18–23]. These phthalocyanine complexes show interesting photophysical and photochemical properties especially high singlet oxygen quantum

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yields which are very important for PDT of cancer. In this study, we report the effects of the peripherally 4-benzyloxybenzoxy substituted metal-free (**H₂Pc**), zinc (**ZnPc**) and lead (**PbPc**) phthalocyanines on the photophysical and photochemical parameters. Aggregation behaviour, photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties of newly synthesized compounds (Scheme 1) are investigated in different solvents. Since PDT activity is mainly based on singlet oxygen, its production is determined by the dye-sensitized photooxidation of 1,3-diphenylisobenzofuran (DPBF), a specific scavenger of this species [24]. The studies of the photostability of **H₂Pc**, **ZnPc** and **PbPc** complexes during photosensitized reactions are also immense importance.

2. Experimental

2.1. Materials

4-Benzyloxybenzyl-alcohol (**1**) was purchased from Aldrich. 1,3-diphenylisobenzofuran (DPBF) was purchased from Fluka. 4-Nitrophthalonitrile (**2**) [25] was prepared according to the literature. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perin and Armarego [26].

2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl₃, and chemical shifts (δ) were reported relative to Me₄Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC−MS/MS spectrometer. UV−visible spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter using 1 cm pathlength cuvettes at room temperature.

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 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 (Eq. (1)) [27,28],

$$\Phi_F = \Phi_F(\text{Std})\frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**H₂Pc**, **ZnPc** and **PbPc**) and the standard, respectively. A and A_{Std} are the respective absorbance of the samples and standard at the excitation wavelength, respectively. n^2 and n_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted **ZnPc** (**Std-ZnPc**) (in DMSO) ($\Phi_F = 0.20$) [29] was employed as the standard. Both the
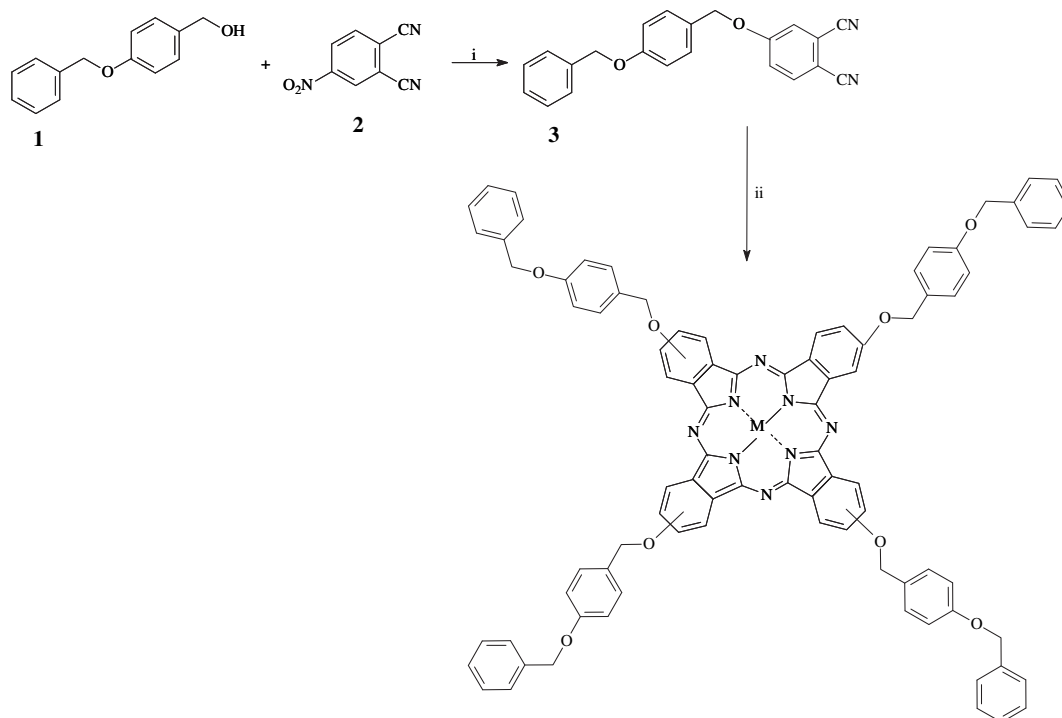
Compound	H₂Pc	ZnPc	PbPc
M	2H	Zn	Pb

Scheme 1. Synthetic pathway for the preparation of phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**): (i) anhydrous K₂CO₃, dry DMF, 50 °C, (ii) 160 °C, n-pentanol, DBU for **H₂Pc**; anhydrous Zn(CH₃COO)₂ and PbO for **ZnPc** and **PbPc**, respectively.

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 [30]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \qquad (2)$$

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 literature [31,32]. Typically, 2 cm^3 portions of the respective metal-free, zinc and lead phthalocyanine (**H$_2$Pc**, **ZnPc** and **PbPc**) solutions containing the singlet oxygen quencher were irradiated in the Q band region with the photo-irradiation set-up described in Refs. [31,32]. Φ_Δ values were determined in air using the relative method with DPBF as singlet oxygen chemical quencher in different solvents (Eq. (3)):

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R \cdot I_{abs}^{Std}}{R^{Std} \cdot I_{abs}} \qquad (3)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard, **ZnPc** ($\Phi_\Delta^{ZnPc} = 0.67$ in DMSO [33], 0.56 in DMF [34], 0.58 in toluene [35] and 0.53 in THF [36]). R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**H$_2$Pc**, **ZnPc** and **PbPc**) and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples (**H$_2$Pc**, **ZnPc** and **PbPc**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [34], the concentration of DPBF was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (absorbance ~ 1.5 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q band region. DPBF degradation at 417 nm was monitored. The light intensity used for Φ_Δ determinations was found to be 6.48×10^{15} photons s^{-1} cm^{-2}. The error in the determination of Φ_Δ was $\sim 10\%$ (determined from several Φ_Δ values).

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [31,32]. Photodegradation quantum yields were determined using Eq. (4),

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

where C_0 and C_t are the samples (**H$_2$Pc**, **ZnPc** and **PbPc**) 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 (**H$_2$Pc**, **ZnPc** and **PbPc**). A light intensity of 2.16×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments of the substituted phthalocyanines (**H$_2$Pc**, **ZnPc** and **PbPc**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the samples, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of substituted phthalocyanines (**H$_2$Pc**, **ZnPc** and **PbPc**) at each BQ concentration were recorded, and the changes in

fluorescence intensity related to BQ concentration by the Stern–Volmer (S-V) equation [37] were shown in Eq. (5):

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \qquad (5)$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Stern–Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F and is expressed in Eq. (6).

$$K_{SV} = k_q \cdot \tau_F \qquad (6)$$

The ratios of I_0/I were calculated and plotted against [BQ] according to equation (5), and K_{SV} is determined from the slope.

2.5. Synthesis

2.5.1. 4-(4-Benzyloxybenzoxy)phthalonitrile (3)

4-(Benzyloxybenzyl)alcohol (**1**) (5 g, 23.33 mmol) was dissolved in dry DMF (40 cm^3) under an inert nitrogen atmosphere and 4-nitrophthalonitrile (**2**) (4.66 g, 23.33 mmol) was added to the solution. After stirring 10 min, finely ground anhydrous K$_2$CO$_3$ (10.0 g, 69.25 mmol) was added portion wise within 2 h with efficient stirring. The reaction mixture was stirred under nitrogen atmosphere at 50 °C for 3 days. Then the solution was poured into ice-water (100 cm^3). The precipitate formed was filtered off, washed with water until the filtrate was neutral and then washed with diethyl ether and dried in vacuum over P$_2$O$_5$. The crude product was crystallized from ethanol. Yield: 6.35 g (80%), mp: 140–142 °C. Anal. Calcd for C$_{22}$H$_{16}$N$_2$O$_2$: C, 77.64; H, 4.70; N, 8.23%. Found: C, 77.67; H, 4.71; N, 8.22%. IR (KBr tablet) ν_{max}/cm^{-1}: 3076 (Ar-H), 2941, 2875 (Aliph. C–H), 2235 (C≡N), 1587 (C=C), 1174 (Ar–O–C). ^{1}H NMR. (CDCl$_3$), (δ: ppm): 7.68 (d, 1H, Ar-H), 7.37–7.45 (m, 5H, Ar-H), 7.30–7.25 (m, 2H, Ar-H), 6.99–7.03 (m, 4H, Ar-H) 5.01 (s, 4H, CH$_2$–O). ^{13}C NMR. (CDCl$_3$), (δ: ppm): 162.69, 156.83, 136.53, 135.73, 130.07, 128.61, 127.82, 127.05, 126.65, 119.73, 118.56, 117.26, 116.38, 115.71, 109.18, 69.87, 69.73. MS (ES$^+$), (m/z): 340 [M]$^+$.

2.5.2. 2,(3)-Tetrakis(4-benzyloxybenzoxy)phthalocyanine (H$_2$Pc)

4-(4-Benzyloxybenzoxy)phthalonitrile (**3**) (1.50 g, 4.41 mmol) was dissolved in dried n-pentanol (5 cm^3) under an inert nitrogen atmosphere. 1.8-diazabicyclo [5.4.0]undec-7-ene (DBU) (0.583 cm^3, 3.91 mmol) was added to the solution and the mixture was heated to 160 °C for 16 h. After cooling, the solution was dropped in ethanol. The green solid product was precipitated and collected by filtration and washed with ethanol. The crude product was purified by passing through a silica gel column, using THF as eluting solvent. Furthermore this product was purified with preparative thin layer chromatography (silica gel) using CHCl$_3$:MeOH (95:5) as a solvent system. Yield: 0.540 g (36%). Anal. Calcd for C$_{88}$H$_{66}$N$_8$O$_8$: C, 77.53; H, 4.84; N, 8.22%. Found: C, 77.76; H, 4.85; N, 8.31%. IR (KBr tablet) ν_{max}/cm^{-1}: 3294 (N–H), 3060–3027 (Ar-H), 2924–2851 (Aliph. C–H), 1602 (N–H bending), 1569 (C=C), 1174 (Ar–O–C). ^{1}H NMR (CDCl$_3$), (δ: ppm): 7.87–7.26 (m, 4H, Pc-H), 7.11–6.63 (m, 44H, Pc-H, Benzyl-H), 4.88 (s, 16H, CH$_2$-O), −6.66 (s, 2H, N–H). ^{13}C NMR (CDCl$_3$), (δ: ppm) 162.36, 156.45, 154.88, 139.12, 137.70, 136.46, 134.67, 132.48, 131.09, 129.02, 127.67, 124.78, 124.34, 119.92, 108.86, 108.26, 70.21, 69.89. MS (ES$^+$), (m/z): 1363 [M + H]$^+$.

2.5.3. 2,(3)-Tetrakis[(4-benzyloxybenzoxy)phthalocyaninato] zinc (II) (ZnPc)

A mixture of 4-(4-benzyloxybenzoxy)phthalonitrile (**3**) (1.50 g, 4.41 mmol), anhydrous Zn(CH$_3$COO)$_2$ (1.51 g, 8.82 mmol) and dried

n-pentanol (5 cm^3) was heated at 160 °C for 16 h. After cooling to room temperature the reaction mixture was dropped in hot ethanol (40 cm^3) to precipitate the product which was filtered off. The green solid product was purified by passing through a silica gel column, using CHCl$_3$:MeOH (95:5) as eluting solvent system. Yield: 0.597 g (38%). Anal. Calcd for C$_{88}$H$_{64}$N$_8$O$_8$Zn: C, 74.00; H, 4.48; N, 7.85%. Found: C, 74.06; H, 4.46; N, 7.88%. IR (KBr tablet) ν_{max}/cm^{-1}: 3064 (Ar-H), 2922−2862 (Aliph. C−H), 1596 (C=C), 1172 (Ar−O−C). ^{1}H NMR (CDCl$_3$), (δ: ppm): 7.90−7.72 (m, 4H, Pc-H), 7.26−6.79 (m, 44H, Pc-H, Benzyl-H), 4.92 (s, 16H, CH$_2$). ^{13}C NMR (CDCl$_3$), (δ: ppm) 159.74, 156.45, 153.67, 152.45, 138.79, 136.62, 135.52, 132.90, 130.88, 129.23, 128.84, 124.88, 124.53, 120.68, 119.12, 110.24, 69.80, 68.21. MS (ES$^+$), (m/z): 1427 [M + H]$^+$.

2.5.4. 2,(3)-Tetrakis[(4-benzyloxybenzoxy)phthalocyaninato] lead (II) (**PbPc**)

A mixture of 4-(4-benzyloxybenzoxy)phthalonitrile (**3**) (1.50 g, 4.41 mmol), anhydrous PbO (1.96 g, 8.82 mmol) and dried n-pentanol (5 cm^3) was heated at 160 °C for 16 h. After cooling to room temperature the reaction mixture was dropped in hot ethanol (40 cm^3) to precipitate the product which was filtered off. The green solid product was purified by passing through a silica gel column, using CHCl$_3$:MeOH (95:5) as eluting solvent system. Yield: 0.530 g (32%). Anal. Calcd for C$_{88}$H$_{64}$N$_8$O$_8$Pb: C, 67.34; H, 4.08; N, 7.14%. Found: C, 67.30; H, 4.06; N, 7.16%. IR (KBr tablet) ν_{max}/cm^{-1}: 3060 (Ar-H), 2924−2862 (Aliph. C−H), 1508 (C=C), 1174 (Ar−O−C). ^{1}H NMR (CDCl$_3$), (δ: ppm): 7.92−7.36 (m, 4H, Pc-H), 7.28−7.12 (m, 44H, Pc-H, Benzyl-H), 4.86 (s, 16H, CH$_2$-O). ^{13}C NMR (CDCl$_3$), (δ: ppm) 160.74, 158.72, 154.45, 138.52, 136.74, 135.90, 133.56, 131.23, 128.84, 125.88, 124.53, 123.68, 122.80, 120.61, 119.72, 108.24, 69.80, 68.21. MS (ES$^+$), (m/z): 1570 [M + 2H]$^+$.

3. Results and discussion

3.1. Synthesis and characterization

4-(4-benzyloxybenzoxy)phthalonitrile (**3**) was prepared by reaction of 4-(benzyloxybenzyl)alcohol (**1**) with 4-nitrophthalonitrile (**2**) in dried DMF as a solvent at 50 °C in the presence of solid anhydrous K$_2$CO$_3$ as a base. Therefore, 4-benzyloxybenzoxy substituted metal-free phthalocyanine compound (**H$_2$Pc**) was obtained directly from the reaction of 4-(4-benzyloxybenzoxy) phthalonitrile (**3**) and DBU in n-pentanol at reflux temperature. Also, cyclotetramerization of 4-(4-benzyloxybenzoxy)phthalonitrile (**3**) in the presence of anhydrous Zn(CH$_3$COO)$_2$ or PbO and DBU in n-pentanol gave the 4-benzyloxybenzoxy substituted zinc or lead phthalocyanine derivatives **ZnPc** and **PbPc**, respectively.

All new synthesized compounds (**H$_2$Pc**, **ZnPc** and **PbPc**) were characterized by elemental analyses, IR, ^{1}H NMR, ^{13}C NMR and mass spectra. In the IR spectrum, the formation of compound **3** was clearly confirmed by the disappearance of the −OH and −NO$_2$ bands at 3335 and 1530−1357 cm^{-1} and appearance of −C≡N band at 2235 cm^{-1}. In the ^{1}H NMR spectrum of **3**, OH group of compound **1** disappeared as expected. ^{1}H NMR (in CDCl$_3$) spectrum of compound **3** showed new signals at δ = 7.68 (d, 1H, Ar-H), 7.37−7.45 (m, 5H, Ar-H), 7.30−7.25 (m, 2H, Ar-H), 6.99−7.03 (m, 4H, Ar-H) and 5.01 (s, 4H, CH$_2$−O) belonging to aromatic protons and aliphatic ether protons, respectively. The ^{13}C NMR (in CDCl$_3$) spectrum of compound **3** indicated the presence of nitrile carbon atoms δ = 115.71 ppm. The mass spectrum of compound **3** showed an intense peak at m/z = 340 [M]$^+$ support the proposed formula for this compound.

The sharp vibration for the −C≡N group in the IR spectrum of phthalonitrile compound **3** at 2235 cm^{-1} disappeared after formation of metal-free phthalocyanine (**H$_2$Pc**). The ^{1}H NMR spectrum of metal-free phthalocyanine (**H$_2$Pc**) showed new aromatic protons at δ = 7.87−7.26 (m, 4H, Pc-H), 7.11−6.63 (m, 44H, Pc-H, Benzyl-H) and aliphatic ether protons at δ = 4.88 (s, 16H, CH$_2$). The inner core protons (N−H) of this compound (**H$_2$Pc**) were observed at δ = −6.66 (br s, 2H, N−H). The peak for the nitrile carbon atoms in the ^{13}C NMR (CDCl$_3$) spectrum of **H$_2$Pc** was not seen. The mass spectrum of compound **H$_2$Pc** exhibited an intense peak at 1363 m/z for [M + H]$^+$.

After conversion into zinc or lead phthalocyanine, the characteristic C≡N stretch at 2235 cm^{-1} of phthalonitrile **3** disappeared, indicative of metallophthalocyanine formation. The ^{1}H NMR spectrum of **ZnPc** showed new signals at δ = 7.90−7.72 (m, 4H, Pc-H), 7.26−6.79 (m, 44H, Pc-H, Benzyl-H), 4.92 (s, 16H, CH$_2$). ^{13}C NMR spectrum of **ZnPc** showed 16 aromatic carbon atoms signals and 2 aliphatic carbon atoms signals. These signals were observed at (δ: ppm): 159.74, 156.45, 153.67, 152.45, 138.79, 136.62, 135.52, 132.90, 130.88, 129.23, 128.84, 124.88, 124.53, 120.68, 119.12, 110.24, 69.80, 68.21. In the ^{1}H NMR spectrum of **PbPc** complex, signals were observed at (δ: ppm): 7.92−7.36 (m, 4H, Pc-H), 7.28−7.12 (m, 44H, Pc-H, Benzyl-H), 4.86 (s, 16H, CH$_2$-O). The new signals were observed at (δ: ppm): 160.74, 158.72, 154.45, 138.52, 136.74, 135.90, 133.56, 131.23, 128.84, 125.88, 124.53, 123.68, 122.80, 120.61, 119.72, 108.24, 69.80, 68.21 in the ^{13}C NMR spectrum of **PbPc**. The mass spectra of compounds **ZnPc** and **PbPc** exhibited intense peaks at (m/z): 1427 [M + H]$^+$ and 1570 [M + 2H]$^+$, respectively and confirmed the proposed structures.

3.2. Ground state electronic absorption and fluorescence spectra

The ground state electronic absorption spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes in different solvents except for **ZnPc** showed a little aggregation in toluene due to broadness in ~650 nm regions, Fig. 1 [38]. The metal-free phthalocyanine complex **H$_2$Pc** gives a doublet Q band in different solvents as a result of the D$_{2h}$ symmetry [38].

The Q band values of the studied phthalocyanine complexes in different solvents are given in Table 1. The Q bands of the lead phthalocyanine complex (**PbPc**) are red-shifted when compared to the corresponding metal-free (**H$_2$Pc**) and zinc (**ZnPc**) phthalocyanine complexes due to the effect of the lead atom as central atom (Table 1). The B-bands are broad due to the superimposition of the B$_1$ and B$_2$ bands in the 340−360 nm region [39].

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, complexed metal ions and temperature [40,41]. In this study, the aggregation behaviour of the phthalocyanine complexes (**H$_2$Pc**, **ZnPc** and **PbPc**) was investigated in different solvents (DMSO, DMF, toluene and THF), Fig. 1. While the metal-free phthalocyanine complex (**H$_2$Pc**) showed a little aggregation in DMSO, the zinc phthalocyanine complex (**ZnPc**) showed a little aggregation in toluene. Lead phthalocyanine complex (**PbPc**) did not show aggregation in all studied solvents. The aggregation behaviour of the studied phthalocyanine complexes (**H$_2$Pc**, **ZnPc** and **PbPc**) was also studied at different concentration in DMSO. In DMSO, as the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species for the metallated complexes (**ZnPc** and **PbPc**) (Fig. 2 as an example for complex **ZnPc**). The metal-free phthalocyanine complex (**H$_2$Pc**) was showed a little aggregation in DMSO. Beer−Lambert law was obeyed for metallated phthalocyanine complexes (**ZnPc** and **PbPc**) in the concentrations ranging from 1.4 × 10^{-5} to 4 × 10^{-6} M.
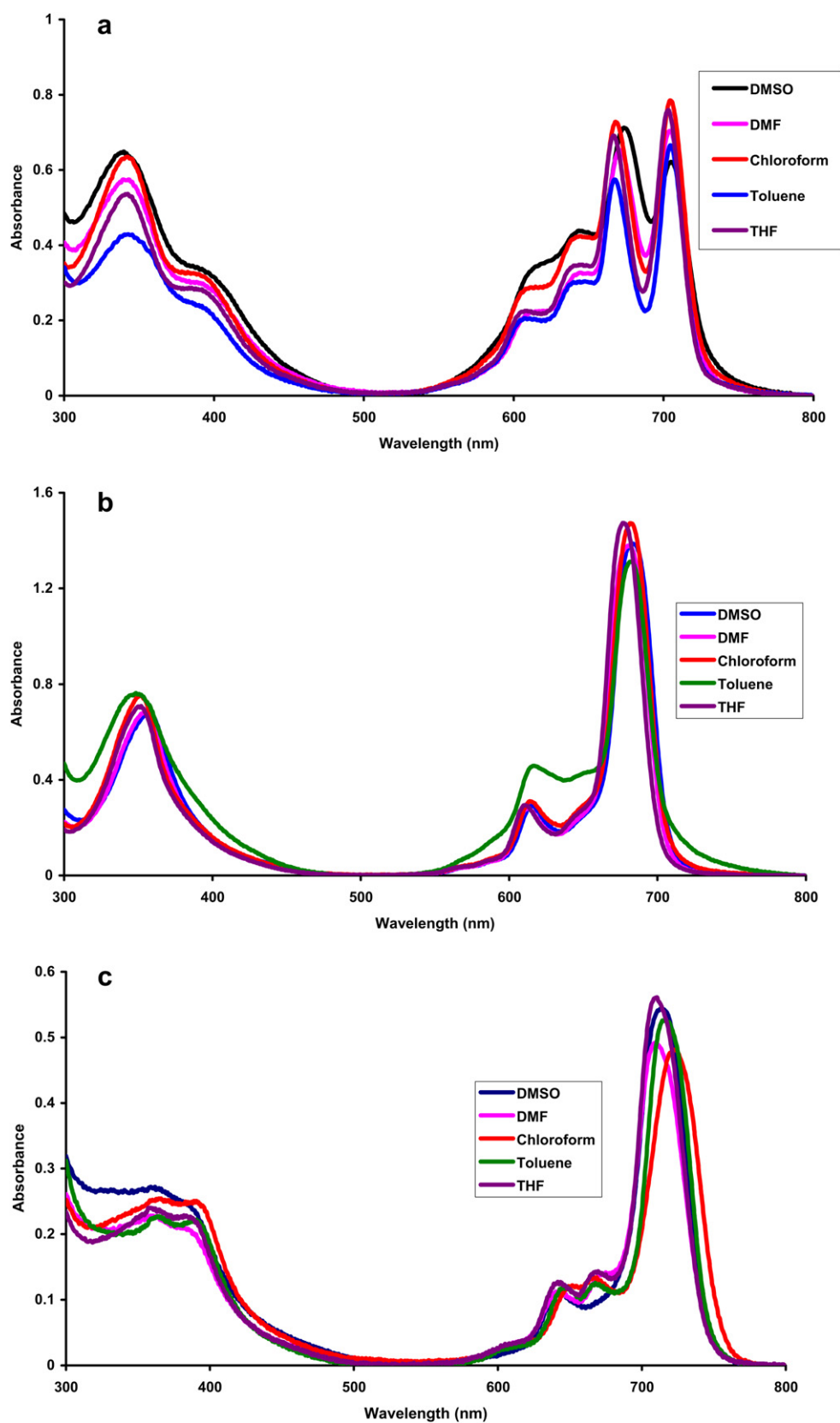
Fig. 1. Absorption spectra of: (a) **H₂Pc**; (b) **ZnPc** and (c) **PbPc** in different solvents. Concentration = 1.2×10^{-5} M.

Table 1
Absorption, excitation and emission spectral data for tetra substituted phthalocyanine complexes (H_2Pc, $ZnPc$ and $PbPc$) in different solvents.

Comp.	Solvent	Q band, λ_{max} (nm)	(log ε)	Excitation, λ_{Ex} (nm)	Emission, λ_{Em} (nm)	Stokes shift, Δ_{Stokes} (nm)
H_2Pc	DMSO	673, 705	4.33, 4.13	676, 708	715	10
	DMF	670, 702	4.58, 4.56	673, 707	711	9
	Toluene	667, 704	4.45, 4.41	668, 707	710	6
	THF	665, 702	4.65, 4.68	668, 705	709	7
$ZnPc$	DMSO	681	5.03	686	697	16
	DMF	678	5.03	679	692	14
	Toluene	681	4.68	682	691	10
	THF	678	5.16	679	689	10
$PbPc$	DMSO	712	4.85	676, 706	716	4
	DMF	710	4.64	672, 706	712	2
	Toluene	716	4.59	669, 706	718	2
	THF	707	4.79	669, 706	710	3
Std-ZnPc	DMSO	672[a]	5.14[a]	672[a]	682[a]	10[a]
	DMF	670[b]	5.37[b]	670[b]	676[b]	6[b]
	Toluene	672[c]	5.14[c]	672	676[d]	4[d]
	THF	666	5.19	666	673	7

[a] Ref. [19].
[b] Ref. [48].
[c] Ref. [23].
[d] Ref. [35].

The fluorescence behaviour of the phthalocyanine complexes was studied in different solvents. Fig. 3 shows the absorption, fluorescence emission and excitation spectra of the phthalocyanine complexes (H_2Pc, $ZnPc$ and $PbPc$) in DMF. The zinc phthalocyanine complex is more fluorescent than other studied phthalocyanine complexes. The lead phthalocyanine complex showed that lowest emission could be due to the larger lead metal being more displaced from the core of the Pc ring, and the displacement being more pronounced on excitation hence a loss of symmetry.

The shapes of the excitation spectra were similar to absorption spectra for the metal-free (H_2Pc) and zinc phthalocyanine ($ZnPc$) complexes (Fig. 3a and b) suggesting that the proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for phthalocyanines H_2Pc and $ZnPc$ suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation. For the lead phthalocyanine complex ($PbPc$), the shape of excitation spectra was different from the absorption spectra in that the Q band of the former showed two peaks in the Q band region, Fig. 3c, unlike the narrow Q band of the latter. This suggests that there are changes in the molecule following excitation most likely due to the larger lead metal being out of the plane of the phthalocyanine ring.

Fluorescence emission and excitation peaks in different solvents are listed in Table 1. While the observed Stokes shift of the substituted zinc phthalocyanine complex ($ZnPc$) is higher, the lead phthalocyanine complex ($PbPc$) is lower than standard $ZnPc$ (**Std-ZnPc**) (Table 1). The observed Stokes shift of metal-free phthalocyanine complex (H_2Pc) is similar for standard $ZnPc$ (**Std-ZnPc**) (Table 1).
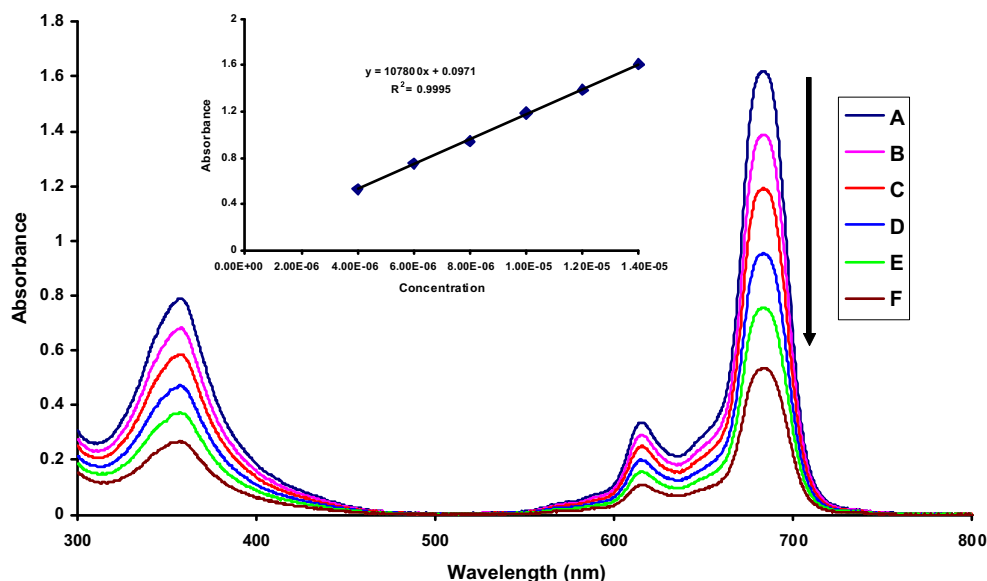

Fig. 2. Absorption spectra of **ZnPc** in DMSO at different concentrations. 14×10^{-6} M (A), 12×10^{-6} M (B), 10×10^{-6} M (C), 8×10^{-6} M (D), 6×10^{-6} M (E), 4×10^{-6} M (F) (Inset: Plot of absorbance versus concentration).
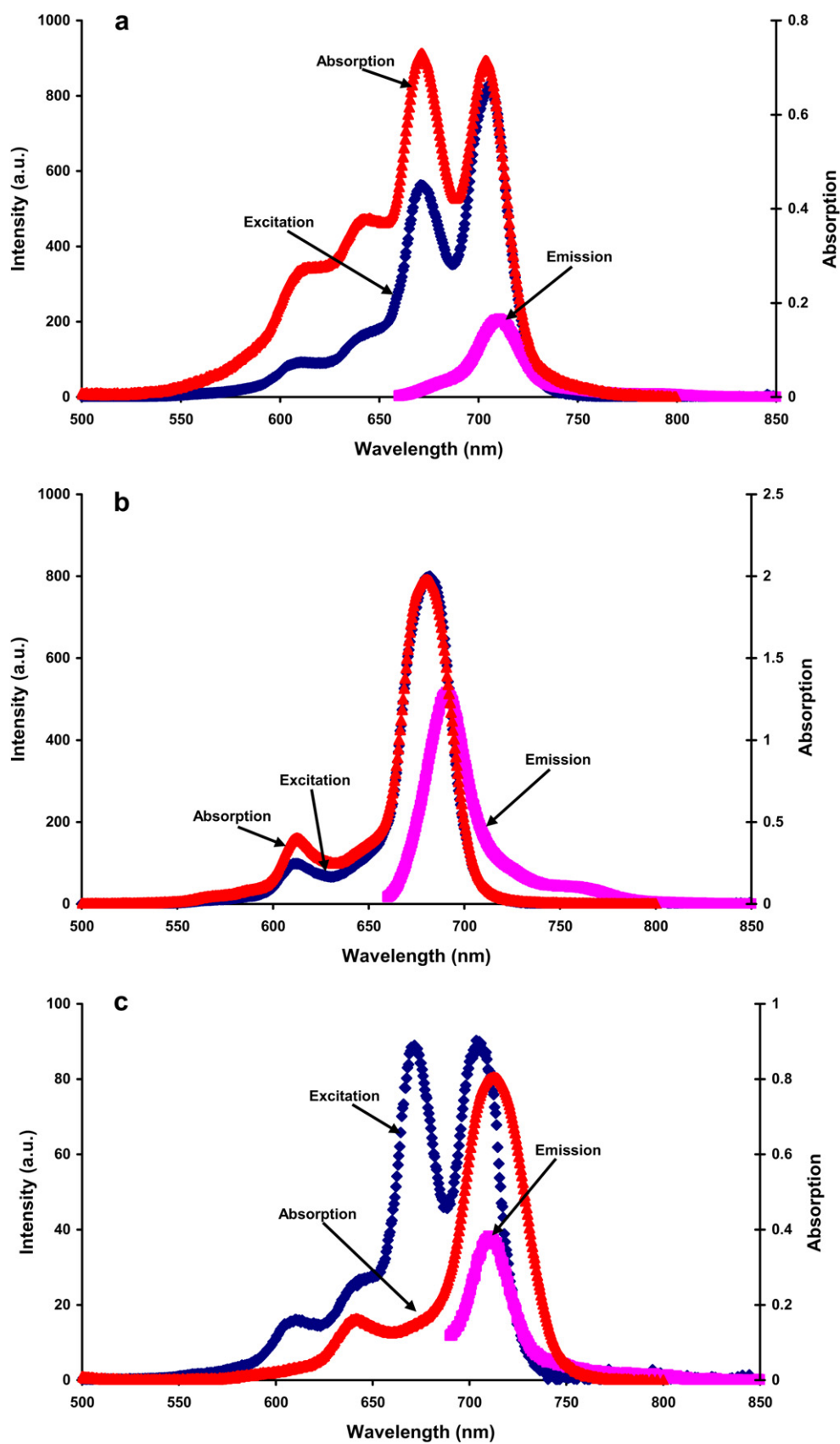
Fig. 3. Absorption, fluorescence emission and excitation spectra of (a) **H₂Pc**, (b) **ZnPc** and **PbPc** in DMF. Excitation wavelength = 650 nm for **H₂Pc** and **ZnPc**, 680 nm for **PbPc**.

Table 2
Photophysical and photochemical parameters of tetra substituted phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) in different solvents.

Comp.	Solvent	Φ_F	τ_F (ns)	τ_0 (ns)	k_F[a] (s^{-1}) ($\times 10^7$)	Φ_d ($\times 10^{-3}$)	Φ_Δ
H₂Pc	DMSO	0.21	8.12	42.75	2.34	0.34	0.34
	DMF	0.32	7.27	22.71	4.40	1.14	0.28
	Toluene	0.30	9.40	31.33	3.19	0.69	0.49
	THF	0.35	7.19	20.55	4.86	0.01	0.43
ZnPc	DMSO	0.19	2.40	11.42	8.75	0.009	0.74
	DMF	0.29	3.56	12.28	8.14	0.19	0.65
	Toluene	0.20	5.19	25.96	3.85	0.74	0.79
	THF	0.22	1.95	8.89	11.23	0.008	0.46
PbPc	DMSO	0.043	0.64	15.08	6.63	1.92	0.16
	DMF	0.063	1.75	27.79	3.59	29.32	0.55
	Toluene	0.24	6.26	26.08	3.83	61.26	0.72
	THF	0.29	5.29	18.25	5.47	25.73	0.22
Std-ZnPc	DMSO	0.20[b]	1.22[c]	6.80[c]	1.47[c]	0.26[c]	0.67[c]
	DMF	0.17[d]	1.03[d]	6.05[d]	1.65[d]	0.023[d]	0.56[d]
	Toluene	0.07[e]	0.90[d]	12.97[d]	7.70[d]	0.062[f]	0.58[e]
	THF	0.25	2.72	10.90	9.17	0.002	0.53[g]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F / \tau_F$.
[b] Ref. [29].
[c] Ref. [19].
[d] Ref. [48].
[e] Ref. [35].
[f] Ref. [22].
[g] Ref. [36].

3.3. Photophysical properties

3.3.1. Fluorescence lifetimes and quantum yields

The fluorescence quantum yields (Φ_F) of phthalocyanine complexes **H₂Pc**, **ZnPc** and **PbPc** are typical of MPc complexes in different solvents, but the Φ_F values of **PbPc** in DMSO and DMF are lower than for the **Std-ZnPc** (Table 2) suggesting that there are more changes in the molecule following excitation in DMSO and DMF for complex **PbPc** most likely due to the larger lead metal being out of the plane of the phthalocyanine ring. Generally, the Φ_F values of the substituted complexes are higher than **Std-ZnPc**. An increase in fluorescence intensity (hence yield) may occur in the presence of ligands which decreasing of the fluorescence quenching. Thus the increasing in the Φ_F value for substituted phthalocyanine complexes in the presence of the ring substituents suggests that the substituents less quench the excited singlet state, hence the fluorescence. The substituted **H₂Pc** complex shows larger Φ_F values in all studies solvents (Table 2). All phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) showed largest Φ_F values in THF among the studied solvents.

Fluorescence lifetime (τ_F) refers to the average time a molecule stays in its excited state before fluorescing, and its value is directly related to that of Φ_F; i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Any factor that shortens the fluorescence lifetime of a fluorophore indirectly reduces the value of Φ_F. Such factors include internal conversion and intersystem crossing. As a result, the nature and the environment of a fluorophore determine its fluorescence lifetime.

Lifetimes of fluorescence (τ_F, Table 2) were calculated using the Strickler–Berg equation. Using this equation, a good correlation has been [28] found between experimentally and the theoretically determined lifetimes for the unaggregated molecules as is the case in this work. Thus we suggest that the values obtained using this equation are an appropriate measure of fluorescence lifetimes. Generally, the τ_F values are within the range reported for MPc complexes [42]. τ_F values are higher for substituted complexes **H₂Pc**, **ZnPc** and **PbPc** when compared to **Std-ZnPc**, except for **PbPc** in DMSO (Table 2), again suggesting less quenching of fluorescence by the ring substituents. For the substituted complexes, longer τ_F values are obtained for the **H₂Pc** complex compared to other studied phthalocyanine complexes (**ZnPc** and **PbPb**).

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also given in Table 2. τ_0 values of the substituted phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) are higher than **Std-ZnPc** in all studied solvents except for complex **ZnPc** in THF. The substituted **H₂Pc** complex showed the highest τ_0 values in all studied solvents when compared to other substituted complexes (**ZnPc** and **PbPc**). There was no clear trend found for the rate constants for fluorescence (k_F) values among the substituted **H₂Pc**, **ZnPc** and **PbPc** complexes.
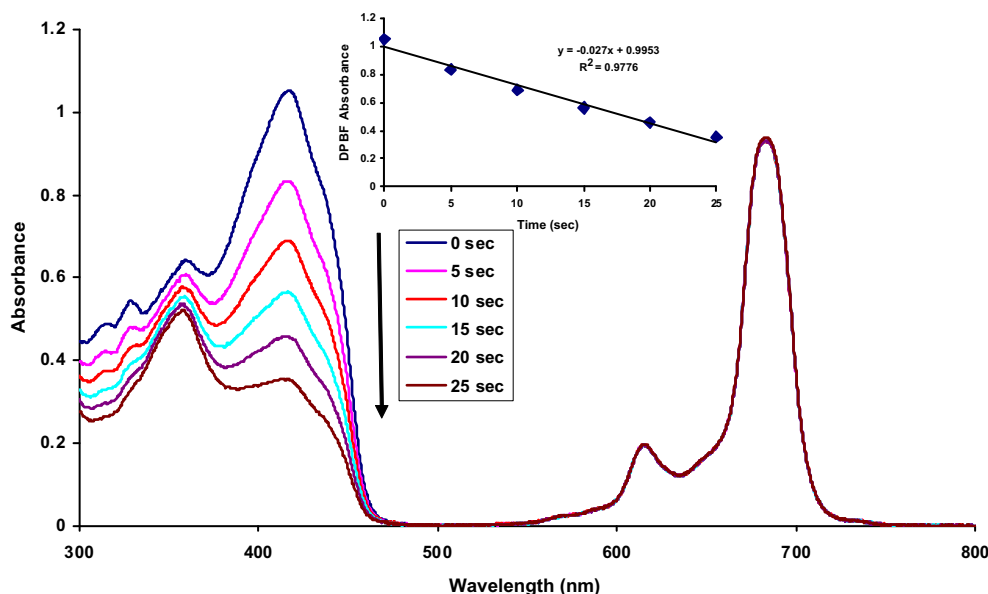

Fig. 4. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **ZnPc** in DMSO at a concentration of 1.2×10^{-5} M (Inset: Plots of DPBF absorbance versus time).

3.4. Photochemical properties

3.4.1. Singlet oxygen quantum yields

A good photosensitizer must be very efficient in generating singlet oxygen, the active species of a photodynamic therapy treatment. Energy transfer between the triplet state of a photosensitizer (such as phthalocyanines) and the ground state of molecular oxygen leads to the production of singlet oxygen and must be highly efficient to generate large amounts of singlet oxygen. This can be 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 (e.g. for Type II mechanism). In this study, Φ_Δ values of the substituted phthalocyanines (**H₂Pc**, **ZnPc** and **PbPc**) were determined in different solvents (DMSO, DMF, toluene and THF) using a chemical method. 1,3-Diphenylisobenzofuran (DPBF) used as a singlet oxygen quencher. The disappearance of DPBF absorbance was monitored using UV–Vis spectrophotometer (Fig. 4 as an example for **ZnPc** in DMSO).

Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including: triplet excited state energy, ability of substituents and solvents to quench the generated singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen. There was no decrease in the Q band or formation of new bands during Φ_Δ determinations (Fig. 4 as an example for **ZnPc** in DMSO): this indicates that the phthalocyanines are not degradated during singlet oxygen studies. It is believed that during photosensitization, the phthalocyanine is firstly excited to the singlet state and through intersystem crossing reaches the triplet state, then transfers its energy to ground state oxygen, $O_2(^3\Sigma_g)$, itself converted into its excited state (singlet oxygen), $O_2(^1\Delta_g)$. This singlet oxygen is the chief cytotoxic species, which subsequently oxidizes the surrounding substrates: this oxidation is the key of the Type II mechanism.

The values of Φ_Δ are higher for substituted **ZnPc** complex when compared to respective **Std-ZnPc** complex in all studied solvents except for THF. The Φ_Δ values of substituted **H₂Pc** and **PbPc** are lower than **Std-ZnPc** in all studied solvents except for complex **PbPc** in toluene (Table 2). When compared to the Φ_Δ values among the substituted complexes (**H₂Pc**, **ZnPc** and **PbPc**), substituted **ZnPc** complex shows highest Φ_Δ values in all studied complexes.
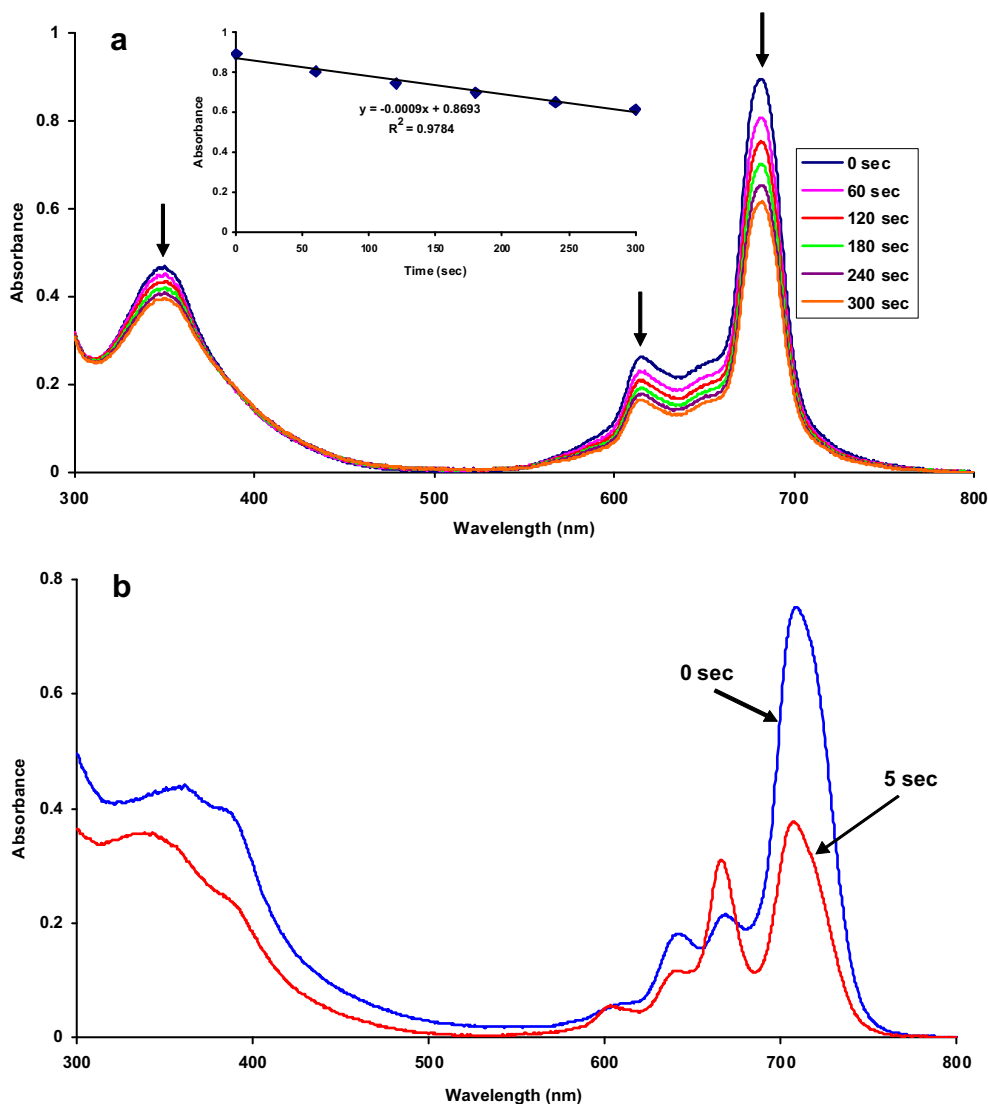

Fig. 5. The photodegradation of compound: (a) **ZnPc** in toluene (b) **PbPc** in THF showing the disappearance of the Q-band at sixty seconds intervals for **ZnPc** and five seconds intervals for **PbPc** (Inset: Plot of Q band absorbance versus time for **ZnPc** in toluene).
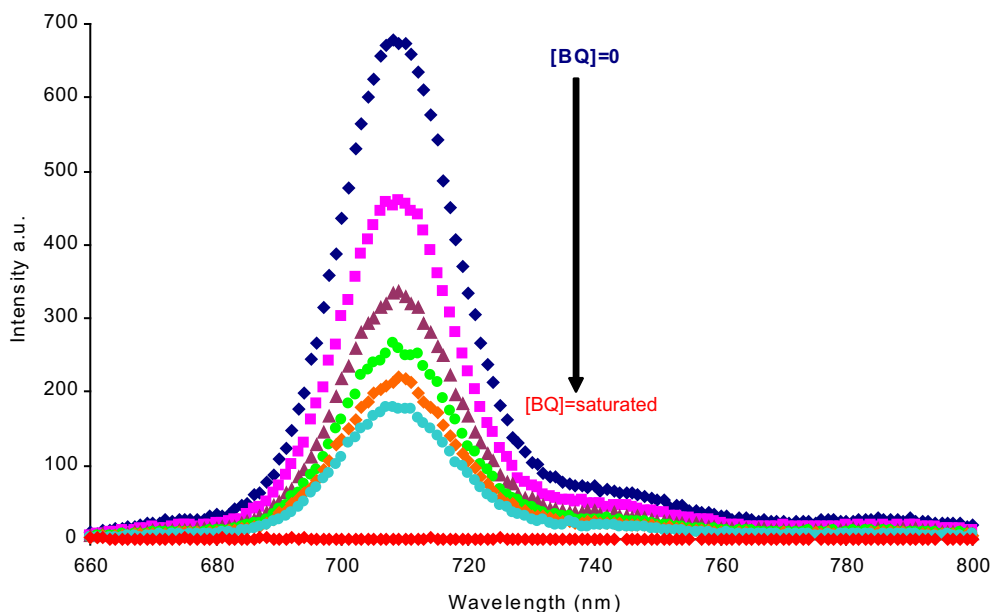
Fig. 6. Fluorescence emission spectral changes of **H₂Pc** (1.00×10^{-5} M) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M and saturated with BQ.

The Φ_{Δ} values of the substituted complexes are higher in toluene than other studied solvents.

3.4.2. Photodegradation studies

Degradation of the molecules under irradiation can be used to study their stability and this is important for their application as photocatalysts (such as photosensitizers). Photodegradation is the oxidative degradation of a photosensitizer molecule with time into lower molecular weight fragments under light [34]. Photodegradation generally depends on the structure of the molecule, concentration, solvent and light intensity. It is believed that photodegradation is a singlet oxygen mediated process, since singlet oxygen is highly reactive and it can react with phthalocyanines [17]. Generally, phthalimide residue was found to be the photooxidation product following degradation of phthalocyanines [43].

The spectral changes observed for all the complexes (**H₂Pc**, **ZnPc** and **PbPc**) during irradiation are as shown in Fig. 5 (using complex **ZnPc** in toluene and complex **PbPc** in THF as examples). The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation for complexes **H₂Pc** and **ZnPc** (Fig. 5a as an example for complex **ZnPc** in toluene). For substituted **PbPc** complex, the shape of the absorption spectra changed during the photodegradation studies in all studied solvents (Fig. 5b as an example for complex **PbPc** in THF). The single narrow Q band of the **PbPc** split two bands during photodegradation under light irradiation. This suggests that there are changes in the molecule following photodegradation most likely due to the larger lead metal being out of the plane of the phthalocyanine ring.

The photodegradation quantum yield (Φ_d) values of the phthalocyanine complexes in different solvents are given in Table 2. Stable phthalocyanine molecules show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [42]. While the substituted **H₂Pc** and **ZnPc** complexes have an intermediate photostability, the substituted **PbPc** is less stable than other studied phthalocyanine complexes.

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

The fluorescence quenching of substituted phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) by BQ in different solvents was found to obey Stern–Volmer kinetics. Fig. 6 shows the quenching of **H₂Pc** complex by BQ in toluene as an example. The slope of the plots shown at Fig. 7 gave K_{SV} values. The Stern–Volmer plots for all studied complexes (**H₂Pc**, **ZnPc** and **PbPc**) gave straight lines, depicting diffusion-controlled quenching mechanisms. Quinones have high electron affinities, and their involvement in electron transfer processes is well documented [44]. The energy of the lowest excited state for quinones is greater than the energy of the excited singlet state of MPc complexes [45], hence, energy transfer from the excited MPc to BQ is not likely to occur. Moreover, MPcs are known to be easily reduced. Therefore MPc fluorescence quenching by BQ is via excited state electron transfer, from the MPc to the BQ [46]. The K_{SV} and bimolecular quenching constant (k_q) values for the BQ quenching of phthalocyanine complexes in different solvents are listed in Table 3. The K_{SV} values of the substituted phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) are lower than **Std-ZnPc** in all studied solvents. When compared the substituted complexes, **H₂Pc** complex showed the highest K_{SV} values, while complex **PbPc** showed the lowest K_{SV} values in all studied solvents. The substitution with 4-benzyloxybenzoxy group seems to decrease the K_{SV} values of the complexes. The order of K_{SV} values for substituted complexes among the studied solvents was as follows: toluene > THF > DMF > DMSO. In different solvents, the K_{SV} values for BQ quenching of phthalocyanine complexes vary directly with the solvents' polarity. The bimolecular quenching constant (k_q) values of the substituted phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) were also lower than for **Std-ZnPc** in studied solvents except for **ZnPc** complex in THF, thus substitution with 4-benzyloxybenzoxy group seems to decrease the k_q values of the complexes. The k_q values were found to be close to the diffusion-controlled limits, $\sim 10^{10}$ M^{-1} s^{-1}, which is in agreement with the Einstein–Smoluchowski approximation at room temperature for diffusion-controlled bimolecular interactions [47].
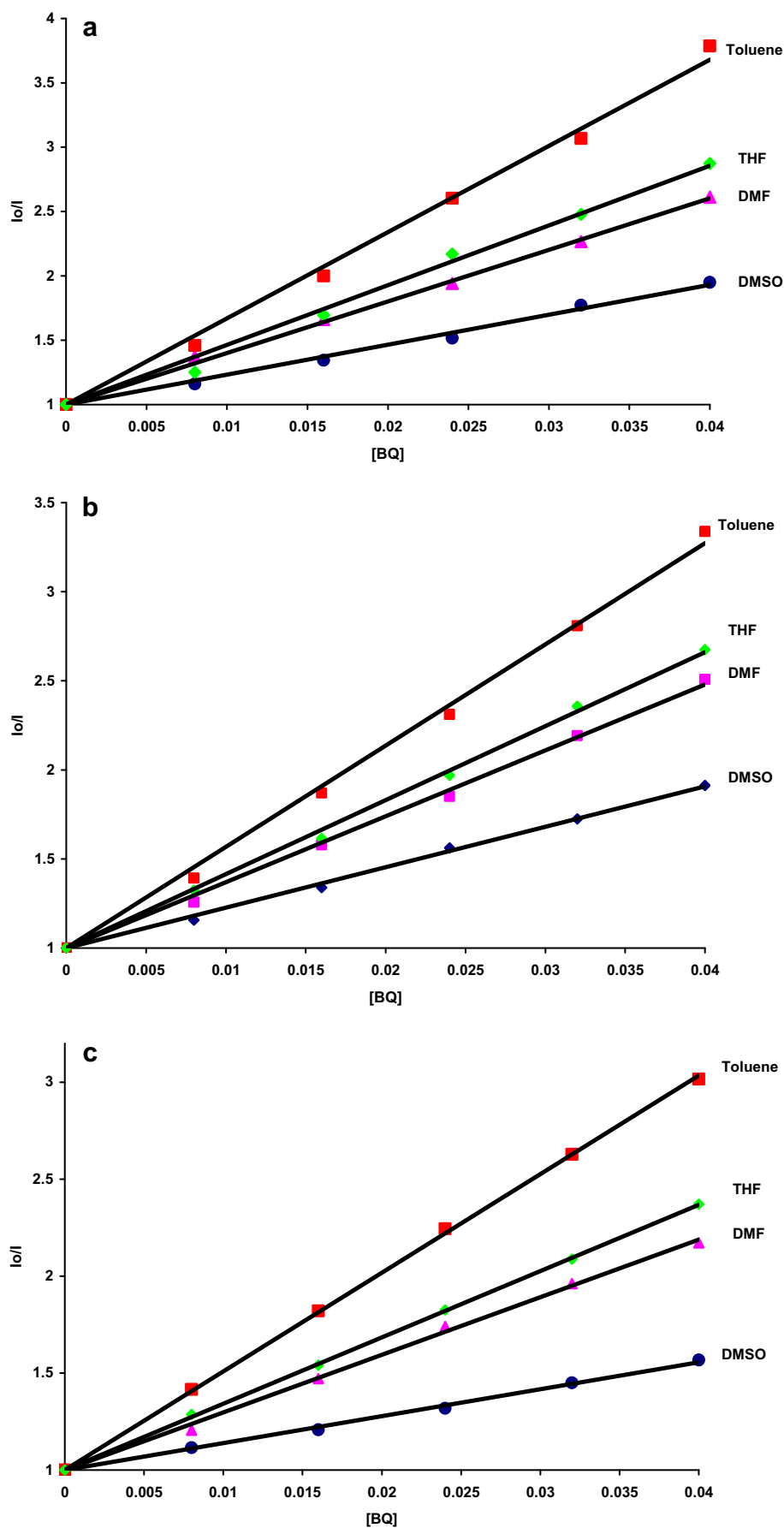
Fig. 7. Stern–Volmer plots for benzoquinone (BQ) quenching of substituted phthalocyanine complexes in different solvents (a) for **H₂Pc** (b) for **ZnPc** and for **PbPc**. [MPc] ∼ 1.00×10^{-5} M. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M in all studied solvents.

Table 3
Fluorescence quenching data for tetra substituted phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) in different solvents.

Comp.	Solvent	K_{SV} (M^{-1})	$k_q/10^{10}$ (M^{-1} s^{-1})
H₂Pc	DMSO	23.26	0.28
	DMF	40.10	0.55
	Toluene	60.38	0.71
	THF	46.42	0.64
ZnPc	DMSO	22.70	0.94
	DMF	36.99	1.04
	Toluene	56.82	1.09
	THF	41.52	2.13
PbPc	DMSO	13.69	2.13
	DMF	32.19	1.84
	Toluene	50.51	0.81
	THF	33.37	0.63
Std-ZnPc	DMSO	31.90[a]	2.61[a]
	DMF	57.60[b]	5.59[b]
	Toluene	61.53[c]	2.19[c]
	THF	48.48	1.78

[a] Ref. [19].
[b] Ref. [48].
[c] Ref. [22].

4. Conclusions

In the presented work, the syntheses of new peripherally tetra-4-benzyloxybenzoxy substituted metal-free (**H₂Pc**), zinc (**ZnPc**) and lead (**PbPc**) phthalocyanines were described and the compounds were characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy, electronic spectroscopy and mass spectrometry. The photophysical and photochemical properties of these phthalocyanine complexes (**H₂Pc**, **ZnPc** and **PbPc**) were also described in different solvents (DMSO, DMF, toluene and THF) for comparison. All the compounds are soluble in most solvents such as chloroform, toluene, DMSO etc. In solution, the absorption spectra showed monomeric behaviour evidenced by a single (narrow) Q band, for **ZnPc** and **PbPc** in different solvents typical of metallated phthalocyanine complexes except for **ZnPc** in toluene. The metal-free phthalocyanine complex **H₂Pc** showed a doublet Q band in different solvents. The substitution of the 4-benzyloxybenzoxy substituents on the phthalocyanine ring increased the wavelength of the Q band. The fluorescence behaviour of the phthalocyanine complexes was studied in different solvents. The zinc phthalocyanine complex is more fluorescent than other studied phthalocyanine complexes. The lead phthalocyanine complex showed that lowest emission could be due to the larger lead metal ion. Generally, the Φ_F values of the substituted complexes are higher than **Std-ZnPc**. The substituted complexes (**H₂Pc**, **ZnPc** and **PbPc**) have good singlet oxygen quantum yields (Φ_Δ), especially complex **ZnPc** results in the highest values. The value of Φ_Δ ranged from 0.16 (for complex **PbPc** in DMSO) to 0.79 (for complex **ZnPc** in toluene) gives an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism). While the substituted **H₂Pc** and **ZnPc** complexes showed similar stability, the substituted **PbPc** is less stable than other studied phthalocyanine complexes most likely due to the larger lead metal being out of the plane of the phthalocyanine ring during photodegradation studies. The substituted complexes showed lower K_{SV} values when compared to the **Std-ZnPc** in all studied solvents.

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