Dyes and Pigments 95 (2012) 280–289

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A novel phthalocyanine conjugated with four salicylideneimino complexes: Photophysics and fluorescence quenching studies

Gülşah Gümrükçü [a,*], Gülnur Keser Karaoğlan [a], Ali Erdoğmuş [a], Ahmet Gül [b,**], Ulvi Avcıata [a]

[a] Department of Chemistry, Technical University of Yildiz, Davutpasa, Istanbul 34210, Turkey
[b] Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul 34469, Turkey

ARTICLE INFO

Article history:
Received 11 November 2011
Received in revised form
27 April 2012
Accepted 9 May 2012
Available online 24 May 2012

Keywords:
Phthalocyanine
Schiff base complex
8-Hydroxyquinoline
Salicylaldimine
Photophysics
Fluorescence quenching

ABSTRACT

A novel phthalocyanine with four salicylideneimino ligating groups directly conjugated to the macrocyclic core has been synthesized by the condensation of tetramino-phthalocyanine with salicylaldehyde. Complexation on the periphery to obtain pentanuclear complex has been accomplished either directly through the reaction of this phthalocyanine, 8-hydroxyquinoline as the second ON donor ligand and zinc (II) salt or zinc (II) complex of 8-hydroxyquinoline has been isolated first and then it has been reacted with the phthalocyanine carrying salicylideneimino ligating groups. Also a new mixed ligand Schiff base complex of Zn (II) as a model containing salicylaldimine ligand and 8-hydroxyquinoline has been synthesized to compare with the complex. The new compounds have been characterized by elemental analysis FTIR, ^{1}H NMR, UV–Vis spectroscopy and mass spectrometry. General trends are described for fluorescence lifetimes and fluorescence of these compounds in dimethylsulfoxide, dimethylformamide and tetrahydrofurane. The solvent effect on the photophysical parameters of the zinc (II) phthalocyanines and the model zinc (II) complex is also studied. The fluorescence of the substituted zinc (II) phthalocyanine complexes is effectively quenched by 1,4-benzoquinone (BQ) in these solvents.

1. Introduction

The design of novel substituted phthalocyanines (Pcs) closely follows the requirements of their intended applications [1]. The increasing importance and use of phthalocyanines as advanced materials have created impetus for design variables of the central metal ion and peripheral substituents to reach the desired properties [2]. Phthalocyanines are used in a number of applications in many areas such as in medicinal and material science due to their increased stability, architectural flexibility, diverse coordination properties and improved spectroscopic characteristics [3]. The interesting properties of Pcs are the presence of a highly conjugated π-electron system, intense absorption in the red/near-IR (Q band) region [4], capability to exhibit changeable conductivity and photocatalytic effects [5,6]. Some technological applications in fields such as chemical sensors [7], liquid crystals [8], semiconductors [9], non-linear optics [10] and photosensitizers in photodynamic therapy (PDT) [11] have shown the increased importance of these intensely colored macrocyclic compounds. The metallophthalocyanines (MPcs) can be modulated in a number of ways by changing the peripheral or non-peripheral substitution on the Pc ring in addition to changing the central metal ion and the axial ligands [12].

Over the last decade, a substantial number of phthalocyanine-based photosensitizing agents for PDT have been prepared and evaluated for their photodynamic activity with the focus being on silicon, zinc and aluminum analogs as a result of their desirable photophysical properties [13] and their applications for the detection and cure of tumors are under investigation [14].

Coordination compounds from ligand systems capable of binding multiple metal centers are of importance due to their physical properties being totally different than mononuclear systems. One strategy for the design of multimetallic systems has involved the use of polynucleating macrocyclic ligands [15] and, in particular, much work has been devoted to the synthesis of porphyrins [16] and phthalocyanines [17] that have been functionalized with appendages capable of coordinating metal ions as well. Several different approaches in designing polynucleating porphyrins and phthalocyanines have emerged. These include meso substitution with ferrocenes [18] or crown ethers [19] as well as substitution with metal-ion-coordinating pendant-arms and basket-handles [20]. There are also examples of

---

* Corresponding author.
** Corresponding author.
E-mail addresses: gumrukcugulsah@hotmail.com (G. Gümrükçü), ahmetg@itu.edu.tr (A. Gül).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2012.05.005

meso-tetrapyridylporphyrins that coordinate metal ions peripherally *via* the pyridyl groups [21]. However, for most of these complexes, the extent of electronic interaction between metal sites is quite low.

In a recent review, π- conjugated salen systems have been reported and the related conjugated multi-salphen structures might be considered as complementary systems to phthalocyanines with excellent building block potential [22]. Recently, we have reported Pcs with unsaturated cinnamaldimine moieties attached to the inner core through phenoxy-bridges [23] and a new water-soluble tetra-cationic zinc phthalocyanine [24] which contains four conjugated Schiff's base groups at the peripheral positions. In the present study, we are combining the completely planar 18 π-electron system of aromatic phthalocyanine core with salicylideneimino groups to enhance conjugation. We start with the synthesis of a zinc (II) phthalocyanine containing salicylideneimino moieties on the periphery and subsequently, complexation of its Schiff's base groups with zinc (II) ions in the presence of a second ON donor ligand, 8-hydroxy-quinoline (**4**), pentanuclear zinc (II) complex is isolated. A model compound has been also prepared.

2. Experimental

2.1. Instruments and chemicals

All chemicals used were of reagent grade quality. The solvents were dried over molecular sieves (4 Å). 4-Nitrophthalonitrile, [2,9,16,23-tetra-(4-nitro)-phthtalocyaninatozinc(II)] (**npc**), [2,9,16,23-tetra-(4-amino)-phthtalocyaninatozinc(II)] (**1**) and 2-[(E)-(phenylimino)methyl]-phenol (**8**) were synthesized according to the methods described previously in the literature, respectively [14,23,25,26]. The compounds **2**, **4** and **7** were used as supplied commercially. All reactions were carried out under dry argon atmosphere unless otherwise noted. Column chromatography was performed on silica gel 60 (Merck, 0.040–0.063 mm) for purification of the complexes. The progress of the reactions and the homogeneity of the products were monitored in each step by TLC (SiO_2). IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer; electronic spectra in the UV–Vis region were recorded with an Agilent 8453 UV/Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. ^1H NMR spectra were recorded in *d*-tetrahydrofuran on a Varian UNITY INOVA 500 MHz spectrophotometer using TMS as internal reference. Mass spectra were performed on a Bruker microflex LT MALDI-TOF MS. Melting points were determined on an Electrothermal Gallenkamp apparatus. Elemental analyses were performed on a Thermo Flash EA 1112.

2.2. Synthesis

2.2.1. [2,9,16,23-tetra-(salicylaldimino)phthtalocyaninatozinc(II)] (*3*)

A solution of **1** (150.4 mg, 0.236 mmol) in dry THF (10 mL) was added dropwise to a solution of salicylaldehyde (**2**) (115.2 mg, 0.943 mmol) in dry THF (5 mL) and the mixture was heated under reflux under argon for 20 h. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The product was separated by filtration as a green solid. The precipitate was washed successively with cold water, methanol and ethanol to remove the unreacted starting materials and dried *in vacuo*. The dark green product was isolated from the crude residue by column chromatography over silica gel using $CHCl_3$: THF (1:10, v/v) as eluent. Compound **3** is fairly soluble in THF, acetone, DMF, DMSO and $CHCl_3$. Yield: 86 mg (35%); m.p. > 200 °C. FTIR υ_{max}/cm^{-1}: 3430 (Ar–OH, m), 3058 (Ar–H, w), 2921–2840 (–CH, m), 1619 (–N=C, s), 1568, 1490 (Ar C=C); ^1H NMR (DMSO-d_6) δ, ppm: 13.56 (s, 4H, –OH, D-exchangeable), 8.90 (s, 4H, –N=CH), 9.42, 8.51–7.01 (m, 28H, Ar–H); UV–Vis (THF): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 694 (5.08), 629 (4.48), 356 (4.88); (DMF): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 698 (5.06), 632 (4.46), 361 (4.86); (DMSO): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 702 (5.06), 637 (4.50), 361 (4.89); Anal. Calc. for $C_{60}H_{36}N_{12}O_4Zn$ (1054.4148 g/mol): C, 68.35; H, 3.44; N, 15.94; Found: C, 68.11; H, 3.02; N, 15.70; MS (MALDI-TOF): *m*/*z* (100%) 1054.607 $[M]^+$, 844.51 $[M-(C_7H_6NO)-(C_6H_5O)]^+$, 916.59 $[M\text{-}4OH\text{-}(C_6H_5)+2H]^+$, 948 $[M-(C_7H_6O)-2H]^+$, 1018 $[M-2OH-4H]^+$.

2.2.2. Chloroaqua-8-hydroxyquinolinatozinc(II) (*6*)

$ZnCl_2$ (93.7 mg, 0.69 mmol) in ethanol (10 mL) was added to a solution of 8-hydroxyquinoline (100 mg, 0.69 mmol) in ethanol (20 mL). The resulting reaction mixture was stirred under reflux for 4 h under a nitrogen atmosphere. During this time a solid precipitated formed. The reaction mixture was cooled to room temperature and the precipitate was isolated by vacuum filtration and washed with water and ethanol. Yield: 85 mg (47%); m.p. 290 °C (dec). FTIR υ_{max}/cm^{-1}: 3432–3352 (H_2O, br), 3049 (Ar–H, w), 1578 (–N=CH, s), 1498, 1463, (Ar C=C), 1378, 1316, 1271, 1107 (ph C–O, s), 821, 732. ^1H NMR (DMSO-d_6) δ, ppm: 8.80–6.20 (m, 6H, Ar–H), 3.50 (broad, s, 2H, $-OH_2$), UV–Vis (DMSO): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 323 (3.94), 398 (3.64); Anal. Calc. for $C_9H_8ClNO_2Zn$ (263.0279 g/mol): C, 41.10; H, 3.07; N, 5.32; Found: C, 41.24; H, 3.70; N, 5.26. ESI-MS $[M + H]^+$: 264.2418 *m*/*z* (100%).

2.2.3. [2,9,16,23-tetra-{8-hydroxyquinolinato-salicydenaminatozinc (II)} phthtalocyaninato-zinc (II)] (*5*)

2.2.3.1. Method I. Compound 3 (70 mg, 0.066 mmol) and 8-hydroxyquinoline (4) (38.6 mg, 0.264 mmol) were added successively with constant stirring to dry THF (15 mL). After complete dissolution, $Zn(CH_3COO)_2$ (0.048 mg, 0.264 mmol) was added and the mixture was heated under reflux for 24 h and then allowed to stand at room temperature under argon stream. The progress of the reaction was monitored by TLC. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The resulting precipitate was filtered, washed several times with 50% (v/v) ethanol-water to remove any traces of unreacted materials, then washed with methanol and ethanol and dried in a vacuum desiccator over anhydrous calcium chloride. Yield: 56 mg (45%); m.p. > 200 °C.

2.2.3.2. Method II. Compound **3** (60 mg, 0.057 mmol) and chloroaqua-8-hydroxyquinolinatozinc(II) (**6**) (59.9 mg, 0.228 mmol) were added successively with constant stirring to dry DMSO (20 mL) and the reaction mixture was stirred at 85 °C for 48 h under argon stream. The progress of the reaction was monitored by TLC. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The resulting precipitate was filtered, washed several times with water, ethanol and methanol to remove any traces of unreacted materials and dried in a vacuum desiccator over anhydrous calcium chloride. Yield: 42 mg (39%); m.p. > 200 °C.

The products obtained in both cases are identical and they are insoluble in most common organic solvents but soluble in THF, DMF and DMSO. FTIR υ_{max}/cm^{-1}: 3052 (Ar–H, w), 1604 (–N=CH, s), 1579, 1497, 1466 (Ar C=C), 1048, 940, 825, 743, 742; ^1H NMR (DMSO-d_6) δ, ppm: 8.65 (s, 4H, N=C–H), 8.95, 8.45–6.20 (m, 52H, Ar–H); UV–Vis (THF): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 705 (5.11), 640 (4.75), 347 (5.02); (DMF): λ_{max}/nm (–log ε, L. mol^{-1} cm^{-1}): 715 (5.12), 649 (4.78), 352 (5.02); (DMSO): λ_{max}/nm (–log ε, L.

mol^{-1} cm^{-1}): 724 (5.10), 656 (4.81), 354 (5.02); Anal. Calc. for $C_{96}H_{56}N_{16}O_8Zn_5$ (1888.6192 g/mol): C, 61.05; H, 2.99; N, 11.87; Found: C, 61.93; H, 3.02; N, 11.25; MS (MALDI-TOF): *m*/*z* (100%) 1911.475 [M + Na]$^+$.

2.2.4. Synthesis of mononuclear model mixed ligand schiff base complex (9)

A methanolic solution of salicylideneiminobenzene (**8**) (100 mg, 0.51 mmol) was mixed with a methanolic solution of 8-hydroxyquinoline (**4**) (73.6 mg, 0.51 mmol). Subsequently, a methanolic solution of the $ZnCl_2$ (69 mg, 0.51 mmol) was added dropwise with stirring; the mixture was heated under reflux for 4 h under an argon atmosphere and then left to cool at room temperature. The resulting precipitate was filtered, washed several times methanol–water {50% (v/v)} to remove any traces of unreacted materials, then washed with diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride. The product is insoluble in common organic solvents but soluble in DMF and DMSO. Yield: 150 mg (73%); m.p. 290 °C (dec). FTIR υ_{max}/cm^{-1} 3055 (Ar–H, w), 1601 (–N=CH, s), 1579, 1497, 1466 (Ar C=C), 1107 (ph C–O, s), 1036, 822, 786, 745, 731. ^{1}H NMR (DMSO-d_6) δ, ppm: 8.71 (dd, 1H, –N=CH), 8.42–6.43 (m, 15H, Ar–H); UV–Vis (DMSO): λ_{max}/nm (log ε, L. mol^{-1} cm^{-1}): 281 (2.36), 338 (2,98), 400 (2.87); Anal. Calc. for $C_{22}H_{16}N_2O_2Zn$ (405.7836 g/mol): C, 65.12; H, 3.97; N, 6.90; Found: C, 65.39; H, 3.74; N, 6.89. ESI-MS [M + H]$^+$: 406.633 *m*/*z* (100%).

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] using unsubstituted ZnPc ($\Phi_F = 0.20$ in DMSO) [28] as the standard.

$$\Phi F = \Phi F(\mathrm{Std}) \frac{F \cdot A_{\mathrm{Std}} \cdot n^2}{F_{\mathrm{Std}} \cdot A \cdot n^2_{\mathrm{Std}}} \qquad (1)$$

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program which uses the Strickler–Berg equation [29]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

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

2.3.2. Fluorescence quenching by benzoquinone (BQ)

Fluorescence quenching experiments on the substituted zinc phthalocyanine derivatives (**3** and **5**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complexes, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 mol dm^{-3}. The fluorescence spectra of substituted zinc phthalocyanine derivatives (**3** and **5**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [30] was shown in Eq. (3):

$$\frac{I_0}{I} = 1 + K_{SV}[\mathrm{BQ}] \qquad (3)$$

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. (4).

$$K_{SV} = k_q \cdot \tau_F \qquad (4)$$

The ratios of I_0/I were calculated and plotted against [BQ] according to Eq. (3), and K_{SV} is determined from the slope.

3. Results and discussions

3.1. Synthesis and characterization

A novel pentanuclear metallo phthalocyanine (M = Zn) containing four additional Schiff base complexes of Zn(II) at the peripheral positions was synthesized through a multistep reaction sequence. Starting from 4-nitrophthalonile [25], tetranitrophthalocyanine [14,31,32] and tetraamino- phthalocyanine (**1**) [23,24] the steps are those to reach the precursor for the Schiff's base. A new phthalocyanine with four salicylideneimino moieties (**3**) has been obtained from the reaction of **1** with salicylaldehyde. Complexation on the periphery to obtain the pentanuclear complex (**5**) has been accomplished either directly through the reaction of this phthalocyanine and 8-hydroxyquinoline (**4**) as the second ON donor ligand and zinc (II) salt or from the previously prepared zinc (II) complex of 8-hydroxyquinoline and then reaction with the phthalocyanine carrying salicylideneimino donor sites (Fig. 1). The phthalocyanine (**3**) involving Schiff base ligands at the peripheral positions was obtained by the reaction of compound (**1**) and salicylaldehyde (**2**) in the presence of THF in 35% yield. Product **3** was separated by column chromatography on silica gel using $CHCl_3$: THF (1:10, v/v) as the eluent. In the first method to reach the pentanuclear compound (**5**), interaction of the metal ion with salicylaldimino- substituted phthalocyanine (**3**) and 8-hydroxyquinoline (**4**) in 4: 1: 4 M ratios resulted with the desired product **5** in 45% yield. Pc **5** was purified by successive treatment with various solvents such as 50% (v/v) ethanol-water, chloroform, dichloromethane, ethyl acetate, ethanol and methanol. In the second method, a mononuclear Zn (II) complex of 8-hydroxyquinoline (**6**) was prepared and it was subsequently reacted with salicylaldimino- substituted phthalocyanine (**3**) to yield the desired complex **5** in 39% yield (Fig. 1). It was observed that all the analytical and spectral data for these two products are exactly the same and the yields are comparable. Although the obvious features of the novel Pc **3** have been high solubility in common organic solvents, e.g. chloroform, acetone, DCM, THF, DMF and DMSO, **5** is only soluble to a certain extent only in THF, DMF and DMSO.

Also a new mixed ligand Schiff base model complex (**9**) with bidentate NO donor 2-[(E)-(phenylimino)methyl]phenol (**8**), bidentate NO donor 8-hydroxyquinoline (**4**) ligands and zinc acetate salt was prepared in **73** % yield to compare with the pentanuclear complex **5**. The reaction steps for the synthesis of the mononuclear zinc (II) complex were given in Fig. 2.

The structures of **3**, **5**, **9** and **6** were characterized by FTIR, UV–Vis, ^{1}H NMR, ESI MS and MALDI-TOF MS spectroscopic methods, as well as by elemental analysis. All the analytical and spectral data are consistent with the predicted structures. In the IR-spectrum of **3**, the characteristic stretching vibrations are attributable to aromatic –CH at 3058 cm^{-1}, aliphatic –CH at 2958–2865 cm^{-1} and the characteristic Schiff's base stretching band appears at 1619 cm^{-1}. This intense band is assigned to the –C=N stretching frequency of ligand and is characterized for the azomethine moiety of most Schiff's base compounds. In the spectrum of **5**, stretching vibrations of aromatic CH groups was observed at 3052 cm^{-1}.

The broad stretching vibration at 3242 cm^{-1} due to O–H of the free 8-hydroxyquinoline (**4**) and 3502 cm^{-1}-3360 cm^{-1} belonging to Ar–OH of **3** were absent in the complex **5**, suggesting formation of the M–O bond with **4** and **3** [34]. Thus, 8-hydroxyquinolate in these complexes is a monobasic bidentate chelating ligand. The IR-spectrum of **4** shows a strong band at 1586 cm^{-1} due to stretching of the C=N [35]. This band shifted to 1579 cm^{-1} on coordination for **5** suggesting that the lone pair on nitrogen is involved in formation of a bond with the metal. Coordination of the salicylaldimine

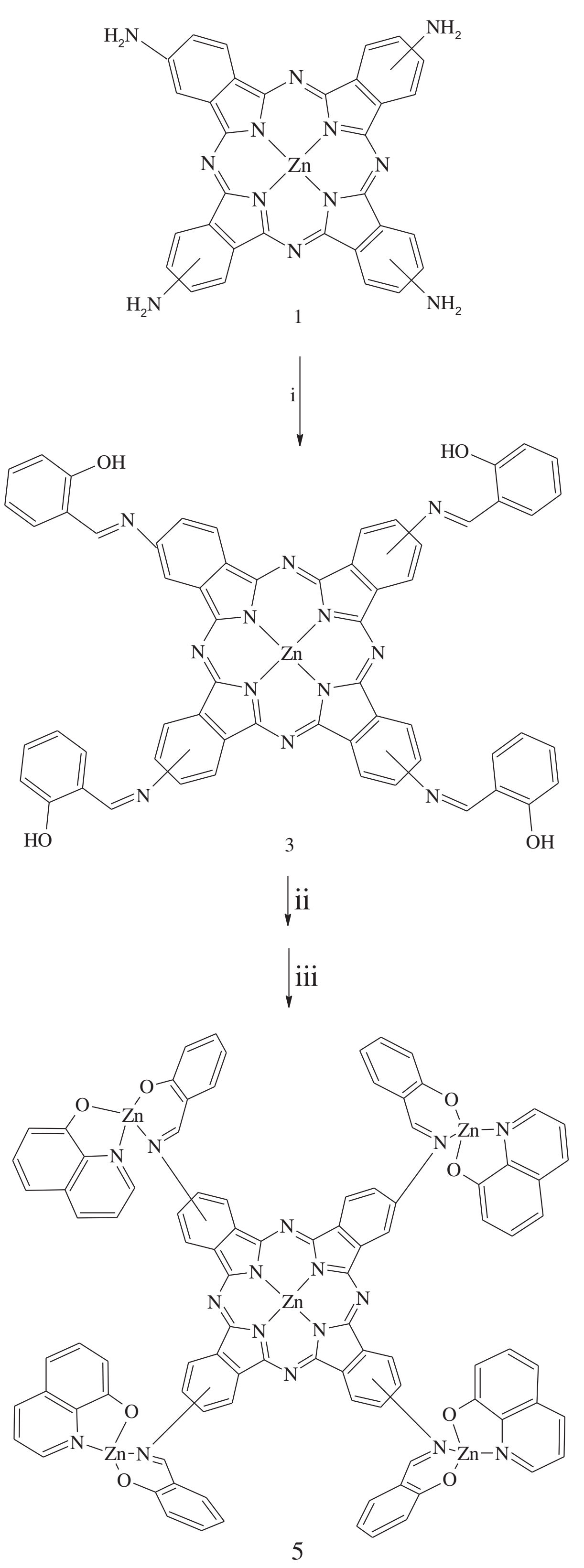

Fig. 1. Synthesis of Pcs **1**, **3** and **5**; (i) salicylaldehyde, THF, reflux; (ii) *Method I*:8-hydroxyquinoline, THF, $Zn(OAc)_2$, reflux; (iii) *Method II*: chloroaqua-8-hydroxyquinolinatozinc(II), DMSO, 85 °C, 48 h.

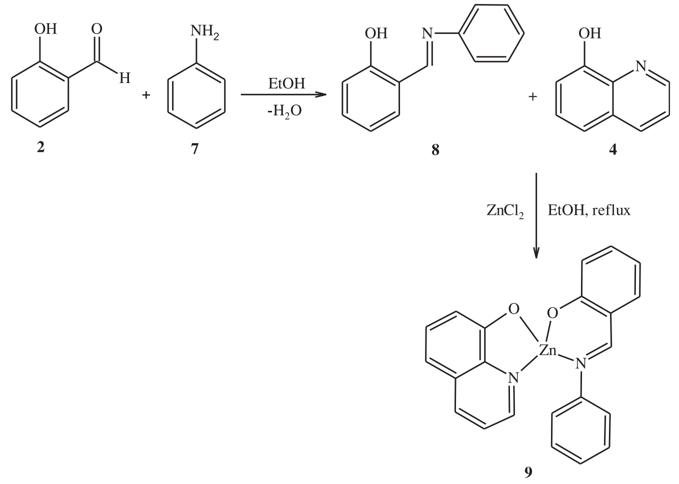

Fig. 2. Synthesis of mononuclear mixed ligand complex.

ligands to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the υ(C═N) absorption frequency. The very strong and sharp band was shifted to lower wavenumber at 1604 cm^{-1} in the mixed ligand complex substituted Pc **5** compared to the Schiff base substituteted Pc **3** (1619 cm^{-1}) confirming the involvement of the imine nitrogen in complex formation. All these shifts to lower wavenumbers support the participation of the azomethine group of these compounds in binding to the zinc ion [36,37].

The ^{1}H NMR spectra were in good correlation with the structures of **3** and **5**. The proton NMR spectra of **3** showed a peak as singlet at δ 13.56 ppm, characteristic of intramolecular hydrogen bonded OH proton in DMSO-d_6. It was observed that the signal due to this proton (13.56, phenolic-OH) disappeared completely on addition of D_2O, while the other signals still exist at their expected positions. The −OH proton peak did not appear in the complex **5** as expected. In the ^{1}H NMR spectra, chemical shifts of aromatic protons appeared at δ 9.42, 8.51–7.01 ppm for **3** as multiplet and at δ 8.95, 8.45–6.20 ppm for **5** as multiplet, while the protons of azomethine groups were observed as singlet at δ 8.90 ppm for **3** and at δ 8.65 ppm for **5**.

Interaction of $ZnCl_2$ with model Schiff base ligand (**8**) and 8-hydroxyquinoline (**4**) in 1: 1: 1 M ratio resulted in complex **9**. The salicylaldimine ligand (**8**) was prepared via Schiff base condensation of salicylaldehyde (**2**) and aniline (**7**) using a published procedure [26,38]. In the zinc complex (**9**), coordination through the phenolic oxygen after deprotonation is revealed by the disappearance of the υ(O–H) phenolic band at 3432–3352 cm^{-1} and the appearance of a band due to υ(C–O) at much lower frequencies (1107 cm^{-1}) as compared to that of the ligand (**8**) at 1148 cm^{-1} [33,39]. The azomethine stretching band was shifted to lower energy at 1601 cm^{-1} in **9** compared to the free ligand **8** (1614 cm^{-1}), confirming involvement of the azomethine nitrogen in complex formation [38]. The ^{1}H NMR spectra of the monomeric zinc complexes **9**, **6** provided the characteristic chemical shifts and confirmed the proposed structures. DMSO-d_6 was used as the solvent owing to good solubility for both complexes. The proton NMR spectra of the uncoordinated OH groups in **4** and **8** show a singlet at δ 8.45 ppm and δ 12.56 ppm, respectively, and these are of characteristic values for intramolecular hydrogen bonded OH protons [26,33,38]. The absence of the phenolic-OH proton signals in the Zn (II) complex (**9**) indicates coordination by phenolic oxygen to the metal ion after deprotonation [39]. Moreover, the spectrum of the complex (**9**) shows new signals due to the participation of the

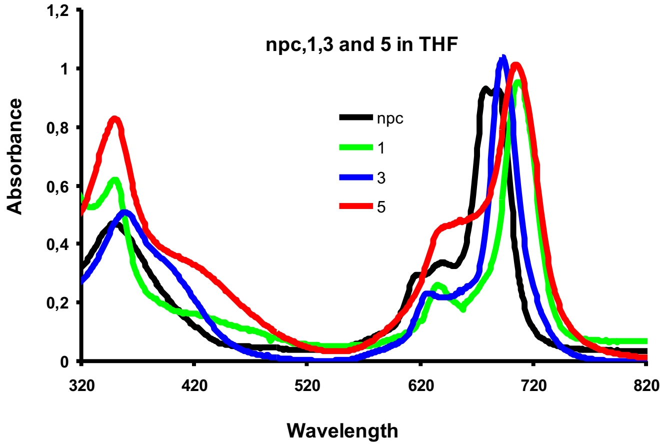

Fig. 3. UV–Vis spectra of phthalocyanines in a THF solution for (npc), **1**, **3** and **5**.

Table 1
Absorption, excitation and emission spectral data for substituted zinc phthalocyanine complexes (**3** and **5**) in DMSO, DMF and THF.

Comp.	Solvent	Q band λ_{max}, (nm)	(log ε)	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
3	DMSO	702	5.06	715	716	14
	DMF	698	5.05	711	716	18
	THF	694	5.08	694	711	17
5	DMSO	724	5.10	750	753	29
	DMF	715	5.12	741	743	28
	THF	705	5.11	721	725	21
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]
	THF	666[c]	5.19[c]	666[c]	673[c]	7[c]

[a] Ref. [50].
[b] Ref. [51].
[c] Ref. [52].

aromatic protons of **4** and **8** suggesting that these ligands are involved in complex formation. The ^{1}H NMR spectra of Zn (II) complex (**9**) have the azomethine (–CH = N–) proton signals shifting downfield (from δ 8.65 to δ 8.71) when compared with the Schiff base (**8**) on coordination of azomethine nitrogen to the metal ions [26,33,38,40]. The peaks at range δ 8.42–6.43 ppm for **9** as multiplet are assignable to the protons of different Ar–H groups. The ^{1}H NMR spectrum of complex **6** has the protons of water molecules at δ 3.50 ppm as broad singlet and aromatic protons as multiplet at δ 8.80–6.20 ppm.

3.2. Ground state electronic absorption and fluorescence spectra

The formation of **9** and **6** was also confirmed by electronic spectra. In the electronic spectra of **9**, the absorption bands may be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand transitions, involving the π-system of the quinoline residue, in addition to metal ligand charge–transfer transitions [41]. Compound **8** shows a peak at 340 nm [42]. Compound **9** exhibits three absorption maxima at 281, 338 and 400 nm. The band at 281 nm can be attributed to $\pi \rightarrow \pi^*$ transition in the benzene ring or azomethine groups for (**9**). The band observed at about 341 nm is most probably due to the transition of $n \rightarrow \pi^*$ of the imine group [43]. The band at 400 nm was attributed to the ligand→metal charge-transfer transitions, which overlap with the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the free ligands [39]. These modifications in shifts and intensity for the absorption bands supported the coordination of the ligand to the central Zn (II) ion.

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*003F transition from HOMO (highest occupied molecular

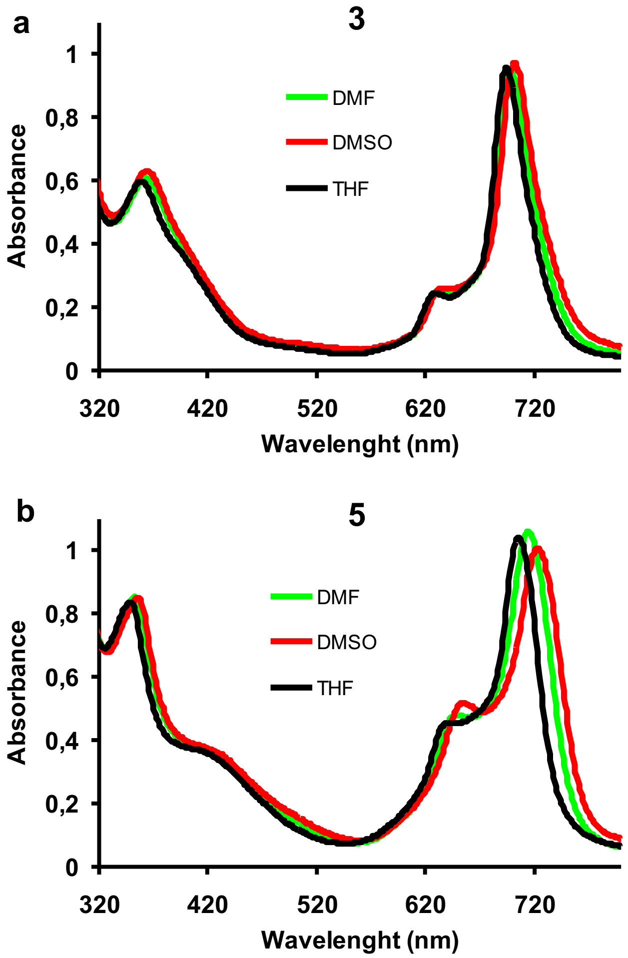

Fig. 4. UV–Vis spectra of **3** (a) and **5** (b) in DMSO, DMF and THF solution.

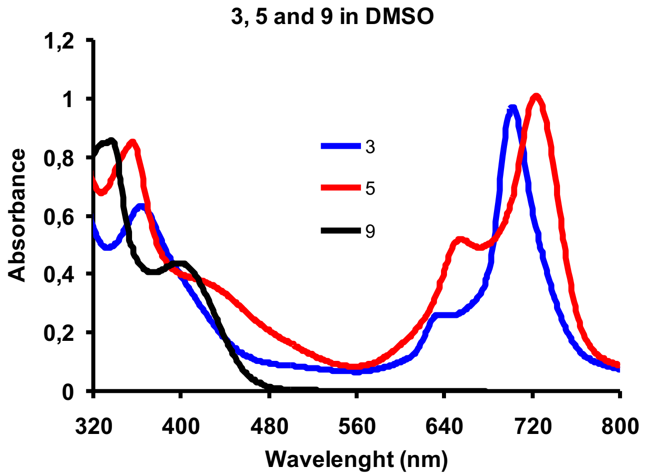

Fig. 5. UV–Vis spectra of **3**, **5** and **9** in DMSO solution.

orbital) to the 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, but contains a small contribution from *n*–π* transition [44].

The ground state electronic absorption spectra of the peripherally tetra-substituted phthalocyanine complexes (**3** and **5**) showed monomeric behavior evidenced by a single (narrow) Q band, typical of metalated phthalocyanine complexes in DMSO, DMF and THF. The electronic spectra of phthalocyanine compounds (**npc**), **1**, **3** and **5** are given in Fig. 3. The UV–Vis absorption spectra of metallophthalocyanines **3** and **5** in DMSO, DMF and THF showed intense Q absorption at 702 and 724 nm, respectively (Fig. 4, Table 1).

The Q band of the phthalocyanine complex (**5**) with Zn (II) complexes on the periphery was red-shifted when compared to the corresponding phthalocyanine complex (**3**) in all studied solvents; the reason for this shift might be the coordination of N atom on the periphery to Zn (II) ion in the case of **5.** The Q band absorption maximum of **5** is about 20 nm longer than that of **3**. The Q bands for complex **5** are broader compared to that of **3**, suggesting some aggregation in DMSO, DMF and THF (Fig. 4). Fig. 5 shows UV–Vis spectra of compounds **3**, **5** and **9** in DMSO. 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. In this study, the aggregation behavior of the phthalocyanine complexes (**3** and **5**) is investigated in DMSO, DMF and THF. For complexes, as the concentration was increased, the intensity of absorbance of the Q band also increased and there were no new bands (normally blue shifted) observed in solvents used. At the same time, Beer–Lambert law was obeyed for all of the compounds in the concentration

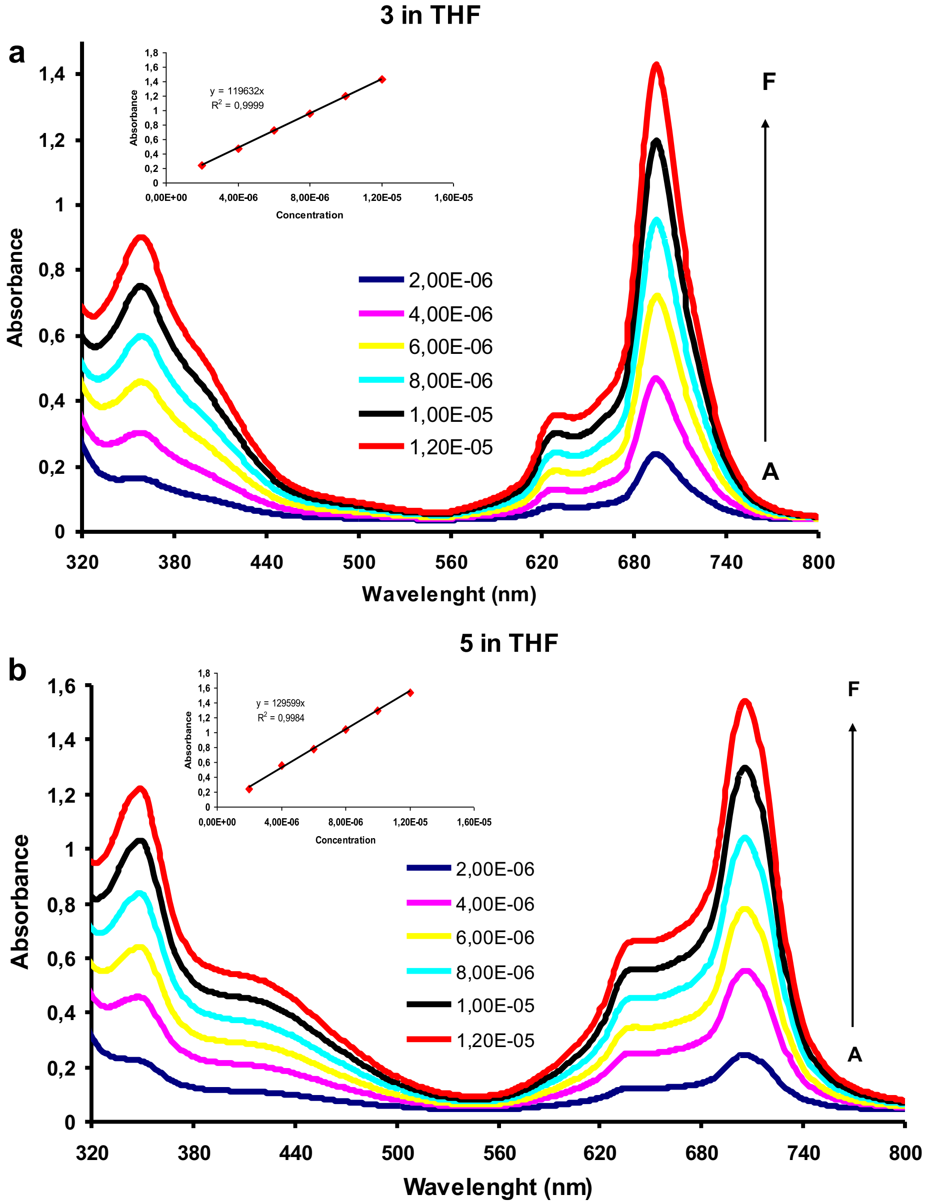

Fig. 6. Absorption spectral changes of **3** (a) and **5** (b) in THF at different concentrations: 2×10^{-6} (A), 4×10^{-6} (B), 6×10^{-6} (C), 8×10^{-6} (D), 10×10^{-6} (E), 12×10^{-6} (F) mol dm^{-3}. (Inset: Plot of absorbance versus concentration).

ranges from 2×10^{-6} to 12×10^{-6} mol dm^{-3} (see Fig. 6) as examples for complexes **3** (a) and **5** (b) in THF), showing that the complexes are not significantly aggregated within this concentration range. Still if we compare the aggregation behavior of compounds **3** and **5**, the latter showed some higher tendency.

The fluorescence behavior of zinc phthalocyanine complexes (**3** and **5**) were studied in DMSO, DMF and THF. Fig. 7 shows the absorption, fluorescence emission and excitation spectra for complex **3** and **5** in THF. Fluorescence emission peaks were observed at 711 nm for **3** and 725 nm for **5** in THF. The fluorescence excitation of **3** (Fig. 7a) was similar to absorption spectra. The proximity of the Q band maxima of the absorption and excitation spectra for **3** suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in THF. Emission spectra of **3** showed a red shift and broadening compared to the "mirror image" absorption spectrum. Excitation spectra of **3** showed similar behavior with about 13 nm red shift in DMSO and DMF.

However there was a disagreement of the absorption, fluorescence excitation and emission of complex **5** in DMSO, DMF and THF (Fig. 7b). For **5**, the excitation spectrum ($\lambda_{\mathrm{Ex}} = 694$ nm for **3** and 721 nm for **5**) was narrower compared to absorption spectrum, due to aggregation. For **5**, the fluorescence excitation spectrum (Fig. 7b) is red-shifted by about 16 nm relative to that of the absorption spectrum, suggesting a change in geometry upon excitation. In the case of **5** (Fig. 7b), the absorption and fluorescence excitation spectra are not similar; although there is almost a peak-to-peak matching, the intensities are reversed, which could be due to excitonic intensity borrowing and exchange between the two major transitions.

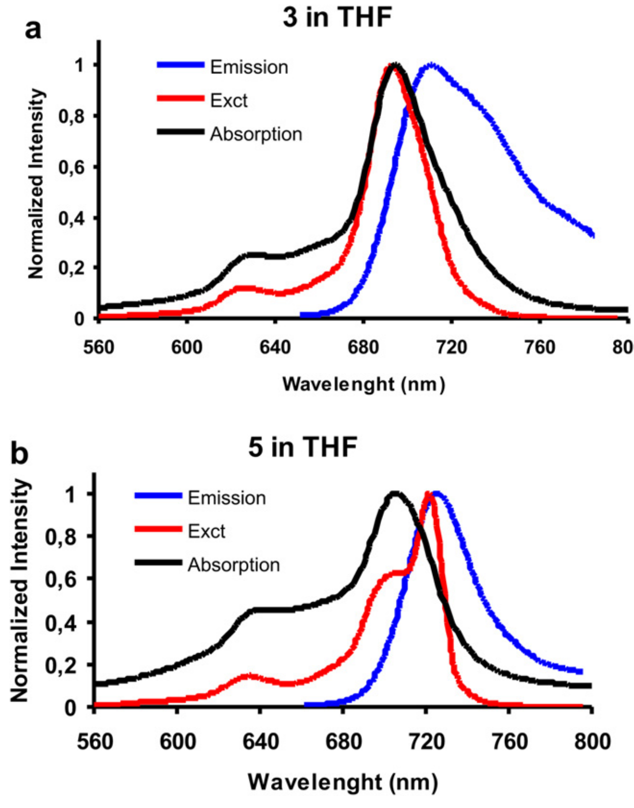

Fig. 7. Absorption, excitation and emission spectra for compound **3** (a) and **5** (b) in THF. Excitation wavelength = 630 nm for **3** and 640 for **5** nm in THF.

The observed Stokes shifts are 17 nm for **3**, and 21 nm for **5** in THF. Fluorescence emission and excitation peaks in different solvents are listed in Table 1.

3.3. Photophysical and photochemical properties

3.3.1. Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of zinc phthalocyanines (**3**) and (**5**) were studied in DMSO, DMF and THF. Φ_F values of zinc phthalocyanine complexes (**3** and **5**) are lower than unsubstituted ZnPc ($\Phi_F = 0.20$) [28] and typical of phthalocyanine complexes (Table 1) in all solvents studied. This implies that the presence of Schiff base Zn (II) complexes as substituents caused some fluorescence quenching of the parent **3** and **5**. Complex **5** has a lower fluorescence quantum yield (Φ_F) compared to **3** due to the quenching of four mononuclear Schiff base complexes of Zn(II) involving mixed ligand at the peripheral positions.

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 the theoretically determined lifetimes for the unaggregated molecules in this work [45]. Thus we suggest that the τ_F values obtained using this equation are an appropriate measure of fluorescence lifetimes. While the τ_F value of the studied zinc phthalocyanine compound (**3**) is within the range ($\tau_F = 0.17$ ns), the τ_F values of the studied complex (**5**) ($\tau_F = 0.13$ ns) phthalocyanine compounds are lower than reported for Pc compounds [1]. All studied phthalocyanine compounds showed lower τ_F values than unsubstituted ZnPc ($\tau_F = 1.22$ ns) in DMSO. For the substituted complexes a longer τ_F value is obtained for compound (**3**) in THF ($\tau_F = 0.49$ ns), complex (**5**) has longer τ_F value in DMSO ($\tau_F = 0.13$ ns) (Table 2).

The natural radiative lifetime (τ_0) and the rate constants for fluorescence (k_F) values are also investigated in this study (Table 2). The τ_0 values of the (**3**) and (**5**) compounds are close to unsubstituted ZnPc ($\tau_0 = 6.80$ ns) in DMSO. The τ_0 value of the studied zinc phthalocyanines (**3**) ($\tau_0 = 5.94$ ns) and (**5**) ($\tau_0 = 6.15$ ns) are slightly lower than unsubstituted ZnPc ($\tau_0 = 6.80$ ns) in DMSO. τ_0 values of the substituted phthalocyanine complexes (**3** and **5**) are lower than Std-ZnPc in all studied solvents except for **3** and **5** in DMF. The complex **3** showed the highest τ_0 values in all studied solvents when compared to complex **5** in THF.

The rate constants for fluorescence (k_F) values of complexes (**3** and **5**) are listed in Table 2 in DMSO, DMF and THF. The k_F values of

Table 2
Photophysical and photochemical parameters of substituted zinc phthalocyanine complexes (**3** and **5**) in DMSO, DMF and THF.

Comp.	Solvent	Φ_F	τ_F (ns)	τ_0 (ns)	k_F (s^{-1}) ($\times 10^7$)[a]
3	DMSO	0.029	0.17	5.94	16.84
	DMF	0.025	0.18	7.11	14.06
	THF	0.070	0.49	7.02	14.24
5	DMSO	0.021	0.13	6.15	16.27
	DMF	0.011	0.07	6.18	16.19
	THF	0.020	0.12	6.02	16.60
ZnPc	DMSO	0.20[b]	1.22[c]	6.80[c]	1.47[c]
	DMF	0.17[d]	1.03[d]	6.05[d]	1.65[d]
	THF	0.25[e]	2.72[e]	10.90[e]	9.17[e]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Ref. [28].
[c] Ref. [51].
[d] Ref. [53].
[e] Ref. [52].

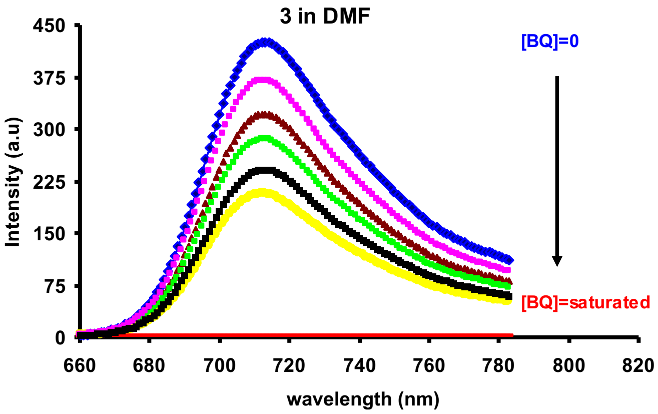

Fig. 8. Fluorescence emission spectral changes of **3** (1.00×10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm^{-3} and saturated with BQ.

studied zinc phthalocyanine complexes (**3** and **5**) are higher than unsubstituted ZnPc in all solvents used.

3.3.2. Fluorescence quenching studies by benzoquinone

The fluorescence quenching of zinc phthalocyanine complexes (**3** and **5**) by benzoquinone (BQ) in DMSO, DMF and THF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 8 shows the quenching of complex **3** by BQ in DMF as an example. The slope of the plots shown at Fig. 8 gave K_{SV} values, listed in Table 3. The Stern–Volmer plots for studied complexes (**3** and **5**) gave straight lines, depicting diffusion-controlled quenching mechanisms (Fig. 9). Quinones have high electron affinities, and their involvement in electron transfer processes is well documented [46]. The energy of the lowest excited state for quinones is greater than the energy of the excited singlet state of MPc complexes [47], 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 [48]. The K_{SV} and bimolecular quenching constant (kq) 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 (**3** and **5**) are lower than Std-ZnPc in all studied solvents. When compared the substituted complexes (**3** and **5**), the K_{SV} values of the complex **3** were lower in DMSO than DMF and THF, the lowest K_{SV} value was calculated in DMF for complex **5**. The substitution with Schiff base Zn(II) complex 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: THF > DMF > DMSO except **3** in DMSO. In different solvents, the K_{SV} values for BQ quenching of phthalocyanine complexes vary directly with the solvents' polarity.

Table 3
Fluorescence quenching data of substituted zinc phthalocyanine complexes (**3** and **5**) in DMSO, DMF and THF.

Comp.	Solvent	K_{sv} (M^{-1})	k_q/($\times 10^{11}$ s^{-1})
3	DMSO	19.72	1.16
	DMF	23.86	1.33
	THF	24.11	0.49
5	DMSO	27.61	2.12
	DMF	23.48	3.35
	THF	28.38	2.36
ZnPc	DMSO	31.90[a]	2.61[a]
	DMF	57.60[b]	5.59[b]
	THF	48.48[c]	1.78[c]

[a] Ref. [50].
[b] Ref. [51].
[c] Ref. [52].

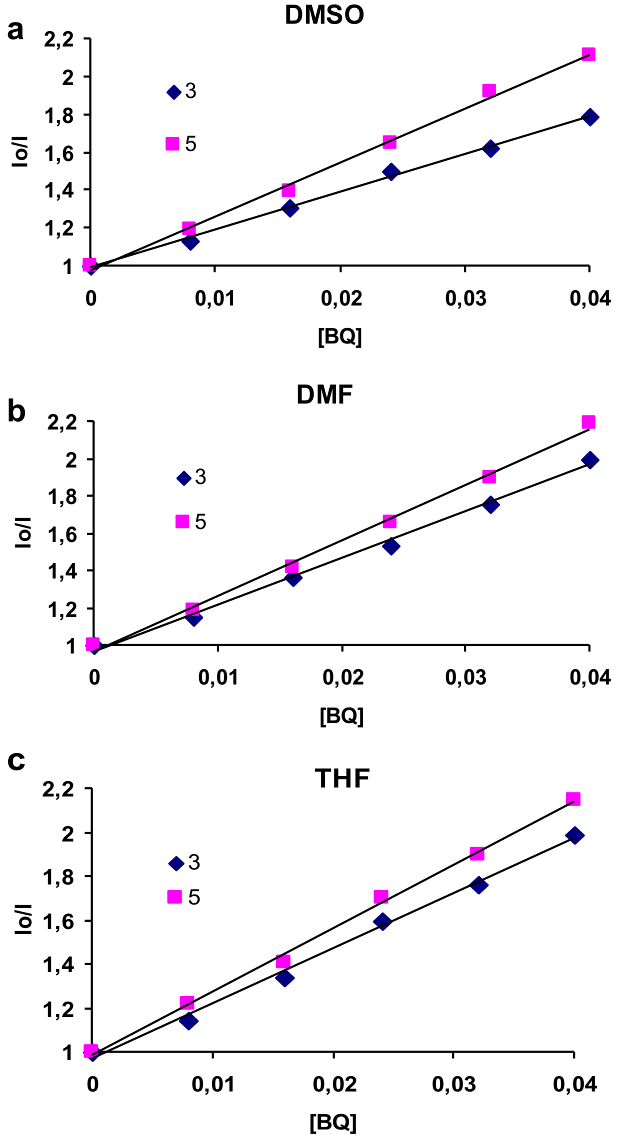

Fig. 9. Stern–Volmer plots for benzoquinone (BQ) quenching of substituted zinc phthalocyanine complexes **3** and **5** (a) in DMSO, (b) DMF and (c) THF. [MPc] $\sim 1.00 \times 10^{-5}$ mol dm^{-3} in DMSO, DMF and THF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm^{-3} in all solvents used.

The bimolecular quenching constant (k_q) values of the substituted zinc phthalocyanine complexes (**3** and **5**) were higher in DMF than DMSO and THF. The k_q values were found to be close to the diffusion-controlled limits, $\sim 10^{11}$ M^{-1} s^{-1} (Table 3), which is in agreement with the Einsteine-Smoluchowski approximation at room temperature for diffusion-controlled bimolecular interactions [49–53].

4. Conclusion

In the presented work, the synthesis of new peripherally tetra-substituted zinc (II) phthalocyanine complexes were described and these new complexes were characterized by elemental analysis, FTIR, ^{1}H NMR spectroscopy, electronic spectroscopy and mass spectrometry. Although **3** has good solubility in common organic solvents such as THF, acetone, toluene, DMF, DCM, DMSO and CHCl$_3$, **5** obtained in both methods is insoluble in most common organic solvents but soluble in THF, DMF and DMSO. The photophysical and fluorescence quenching properties of the zinc (II) phthalocyanine complexes (**3** and **5**) were investigated in solvents DMSO, DMF and THF. While, complexes **3** and **5** show lower fluorescence quantum yields (Φ_F) and shorter lifetime compare to unsubstituted zinc phthalocyanine, complex **5** has lower fluorescence quantum yields (Φ_F) compared to **3** due to the quenching by four mononuclear Schiff base complexes of Zn(II) involving mixed ligand at the peripheral positions. The fluorescence of the substituted zinc (II) phthalocyanine complexes (**3** and **5**) is effectively quenched by 1,4-benzoquinone in DMF, DMSO and THF.

Acknowledgment

This study was supported by Yildiz Technical University (Project No: BAPK-28-01-02-12).

References

[1] Nyokong T. Effects of substituents on the photochemical and photophysical properties of main group phthalocyanines. Coord Chem Rev 2007; 251(13–14):1707–22.

[2] Kantekin H, Gok Y, Kilicaslan MB, Acar I. Synthesis and characterization of new metal-free and nickel(II) phthalocyanines containing hexaazadioxa macrobicyclic moieties. J Coord Chem 2008;61(2):229–36.

[3] Hanabusa K, Shirai H. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 2. New York: VCH Publications; 1993.

[4] Reddy PY, Giribabu L, Lyness C, Snaith HJ, Vijaykumar C, Chandrasekharam M, et al. Efficient sensitization of nanocrystalline TiO$_2$ films by a near-IR-absorbing unsymmetrical zinc phthalocyanine. Angew Chem Int Edit 2007; 46(3):373–6.

[5] Li XQ, Liu LF, Kang SZ, Mu J, Li GD. Differences between Zn-porphyrin-coupled titanate nanotubes with various anchoring modes: thermostability, spectroscopic, photocatalytic and photoelectronic properties. Appl Surf Sci 2011; 257(14):5950–6.

[6] Harish MNK, Keshavayya J, Reddy KV, Mallikarjuna HR, Ali RS, Rajesh T. Decorating nickel phthalocyanine periphery by aryl-1,3,4-oxadiazole pendants: synthesis, characterization, and conductivity studies. J Coord Chem 2010;63(23):4050–60.

[7] Harbeck M, Erbahar DD, Gurol I, Musluoglu E, Ahsen V, Ozturk ZZ. Phthalocyanines as sensitive coatings for QCM sensors: comparison of gas and liquid sensing properties. Sensor Actuat B-Chem 2011;155(1):298–303.

[8] Ayhan MM, Durmus M, Gurek AG. Synthesis, photophysical and photochemical studies of novel liquid crystalline phthalocyanines. J Porphyr Phthalocya 2009;13(6):722–38.

[9] Claessens CG, Blau WJ, Cook M, Hanack M, Nolte RJM, Torres T, et al. Phthalocyanines and phthalocyanine analogues: the quest for applicable optical properties. Monatsh Chem 2001;132(1):3–11.

[10] de la Torre G, Torres T, AgulloLopez F. The phthalocyanine approach to second harmonic generation. Adv Mater 1997;9(3):265–9.

[11] Van Lier JE. In: Kessel D, editor. Photodynamic therapy of neoplastic diseases, vol. 1. Boca Raton, FL: CRC Press; 1990. p. 279–90.

[12] Leznoff CC, . Lever ABP, editors. Phthalocyanines: properties and applications, vol. 1–4. New York: VCH Publications; 1989.

[13] a) Erdoğmuş A, Nyokong T. Novel, soluble, FluXoro functional substituted zinc phthalocyanines; synthesis, characterization and photophysicochemical properties. Dyes Pigm 2010;86(2):174–81;
b) Erdoğmuş A, Nyokong T. Synthesis, photophysical and photochemical properties of novel soluble tetra[4-(thiophen-3-yl)-phenoxy]phthalocyaninato zinc(II) and Ti(IV)O complexes. Inorg Chim Acta 2009;362(14):4875–83;
c) Erdoğmuş A, Nyokong T. New soluble methylendioxy-phenoxy-substituted zinc phthalocyanine derivatives: synthesis, photophysical and photochemical studies. Polyhedron 2009;28(14):2855–62.

[14] Lunardi CN, Rotta JCG, Tedesco AC. Synthesis, photophysical and photobiological study of synergic photosensitizer: zinc-phthalocyanine with Ca^{2+} chelating agent. Curr Org Chem 2007;11(7):647–54.

[15] Stumpf HO, Pei Y, Kahn O, Sletten J, Renard JP. Dimensionality of manganese(II)-copper(II) bimetallic compounds and design of molecular-based magnets. J Am Chem Soc 1993;115:6738–45.

[16] Hamilton A, Lehn JM, Sessler JL. Coreceptor molecules. Synthesis of metalloreceptors containing porphyrin subunits and formation of mixed substrate supermolecules by binding of organic substrates and of metal ions. J Am Chem Soc 1986;108:5158–67.

[17] Kobayashi N, Higashi Y, Osa T. Planar phthalocyanine–pyrazinoporphyrazine heterodinucleates. Chem Commun 1994;15:1785–6.

[18] Wollman RG, Hendrickson DN. Synthesis and physical properties of meso-tetraferrocenylporphyrin, the copper complex, and the corresponding mixed-valence oxidation products. Inorg Chem 1977;6:3079–89.

[19] Sağlam Ö, Gül A. Porphyrazines with appending eight crown ethers. Polyhedron 2001;20:269–75.

[20] Hamilton AD, Rubin HD, Bocarsly AB. Binuclear complexes of a covalently linked porphyrin-bipyridine ligand. J Am Chem Soc 1984;106(23): 7255–7.

[21] Franco C, McLendon G. Bimetallic porphyrins: synthesis and rapid intramolecular electron transfer of (meso-tritolylpyridylporphyrin)pentaammine ruthenium(III). Inorg Chem 1984;23:2370–2.

[22] Whiteoak CJ, Salassa G, Kleij AW. Recent advances with π-conjugated salen systems. Chem Soc Rev 2012;41(2):622–31.

[23] Karaoglan GK, Gumrukcu G, Koca A, Gul A. The synthesis, characterization, electrochemical and spectroelectrochemical properties of a novel, cationic, water-soluble Zn phthalocyanine with extended conjugation. Dyes Pigm 2011;88(3):247–56.

[24] Karaoglan GK, Gumrukcu G, Koca A, Gul A, Avciata U. Synthesis and characterization of novel soluble phthalocyanines with fused conjugated unsaturated groups. Dyes Pigm 2011;90(1):11–20.

[25] Young JG, Onyebuagu W. Synthesis and characterization of di-disubstituted phthalocyanines. J Org Chem 1990;55(7):2155–9.

[26] Li C, Zhang G, Shih HH, Jiang X, Sun P, Pan Y, et al. High-efficient phosphorescent iridium(III) complexes with benzimidazole ligand for organic light-emitting diodes: synthesis, electrochemistry and electroluminescent properties. J Organomet Chem 2009;694(15):2415–20.

[27] Frey-Forgues S, Lavabre D. Are fluorescence quantum yields so tricky to measure? A demonstration using familiar stationery products. J Chem Educ 1999;76(9):1260–4.

[28] Ogunsipe A, Chen J-Y, Nyokong T. Photophysical and photochemical studies of zinc(II) phthalocyanine derivatives – effects of substituents and solvents. New J Chem 2004;28:822–7.

[29] Du H, Fuh R-CA, Li J, Corkan LA, Lindsey JS. PhotochemCAD: a computer-aided design and research tool in photochemistry. Photochem Photobiol 1998; 68(2):141–8.

[30] Rose J. Advanced physico-chemical experiments. London: Sir Isaac Pitman & Sons Ltd; 1964. 257 pp.

[31] Yenilmez HY, Okur Aİ, Gül A. Peripherally tetra-palladated phthalocyanines. J Organomet Chem 2007;692(5):940–5.

[32] Dinçer HA, Gül A, Koçak MB. Tuning of phthalocyanine absorption ranges by additionalsubstituents. Dyes Pigm 2007;74(3):545–50.

[33] Abu-Hussen AAA. Synthesis and spectroscopic studies on ternary bis-schiff-base complexes having oxygen and/or nitrogen donors. J Coord Chem 2006; 59(2):157–76.

[34] Kumar KN, Ramesh R. Synthesis, luminescent, redox and catalytic properties of Ru(II) carbonyl complexes containing 2N$_2$O donors. Polyhedron 2005; 24(14):1885–92.

[35] El-Wahab A, Zeinab H. Mixed ligand complexes of nickel(II) and cerium(III) ions with 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione and some nitrogen/oxygen donor ligands. J Coord Chem 2008;61(20):3284–96.

[36] Pouralimardan O, Chamayou AC, Janiak C, Hosseini-Monfared H. Hydrazone Schiff base-manganese(II) complexes: synthesis, crystal structure and catalytic reactivity. Inorg Chim Acta 2007;360(5):1599–608.

[37] Tas E, Onal IH, Yilmaz I, Kilic A, Durgun M. Synthesis, structural characterization, electrochemistry and spectroelectrochemistry of dinuclear copper (II) metal complexes stabilized by a tetradentate NOOO salicylaldimine ligands. J Mol Struct 2009;927(1–3):69–77.

[38] Bhunora S, Mugo J, Bhaw-Luximon A, Mapolie S, Van Wyk J, Darkwa J, et al. The use of Cu and Zn salicylaldimine complexes as catalyst precursors in ring opening polymerization of lactides: ligand effects on polymer characteristics. Appl Organomet Chem 2011;25(2): 133–45.

[39] Maurya RC, Patel P, Rajput S. Synthesis and characterization of mixed-ligand complexes of Cu(II), Ni(II), Co(II), Zn(II), Sm(III), and U(VI)O-2, with a Schiff base derived from the sulfa drug sulfamerazine and 2,2′-bipyridine. Syn React Inorg Met 2003;33(5):801–16.

[40] van Wyk JL, Mapolie S, Lennartson A, Hakansson M, Jagner S. The synthesis of copper(II) salicylaldiminato complexes and their catalytic activity in the hydroxylation of phenol. Z Naturforsch B 2007;62(3):331–8.

[41] Garcia-Santos I, Sanmartin J, Garcia-Deibe AM, Fondo M, Gomez E. Structural and photophysical studies on a linear trinuclear zinc complex of 2-[(2-hydroxyethylimino)methyl]quinolin-8-ol. Polyhedron 2009;28(14): 3055–9.

[42] Pod'yachev SN, Mustafina AR, Ivanova EG, Morozov VI, Gainullina FK, Galyametdinov YG, et al. Complex formation of dimethylaminomethylcalix[4] resorcinarene and 2-dimethylaminomethylphenol with Cu(II) salicylaldiminates. Russ J Gen Chem 2002;72(1):110–5.

[43] Vafazadeh R, Hayeri V, Willis AC. Synthesis, crystal structure and electronic properties of bis(N-2-bromophenyl-salicydenaminato)copper(II) complex. Polyhedron 2010;29(7):1810–4.

[44] Gouterman M. In: Dolphin D, editor. The porphyrins, vol. 3. New York: Academic Press; 1978.
[45] Maree MD, Nyokong T, Suhling K, Phillips D. Effects of axial ligands on the photophysical properties of silicon octaphenoxyphthalocyanine. J Porphyr Phthalocya 2002;6(6):373–6.
[46] Ogunsipe A, Nyokong T. Effects of central metal on the photophysical and photochemical properties of non-transition metal sulfophthalocyanine. J Porphyr Phthalocya 2005;9(2):121–9.
[47] Darwent JR, McCubbin I, Phillips D. Excited singlet and triplet state electron-transfer reactions of aluminum(III) sulfonated phthalocyanine. J Chem Soc Farad T 2 1982;78(2):347–57.
[48] Idowu M, Nyokong T. Photophysicochemical and fluorescence quenching studies of tetra- and octa-carboxy substituted silicon and germanium phthalocyanines. J Photoch Photobio A 2009;204(1):63–8.
[49] Dutt GB, Periasamy N. Electron-transfer distance in intermolecular diffusion-limited reactions. J Chem Soc Faraday T 1991;87(24):3815–20.
[50] Gürol I, Durmus M, Ahsen V, Nyokong T. Synthesis, photophysical and photochemical properties of substituted zinc phthalocyanines. Dalton Trans 2007;34:3782–91.
[51] Zorlu Y, Dumoulin F, Durmus M, Ahsen V. Comparative studies of photophysical and photochemical properties of solketal substituted platinum(II) and zinc(II) phthalocyanine sets. Tetrahedron 2010;66(17):3248–58.
[52] Saka ET, Durmus M, Kantekin H. Solvent and central metal effects on the photophysical and photochemical properties of 4-benzyloxybenzoxy substituted phthalocyanines. J Organomet Chem 2011;696(4):913–24.
[53] Durmus M, Nyokong T. Photophysicochemical and fluorescence quenching studies of benzyloxyphenoxy-substituted zinc phthalocyanines. Spectrochim Acta A 2008;69(4):1170–7.