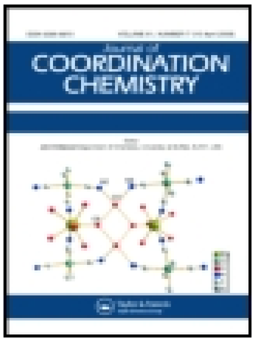

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Phthalocyanines formed from several precursors: synthesis, characterization, and comparative fluorescence and quinone quenching

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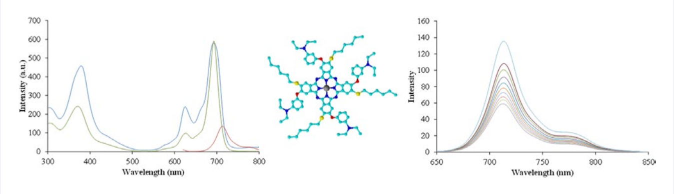
ABSTRACT

We have synthesized a new phthalonitrile with different substituents in 4- and 5-positions (**1**). Cyclotetramerization of **1** yielded phthalocyanines with cobalt(II) (**2**), zinc(II) (**3**), gallium(III)chloride (**4**), and indium(III)chloride (**5**) containing diethylamino-phenoxy and hexylsulfanyl substituents on each benzene unit. Elemental analyses, Fourier transform infrared spectra, ^{1}H-nuclear magnetic resonance spectra, mass spectra, and ultraviolet-visible spectra were used for characterization of the phthalocyanines. The aggregation behavior of the zinc phthalocyanine derivative was studied in different concentrations. Also four chloro and four diethyllaminophenoxy substituted zinc phthalocyanine (**6**) and octa-diethylaminophenoxy substituted zinc phthalocyanine (**7**) were synthesized. These phthalocyanines (**3**, **6**, and **7**) were compared for electronic absorption spectra, fluorescence quantum yields, fluorescent lifetimes, and fluorescence quenching in the presence of benzoquinone. The fluorescence quantum yield gives the efficiency of the fluorescence process. The fluorescence lifetime is an important parameter for practical applications of fluorescence such as fluorescence resonance energy transfer and fluorescence-lifetime imaging microscopy.



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Phthalocyanine; diethylaminophenoxy; aggregation behavior; fluorescence; quinone

1. Introduction

Phthalocyanines constitute an aromatic macrocycle with delocalized two-dimensional 18π-electron systems exhibiting unparalleled optical, electronic, and catalytic properties. They are thus used in many different scientific and technological applications, such as

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photoconducting agents in photocopying devices, chemical sensors, molecular metals, liquid crystals, nonlinear optical materials, and catalysts [1–4]. To promote solubilization of phthalocyanines in these applications is crucial. Because π-stacking, referred to as aggregation, is present between planar macrocycles, phthalocyanines without substitution are poorly soluble in common organic solvents, including chloroform, ethanol, or tetrahydrofuran, as well as in water. The solubility is enhanced dramatically by introduction of substituents on the periphery (*β*) or non-periphery (*α*) of the phthalocyanine ring, and by the presence of axial substituents in the metal center since the distances between stacks are increased [5–15].

The size, nature, and positions of substituents have positive effects on the solubility of the final structures and they improve chemical and physical properties**.** Peripheral octa-substituted phthalocyanines are formed from phthalonitrile derivatives with two identical or different substituents at the 4- and 5-positions of the ring. The superior solubility of those with two different substituents to the octa-substituted phthalocyanines is well known, because four constitutional isomers are formed, and a high dipole moment from the unsymmetrical arrangement occurs [16, 17].

A red-shift in the phthalocyanine is observed in cases when electron-donating substituents are available at non-peripheral positions of phthalocyanine compounds, whereas minor shifts are observed after peripheral substitution [18, 19]. Phthalocyanines bearing axial substituents on the metal ions also induce a bathochromic shift of the Q-band maximum values.

Due to advantages, such as high selectivity, direct and rapid application, and considerable controllability, microwave heating is attractive as an alternative to the conventional thermal synthesis [20].

Owing to the difficult preparation of phthalonitrile precursors with different substituents, phthalocyanines with two or three different substituents on each aromatic ring have been rarely obtained. In previously published studies, we have described the synthesis of octa- and hexadeca-substituted phthalocyanines [16, 20, 21].

In the present paper, we report the synthesis of octa-substituted metallophthalocyanines bearing four diethylaminophenoxy and four hexylsulfanyl substituents in peripheral positions, adjacent to each other. The introduction of diethylaminophenoxy and hexylsulfanyl substituents in peripheral positions and an axial chloro ligand (for gallium (**4**) and indium (**5**) Pcs) increase the solubility of phthalocyanines. Herein, we also examined the aggregation behaviors of the zinc phthalocyanine (**3**) in different concentrations of $CHCl_3$. The octa-substituted metallophthalocyanines were obtained by either conventional thermal processing or microwave heating. We report here the photophysical (fluorescence quantum yields and lifetimes) and quenching properties of **3**, **6** and **7** in DMF. The photophysical and quenching properties of a newly synthesized zinc phthalocyanine were compared with those of previously synthesized zinc phthalocyanines (**6**, **7**) [16, 21, 22].

2. Experimental

2.1. Materials and equipment

All chemicals and solvents were reagent grade from commercial suppliers. Molecular sieves were used to draw extra water from the solvents. Thin layer chromatography on silica was used for testing whether the reaction has finished or not. 1-Chloro-3,4-dicyano-6-[3-(diethylamino)phenoxy]benzene and its corresponding zinc phthalocyanines **6** and **7** were synthesized according to the literature [16, 21, 22].

IR spectra were obtained, on a Universal attenuated total reflectance (UATR) module, with a Perkin Elmer Spectrum One FT-IR spectrometer and electronic spectra were obtained on a Scinco LabPro Plus UV/Vis spectrophotometer. ^{1}H NMR spectra were acquired with an Agilent VNMRS spectrometer, operating at 500 MHz, with TMS as an internal standard. A Micromass Quattro LC/ULTIMA LC–MS/MS spectrometer was used to record the mass spectra. A Thermo Finnigan Flash EA 1112 apparatus was used for elemental analyses at 950–1000 °C. For fluorescence measurements, a Perkin Elmer LS55 fluorescence spectrophotometer and for UV/Vis spectra, a Scinco SD 1000 spectrophotometer, were used.

2.2. Synthesis

2.2.1. *4-[3-(Diethylamino)phenoxy]-5-(hexylthio)phthalonitrile* (1)

1-Chloro-3,4-dicyano-6-[3-(diethylamino)phenoxy]benzene (0.500 g, 1.54 mmol) was dissolved in 10.00 cm^3 of dry DMF, and 0.83 g of n-hexanethiol (2.3 mmol) was added. The mixture was stirred for 15 min, and finely ground anhydrous 2.3 g cesium carbonate (Cs_2CO_3; 6.14 mmol) was added in small portions during 2 h with stirring. The temperature of the reaction mixture was set to 45 °C for 48 h under N_2. The mixture was cooled to room temperature, and the mixture was poured into cracked ice-water mixture (100 cm^3) and the precipitate that formed was filtered, washed with copious amounts of water until the filtrate had a neutral pH, and dried in vacuo. The brown product was purified by column chromatography with silica gel as stationary phase, eluting with n-hexane:ethyl acetate (5:1, v:v).

Compound **1** was soluble in THF, chloroform, dichloromethane, DMF, and DMSO. Yield: 25%. ^{1}H NMR ($CDCl_3$): δ 7.57 (s, H–Ar, H), 7.47 (d, H–Ar, H), 6.96 (s, H–Ar, H), 6.57 (d, H–Ar, H), 6.29 (s, H–Ar, H), 6.24 (d, H–Ar, H), 3.34 (q, N–CH_2, 4H), 2.98 (t, S–CH_2, 2H), 1.76 (q, S–CH_2–CH_2, 2H), 1.50–1.32 (q, CH_2, 4H), 1.16 (t, CH_3, 6H), 0.90 (t, CH_3, 3H); IR (ν, cm^{-1}): 3076 (H–Ar), 2959, 2928 (H-Aliphatic), 2230 (C≡N), 1563 (Ar C=C), 1275 (Ar C–N), 1247 (Ar–O–Ar); $C_{24}H_{29}N_3OS$ calculated %: C, 70.73; H, 7.17; N, 10.31; O, 3.93; S, 7.87. Found %: C, 70.95; H, 7.25; N, 10.29; MS [*m/z*]: 407 $[M]^+$, 392 $[M–CH_3]^+$, 322 $[M–C_6H_{13}]^+$, 290 $[M\text{-}SC_6H_{13}]^+$; m.p.: 137.5 °C.

2.2.2. *General procedures for phthalocyanine derivatives* (2–5)

A mixture, containing **1** (0.150 g, 0.37 mmol), anhydrous metal salts (0.0925 mmol) [$CoCl_2$, 12 mg; $Zn(CH_3COO)_2$, 16.8 mg] in hexan-1-ol (2.0 mL) and a 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, catalytic amount) were charged into a glass tube under nitrogen. The mixture was heated, by stirring efficiently, at 160 °C for 24 h. Instead of conventional heating, microwave heating was used for gallium and indium phthalocyanines. A mixture having **1** (0.150 g, 0.37 mmol) and dried gallium(III)chloride (16 mg, 0.0925 mmol) or indium(III)chloride (20.4 mg, 0.0925 mmol) in freshly distilled quinoline (2 mL) (for **4**) or hexan-1-ol (for **5**) in the presence of a drop of DBU was subjected to irradiation by microwave at 170 °C for 25 min. After cooling to room temprature, the resulting green suspension was turned into a precipitate with methanol or a mixture of methanol and water. The precipitate was isolated from the suspension and washed thoroughly with the same solvents. Pure phthalocyanine derivatives were obtained by column chromatography on silica gel, which is the stationary phase, using a suitable solvent as eluent. Colors: dark green. Solubility: very soluble in chloroform, THF, DMF, and DMSO.

2.2.2.1. *2,9,16,23-Tetrakis-[3-(diethylamino)phenoxy]-3,10,17,24-tetrahexylsulfanyl-phthalocyaninatocobalt(II)* (2).

The crude product was purified by column chromatography, with silica gel as stationary phase, using THF:n-hexane (20:1, v:v) as eluent. Yield: 36 mg, 23%; IR, γmax (cm^{-1}): 3069 (C–H, aromatic) 2957–2926 (C-H aliphatic), 1230 (Ar-O-Ar); UV–vis (CHCl$_3$): λ_{max} = 315, 627, 695; $C_{96}H_{116}CoN_{12}O_4S_4$ calculated %: C, 68.26; H, 6.92; N, 9.95; found %: C, 68.30; H, 6.96; N, 9.92; MS: (ESI) *m/z* 1687.91 [M–H]$^+$.

2.2.2.2. 2,9,16,23-Tetrakis-[3-(diethylamino)phenoxy]-3,10,17,24-tetrahexylsulfanyl-phthalocyaninatozinc(II) (3). The green product was subjected to column chromatography on silica gel (stationary phase) using ethyl acetate:n-hexane (5:1, v/v) as eluent. Yield: 42 mg, 27%; IR, γ_{max} (cm^{-1}): 3068 (C–H, aromatic) 2956–2924 (C–H aliphatic), 1227 (Ar–O–Ar); UV–Vis (CHCl$_3$): λmax (nm) = 361, 626, 698; ^{1}H NMR (CDCl$_3$) δ: 7.19–6.52 (m, Ar–H, 24H), 3.40 (br, N–CH$_2$, S–CH$_2$, 24H), 1.94 (br, S–CH$_2$–CH$_2$, 8H), 1.60 (br, Aliph–CH$_2$, 24H), 1.20 (t, CH$_3$, 24H), 0.93 (t, CH$_3$, 12H); $C_{96}H_{116}ZnN_{12}O_4S_4$ calculated %: C, 68.00; H, 6.90; N, 9.91; found %: C, 68.03; H, 6.88; N, 9.95. MS: (ESI) *m/z* 1694.25 [M]$^+$.

2.2.2.3. 2,9,16,23-Tetrakis-[3-(diethylamino)phenoxy]-3,10,17,24-tetrahexylsulfanyl-phthalocyaninato(chloro)gallium(III) (4). Purification was done with column chromatography (silica gel as adsorbent) with THF:methanol (1:1, v:v) as eluent. Yield: 11 mg, 7%; IR, γ_{max} (cm^{-1}): 3066 (C–H, aromatic) 2957–2919 (C–H aliphatic), 1258 (Ar–O–Ar); UV–vis (CHCl$_3$): λmax (nm) = 359, 715; ^{1}H NMR (CDCl$_3$ δ): 7.39–6.58 (m, Ar–H, 24H), 3.48 (br, N–CH$_2$, S-CH$_2$, 24H), 1.72 (br, S–CH$_2$–CH$_2$, 8H), 1.56 (br, Aliph–CH$_2$, 24H), 0.99 (br, CH$_3$, 36H) ppm; $C_{96}H_{116}ClGaN_{12}O_4S_4$ calculated %: C, 66.44; H, 6.74; N, 9.69; found %: C, 66.46; H, 6.72; N, 9.67.

2.2.2.4. 2,9,16,23-Tetrakis-[3-(diethylamino)phenoxy]-3,10,17,24-tetrahexylsulfanyl-phthalocyaninato(chloro)indium(III) (5). The crude product was purified with column chromatography twice (silica gel as adsorbent, THF:methanol 25:1, v:v and THF:ethyl acetate 1:1, v:v as eluents). Yield: 23 mg, 14%; IR, γmax (cm^{-1}): 3069 (C–H, aromatic), 2954–2924 (C–H aliphatic), 1261–1228 (Ar–O–Ar); UV–vis (CHCl$_3$): λ_{max} (nm) = 362, 728; ^{1}H NMR (CDCl$_3$ δ): 7.53–6.84 (m, Ar–H, 24H), 3.44 (br, N–CH$_2$, S–CH$_2$, 24H), 1.94 (br, S–CH$_2$–CH$_2$, 8H), 1.57 (br, Aliph–CH$_2$, 24H), 0.96 (br, CH$_3$, 36H) ppm; $C_{96}H_{116}ClInN_{12}O_4S_4$ calculated %: C, 64.76; H, 6.57; N, 9.44; found %: C, 64.79; H, 6.60; N, 9.42%; MS: (ESI) *m/z* 1803 [M + Na]$^+$, 1710 [M–5CH$_2$]$^+$, 1675 [M–5CH$_2$–Cl]$^+$.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields (Φ_F) and fluorescence lifetimes (τ_F)

The comparative method for fluorescence quantum yields of zinc phthalocyanines (**3**, **6**, and **7**) was used [23]. Unsubstituted ZnPc, with a Φ_F value of 0.17 [24], was employed as the standard in DMF.

$$\varnothing_F = \varnothing_F(\mathrm{Std})\frac{FA_{\mathrm{Std}}\eta^2}{F_{\mathrm{Std}}A\eta_{\mathrm{Std}}^2} \tag{1}$$

Natural radiative lifetimes, designated as τ_0, were determined with PhotochemCAD software, employing the Strickler-Berg equation [25]. The evaluation was performed using Equation (2).

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

2.3.2. Benzoquinone (BQ)-based fluorescent quenching

Fluorescence quenching experiments with the substituted zinc phthalocyanines (**3**, **6**, and **7**) were performed by adding a series of concentrations of benzoquinone to a constant concentration of the complex. The Stern-Volmer constants of the studied compounds were found by Equation (3) [26]. The I_0/I ratios were calculated and are shown as a plot against [BQ] by using Equation (3), and K_{SV} is determined from the slope.

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \tag{3}$$

The bimolecular quenching constant was found with Equation (4).

$$K_{sv} = k_q * \tau_F \tag{4}$$

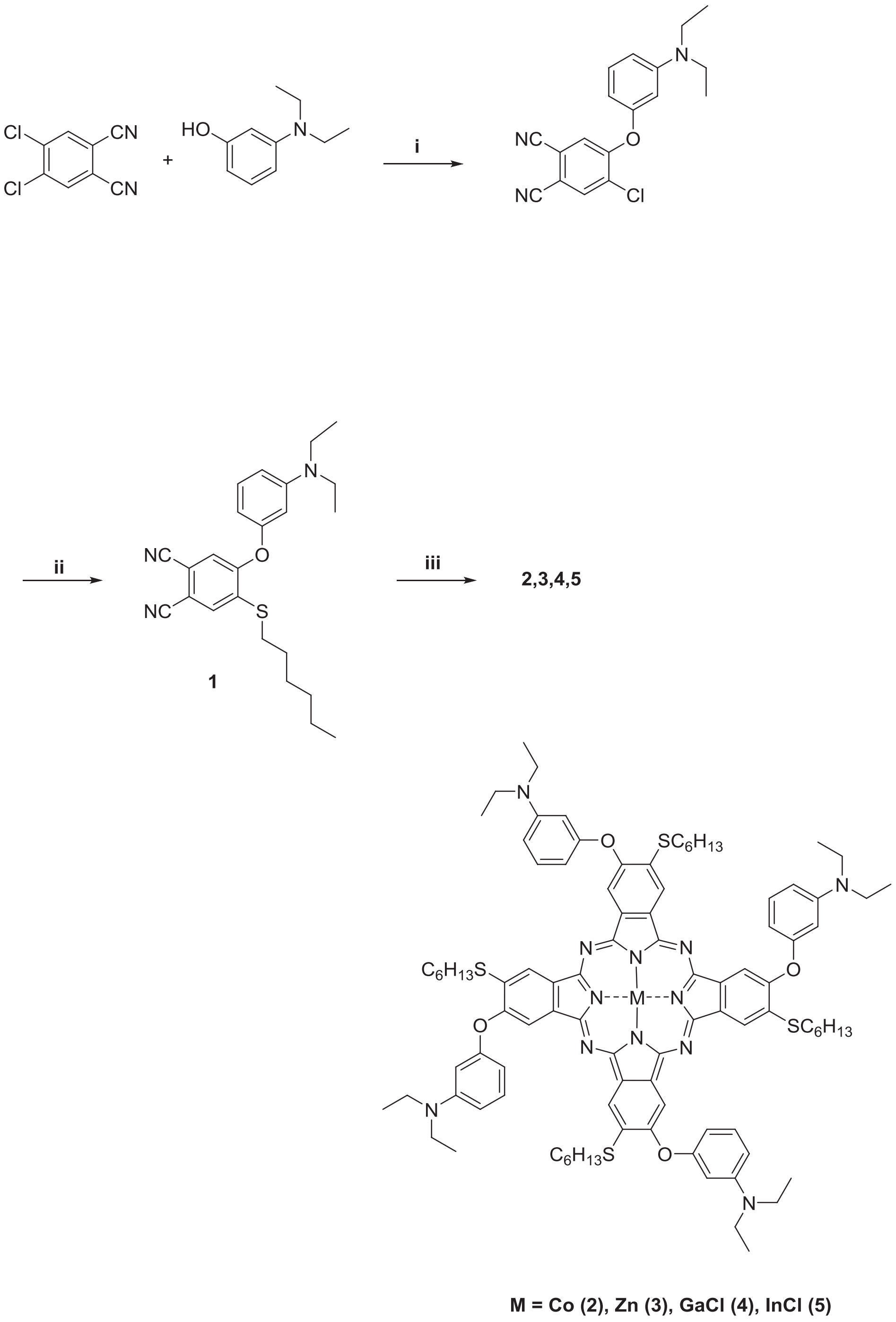
3. Results and discussion

3.1. Synthesis and characterization of the compounds

The procedure for synthesis of phthalocyanines carrying four diethylamino-phenoxy and four hexylsulfanyl substituents at peripheral positions is depicted in Scheme 1, whereas Figure 1 represents phthalocyanine derivatives **6** and **7** which were synthesized according to methods described [16, 21, 22]. The precursor material we chose for the synthesis of the mentioned phthalocyanines was 1-chloro-3,4-dicyano-6-[3-(diethylamino)phenoxy]benzene, whose synthesis and characterization were previously described by our group [16]. First, this compound was reacted with n-hexanethiol in the presence of cesium carbonate in anhydrous DMF at 45 °C for 48 h to yield 4-[3-(diethylamino)phenoxy]-5-(hexylthio)phthalonitrile (**1**). The reaction of this new disubstituted phthalonitrile **1** with metal salts (cobalt(II) chloride, zinc acetate) in hexan-1-ol at 160 °C for 24 h in nitrogen yielded the respective metallophthalocyanines (**2** and **3**) (Scheme 1). The syntheses of gallium and indium phthalocyanines (**4** and **5**) were achieved by treatment of **1** with anhydrous metal salts ($GaCl_3$ for **4** and $InCl_3$ for **5**) and DBU as a catalyst in suitable solvents (quinoline for **4** and hexan-1-ol for **5**) at 170 °C in a sealed tube under microwave irradiation for 25 min (Scheme 1). The new phthalocyanines were obtained pure through silica gel column chromatography by using different mixtures of solvents [THF:hexane (20:1, v:v) for cobalt (**2**), ethyl acetate:n-hexane (5:1, v:v) for zinc (**3**), THF:methanol (1:1, v:v) for gallium (**4**), THF:methanol (25:1, v:v) and THF:ethyl acetate (1:1, v:v) for indium (**5**) phthalocyanines].

As expected, the disubstituted phthalonitrile containing differing substituents in the 4- and 5-positions generated metal phthalocyanines (**2**–**5**) which constitute a mixture of four positional isomers. These isomers are mentioned by their molecular symmetry (C_s, D_{2h}, C_{2v}, and C_{4h}). No separation of these four structural isomers was achieved, employing common column chromatography or by recrystallization was reported. Therefore, we did not attempt to separate the structural isomers **2**–**5**.

The lack of solubility of unsubstituted phthalocyanines in solvents, such as chloroform, methanol, or THF, is well known. Peripheral, non-peripheral, and/or axial substituents can dramatically increase the overall solubility of phthalocyanines in water or common solvents. In general, the presence of a pair of different substituents in each aromatic ring results in better solubility than two identical substituents in the aromatic ring. Thus, due to the presence of four constitutional isomers, phthalocyanines have enhanced solubility. Therefore, **2**–**5** have exceedingly high solubility in chloroform, THF, DMF, and DMSO.



Scheme 1. Synthesis of **2**–**5**. i. Na_2CO_3, DMF, 50 °C, 96 h, ii. Cs_2CO_3, DMF, 45 °C, 48 h, iii. 1-hexanol, 24 h, 160 °C, DBU (for **2**, **3**); quinoline, DBU, 170 °C, 25 min, MW (for **4**); 1-hexanol, DBU, 170 °C, 25 min, MW (for **5**).

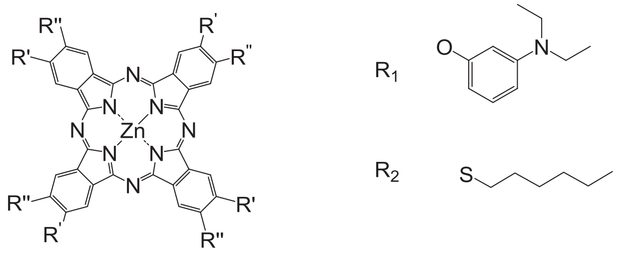
Several spectroscopic techniques were employed to elucidate the structures of the newly obtained compounds, including proton and carbon nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, ultraviolet-visible spectrophotometry, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. The spectral data for **2**–**5** were consistent with the formulations suggested. Vibrations in the relevant IR spectrum at 2230 cm^{-1} for **1** indicated the presence of a C≡N group, whereas those at 1247 cm^{-1} implied the availability of a C–O–C group. Stretches were also observed at 3076 cm^{-1} and 2959, 2928 cm^{-1} for aromatic and aliphatic groups, respectively. The FT-IR spectra of phthalocyanines are generally almost identical. The characteristic vibrations for the ether groups were observed at *ca.* 1230 cm^{-1} for all phthalocyanine derivatives studied.

In the proton nuclear magnetic resonance spectra of the phthalocyanine precursor **1** in deuterio-chloroform, three singlets were displayed at 7.57, 6.96, and 6.29 ppm, three doublets at 7.47, 6.57 and 6.24 ppm, belonging to aromatic protons in the system. The $N–CH_2$ and $N–CH_2–CH_3$ protons of ethylaminophenoxy moiety were observed as a quartet at 3.34 ppm and a triplet at 1.16 ppm, respectively. Aliphatic protons of the hexylthio group were detected at 2.98 ppm as a triplet, at 1.76 ppm as a quartet, at 1.50–1.32 ppm as another quartet, and at 0.90 ppm as a triplet. Due to the use fact of high concentrations of phthalocyanines for recording ^1H NMR spectra of **2**–**5**, the resulting peaks are quite broad, indicating high aggregation of the macrocycles. Another reason for the broad signals in the final phthalocyanine compounds is the presence of positional isomers, which are substituted differently.

The mass spectral results confirmed the presence of the structures we proposed. For **2** and **3**, the molecular ion peaks were observed at *m/z*: $[M–H]^+$ 1687.91 and *m/z*: $[M]^+$ 1694.25, respectively. The mass spectrum of **5** showed peaks, most important of which were at *m/z*: 1803 for $[M+Na]^+$, *m/z*: 1710 for $[M–5CH_2]^+$, and *m/z*: 1675 for $[M–5CH_2–Cl]^+$. The results of the elemental analyses were in agreement with the percentages of carbon, hydrogen, and nitrogen in the structures of all phthalocyanines.

3.2. Electronic absorption (ground-state) and fluorescence spectra

Absorption spectra are useful for obtaining information on whether a phthalocyanine has been formed. Generally, most phthalocyanines have bands in the visible region at 600–700 nm (referred to as the Q-band) resulting from the HOMO→LUMO ($\pi \to \pi^*$) transitions, as well as in the ultraviolet region at 300–350 nm (B-band) due to transitions between lower π-levels to LUMO.



$R' = R_1$, $R'' = R_2$ **(3)**
$R' = R_1$, $R'' = Cl$ **(6)**
$R' = R_1$, $R'' = R_1$ **(7)**

Figure 1. Zinc phthalocyanine derivatives.

The electronic absorption spectra (ground-state) of **2–5** dissolved in chloroform showed the presence of monomeric species along with a single (narrow) Q-band at *ca.* 695–728 nm and a B band at *ca.* 315–362 nm. The Q-bands of the synthesized phthalocyanines were observed at 695 nm (**2**), 698 nm (**3**), 715 nm (**4**) and 728 nm (**5**) (in $CHCl_3$) (Figure 2). We also detected the vibronic bands of **2–5** at 627, 626, 644 and 651 nm, correspondingly, all of which correlated with n–π^* transitions [27]. Because of the central metal ion nature, the Q-band maxima of the series of compounds were in the following descending order In >Ga>Zn>Co.

Within the scope of this work, we studied the aggregation behavior of zinc phthalocyanine in chloroform with different concentrations (Figure 3), which were found to conform to the Beer-Lambert Law at concentrations within the range 4×10^{-6} – 14×10^{-6} mol dm^{-3} for **3**. The increase in the concentration of the substance causes parallel increase of the intensity of the Q band, and no new band due to aggregation is observed [28–30].

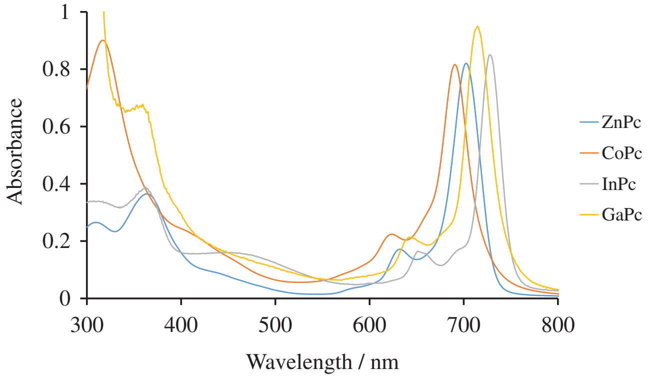


Figure 2. UV spectra of CoPc (**2**), ZnPc (**3**), GaPc (**4**) and InPc (**5**) in $CHCl_3$.

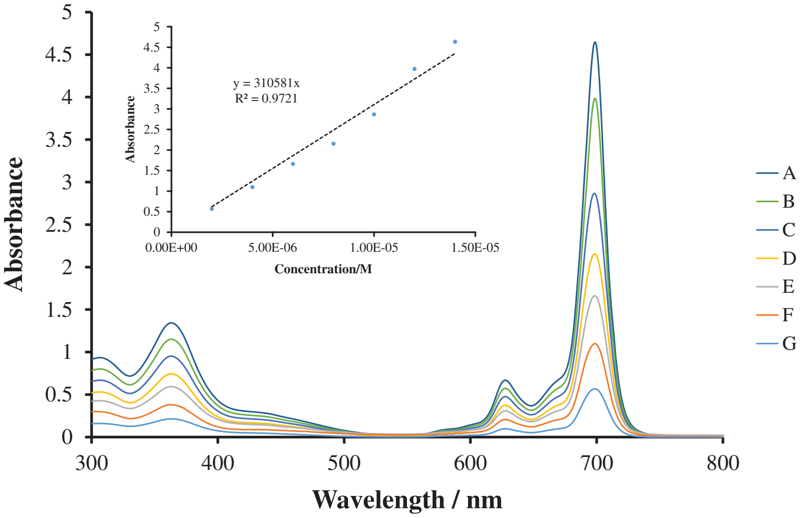


Figure 3. Absorption spectra of ZnPc (**3**) in $CHCl_3$ at different concentrations: 14×10^{-6} (A), 12×10^{-6} (B), 10×10^{-6} (C), 8×10^{-6} (D), 6×10^{-6} (E) and 4×10^{-6} (F) mol dm^{-3}.

The electronic absorption spectra of **3** in various solvents (chloroform, THF, DMF, and DMSO) were also investigated (Figures 4 and 5). The bathochromic shift of the Q band for **3** was due to the effect of the solvent and was changed in the following order: ethyl acetate <THF<DMF<chloroform<DMSO. The electronic absorption spectra of **3** in these solvents were examined by the Bayliss method [30]. The plot of the frequency of the Q band versus $(n^2–1)/(2n^2+1)$ function is depicted in Figure 5, in which n is the refractive index of the solvent used. There is a linear response owing to the solvent used, caused by the solvent itself, not by a ligation effect [31].

In comparison of the diethylaminophenoxy- and chlorine-substituted phthalocyanines reported earlier with the compounds we synthesized in the present paper [16, 21], we found that substitution of the chloro-group for hexylsulfanyl moiety clearly yielded a red-shift of the Q-band maxima at approximately 15–21 nm for **2** and **3** (Figure 6). The Q-band maxima of the gallium and indium phthalocyanines (**4** and **5**) were further bathochromically shifted, when compared to **2** and **3** having divalent metal ions in the core; the reason of this might

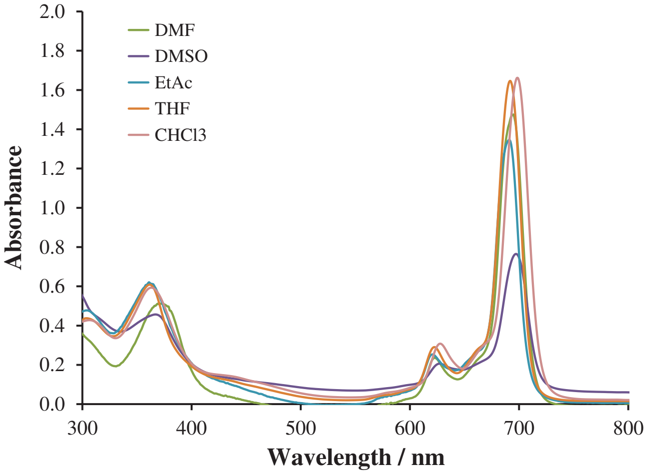


Figure 4. Absorption spectra of ZnPc (**3**) in different solvents (6×10^{-6} mol dm^{-3}).

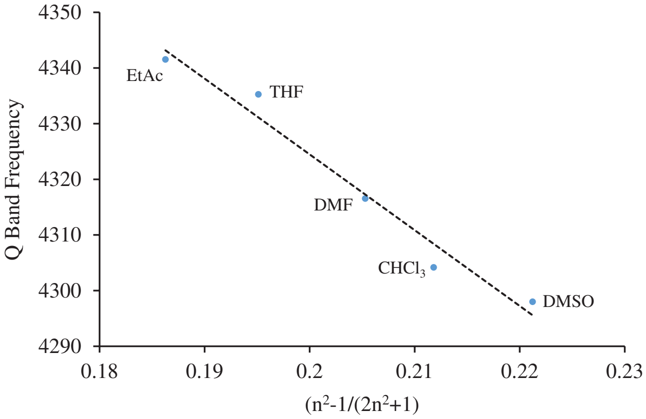


Figure 5. Plot of the Q band frequency of ZnPc (**3**) against $(n^2–1)/(2n^2+1)$, where n is the refractive index of the solvent.

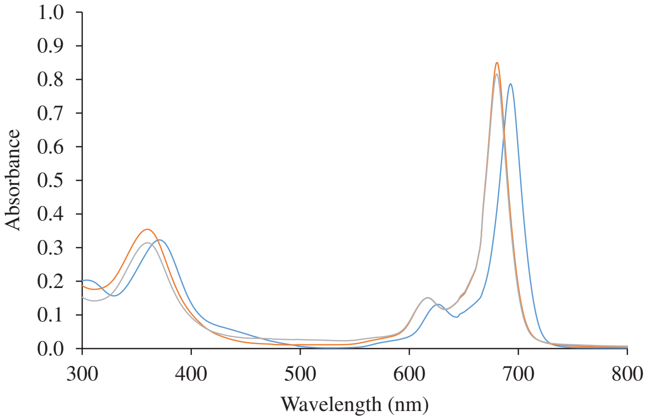


Figure 6. Electronic spectra of the zinc phthalocyanine derivatives (**3**, **6**, and **7**) in DMF. The concentration in this study is 4.00 μmol dm^{-3}.

be the influence of the atom in the axial position and the relevant higher oxidation state of the metal ion in question.

Fluorescence and fluorescence quenching measurements were performed as described [23]. Fluorescence studies of the zinc phthalocyanines have been recorded in DMF. The absorption spectra, fluorescent emission, and subsequent excitation spectra of zinc phthalocyanines (**3**, **6** and **7**) are presented in Figure 7. We detected fluorescence emission peaks at 713, 700 and 702 nm (Table 1). The Stokes' shifts of the ZnPc derivatives were between 5.00×10^5 and 5.26×10^5 cm^{-1}. The fluorescence quantum yields (Φ_F) were calculated by comparison with unsubstituted ZnPc (Table 2).

The fluorescence quantum yield (Φ_F) of a compound is a measure of the molecular efficiency of the fluorescent process. The comparative method is the most reliable approach for calculation of Φ_F. The method known as Φ_F uses a well-characterized sample as a standard. Essentially, when the excitation wavelength of the solutions of the standard and samples are at the same excitation wavelength, it may be speculated that they absorb the same amount of photons. The ratio of two quantum yields is what one gets for a simple ratio of fluorescent intensities of two compared solutions.

Table 1 lists the data of the fluorescence quantum yield, fluorescence lifetimes, and natural radiative lifetimes. The Φ_F values of the zinc phthalocyanines synthesized in this study were lower than that of unsubstituted zinc phthalocyanine in DMF.

Substituent groups may affect the fluorescence properties of phthalocyanines. Structural rigidity plays a role in the fluorescence intensity of a chromophore with a more rigid structure resulting in enhanced fluorescence [32]. Electron-accepting functional groups (such as carboxyl and nitro) result in quenching of the fluorescence [33]. The fluorescence quantum yield of 6-thiohexanoic acid-substituted zinc phthalocyanine is lower than unsubstituted ZnPc in DMF [34]. The fluorescence quantum yields of the poly (aryl benzyl ether) dendrimeric-zinc phthalocyanine are higher than unsubstituted ZnPc in DMF [35]. The bigger Φ_F value in the higher generation dendrimer indicates the dendrimer backbone becomes less rigid as the molecule size grows larger. Salicylhydrazone-zinc complex and its Schiff base metal complex have lower fluorescence quantum yields than standard ZnPc in DMSO because of the bulky substituents which promote intersystem crossing [36].

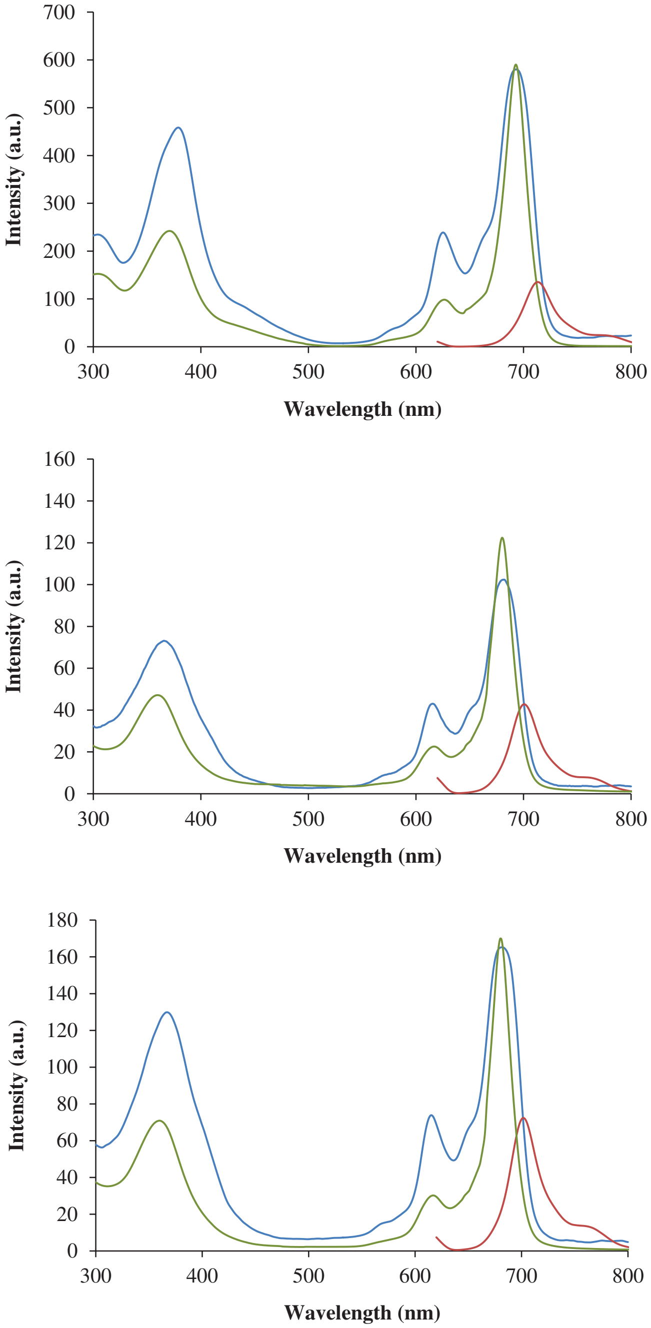


Figure 7. Absorption (top), excitation (middle), and emission (bottom) spectra for **3**, **6** and **7** in DMF; excitation wavelength is 614 nm.

Fluorescence lifetime (τ_F) is the average time of the molecule at the excited state before fluorescing. This value affects the quantum yield, and longer lifetime results in a higher quantum yield of fluorescence. Factors, such as internal conversion and intersystem crossing, reduce the fluorescence lifetime while the value of Φ_F decreases. In the present examination,

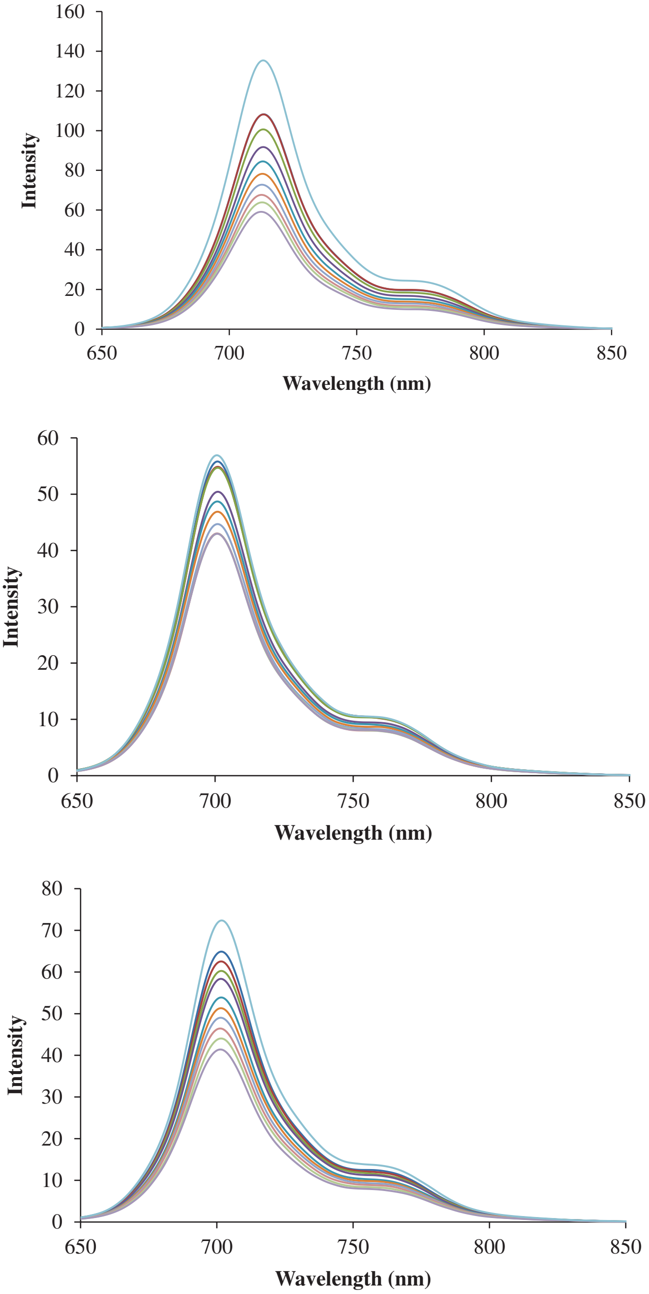


Figure 8a. Fluorescent emission spectral changes of **3**, **6**, and **7** (4.00 μmol dm^{-3}) in which different concentrations of benzoquinone in DMF was added as quencher. The concentration of benzoquinone is 0.000, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm^{-3}.

fluorescent lifetimes (τ_F) were calculated by the equation of Strickler and Berg. [37]. Using this equation, we obtained a good correlation between fluorescent lifetimes, both experimentally and theoretically, of the unaggregated molecules, which was also the case for the octa-(3-(diethylamino)phenoxy- and hexylsulfanyl-substituted Pc compounds in DMF. The

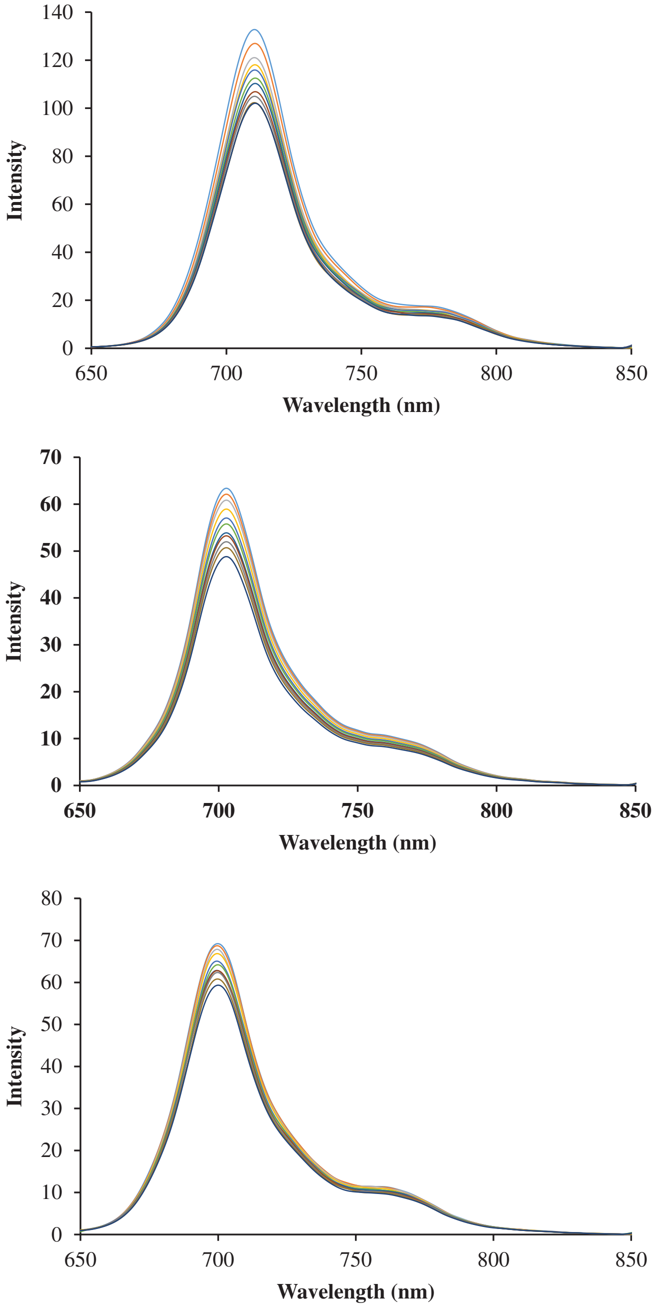


Figure 8b. Fluorescent emission spectral changes of **3**, **6**, and **7** (4.00 μmol dm^{-3}) in which different concentrations of hydroquinone in DMF was added as quencher. The concentration of hydroquinone is 0.000, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm^{-3}.

fluorescence lifetimes (τ_F) and natural radiative lifetimes (τ_0) of ZnPc were calculated by the respective equation, and the corresponding values are displayed in Table 2. The lifetimes of fluorescence (τ_F) values of the octakis(3-(diethylamino)phenoxy and hexylsulfanyl-substituted

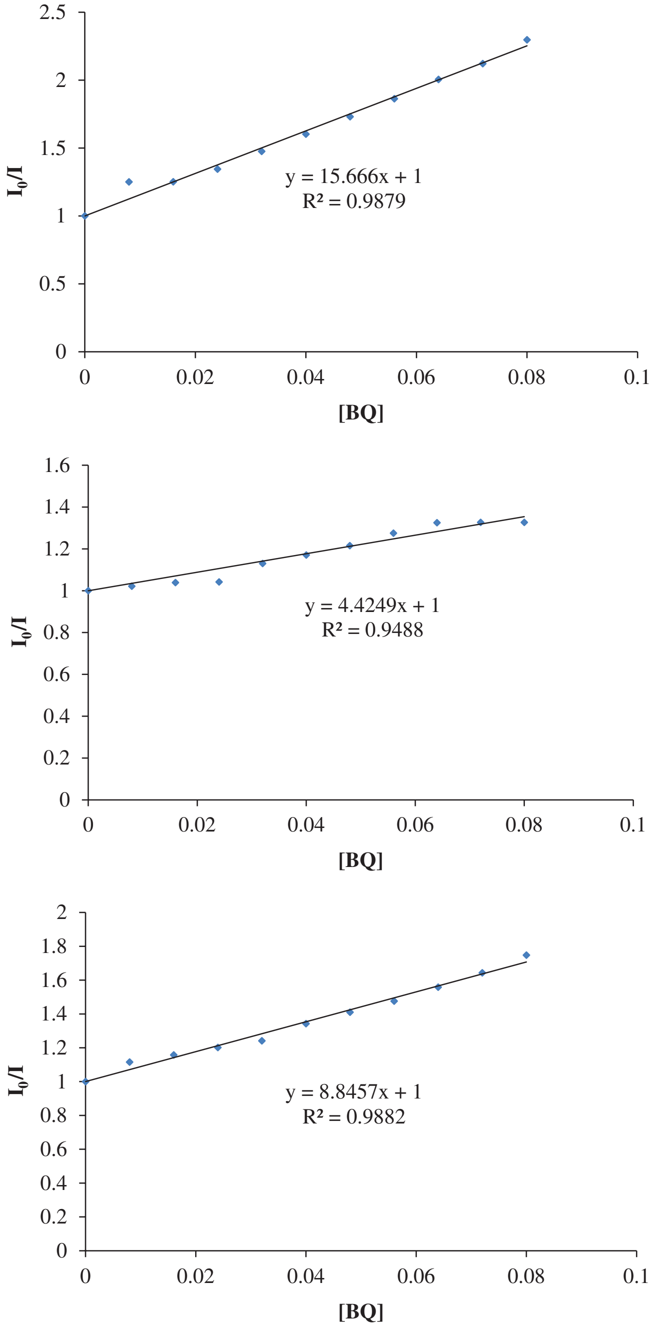


Figure 9a. Stern-Volmer plots of **3**, **6**, and **7** quenched by BQ. [ZnPc] = 4.00 µmol dm^{-3} in DMF. Concentration of the quencher is 0.000, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm^{-3}.

zinc phthalocyanine are lower than that of unsubstituted zinc phthalocyanine in DMF [38]. The k_F value of the substituted zinc phthalocyanines was smaller than that of unsubstituted ZnPc [23].

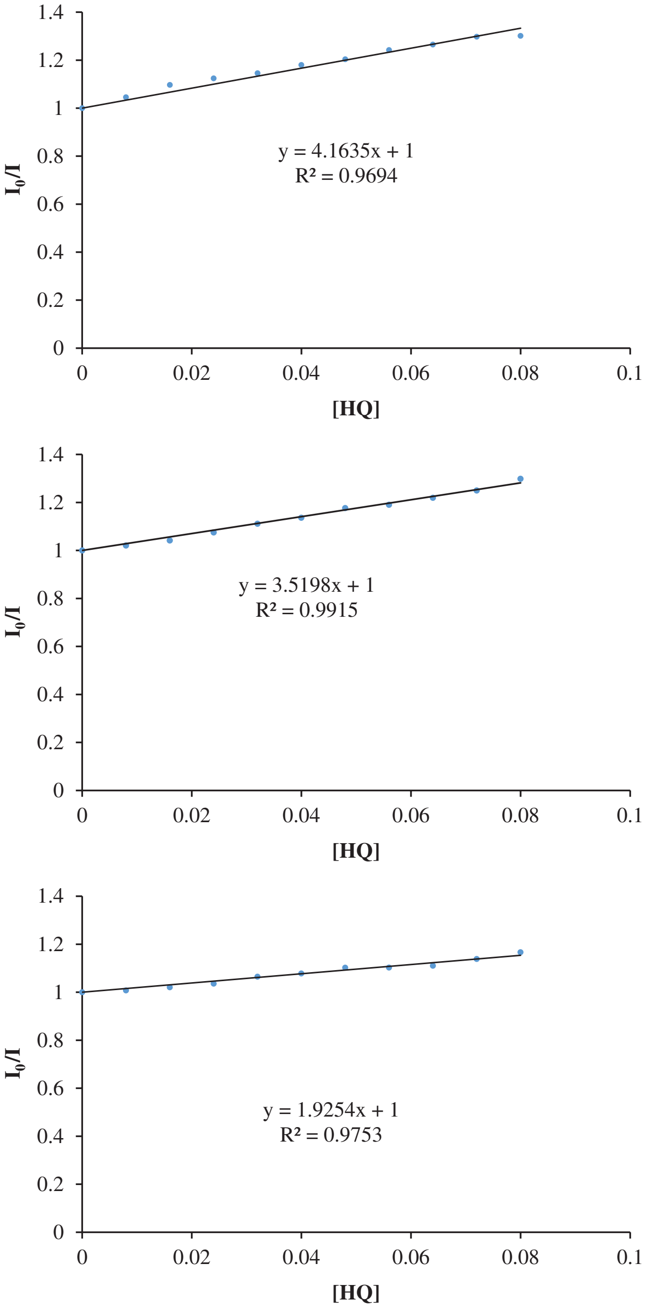


Figure 9b. Stern-Volmer plots of **3**, **6**, and **7** quenched by HQ. [ZnPc] = 4.00 μmol dm^{-3} in DMF. Concentration of the quencher is 0.000, 0.008, 0.016, 0.024, 0.032 and 0.040 mol dm^{-3}.

3.3. Fluorescence quenching studies by BQ

Fluorescence quenching features were investigated by adding benzoquinone (BQ) or hydroquinone (HQ) to the ZnPc solutions. In the presence of quinone, an energy transfer occurred between the excited Zn(II) phthalocyanine (fluorophore) and BQ/HQ (quencher). We

Table 1. Substituted ZnPcs in this paper and unsubstituted ZnPc: absorption, excitation, and emission spectral data (in DMF).

Compound	Q Band λ_{max} (nm)	Log ε	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes' shift Δ_{Stokes} ($\times 10^5$ cm^{-1})
3	693	5.23	693	713	5.00
6	680	5.35	682	700	5.56
7	680	5.34	683	702	5.26
ZnPc[a]	670	5.17	670	676	16.67

[a] Ref. [21].

Table 2. Photophysical and photochemical parameters, and fluorescence quenching of the zinc phthalocyanines in DMF as solvent.

Compound	Φ_F	τ_F (ns)	τ_o (ns)	k_F (s^{-1})($\times 10^8$)[a]	K_{sv}[c]	k_q/($\times 10^{10}$ s^{-1})[c]
3	0.06	0.437	7.29	13.72	15.67	3.59
6	0.01	0.068	6.81	14.68	4.42	1.30
7	0.02	0.138	6.89	14.51	8.85	3.20
ZnPc[b]	0.17	1.03	6.05	16.53	57.60	5.59

[a] k_F is the rate constant for fluorescence. Values were calculated using $k_{F=}\Phi_F/\tau_F$.
[b] Ref. [21].
[c] k_F is the bimolecular quenching constants and K_{sv} is the Stern-Volmer constant (for benzoquinone).

established a progressive decrease in the fluorescence intensity with increase in the concentration of the quencher. The fluorescent quenching of zinc phthalocyanines (**3**, **6** and **7**), obtained by adding known amounts of benzoquinone or hydroquinone in DMF, obeys the kinetics mechanism outlined by Stern and Volmer [39]. The fluorescent spectrum of ZnPc with different amounts of benzoquinone and hydroquinone as the quencher can be seen in Figure 8(a) and 8(b). When we generated the Stern-Volmer plots for **3**, **6**, and **7**, straight lines were obtained; thus, the quenching mechanisms obeyed the diffusion-control hypothesis [39]. The values of zinc phthalocyanines can be observed in the slopes, depicted in Figure 9(a) and 9(b). In addition, the calculated K_{SV} values are presented in Table 2. The K_{sv} values of the phthalocyanines in this study were lower than that for unsubstituted ZnPc ($K_{sv} = 57.60$ M^{-1}). Comparing fluorescence quenching values with BQ and HQ, the phthalocyanines interact better with benzoquinone. The K_{sv} values of the zinc phthalocyanines were reduced when using hydroquinone. The k_q value (bimolecular quenching constants) of the substituted zinc phthalocyanine was smaller than that of unsubstituted ZnPc [23].

4. Conclusion

We described the syntheses and characterizations of metallophthalocyanines (M=Co, Zn, Cl-Ga, Cl-In) substituted with two different substituents on each aromatic group. The electronic absorption spectra of the zinc phthalocyanine in various solvents were investigated. Aggregation behavior of the zinc phthalocyanine was also examined. According to Beer-Lambert Law, no aggregation was observed in chloroform in the concentration range from 4×10^{-6} to 14×10^{-6} mol dm^{-3}. The photophysical properties of three different ZnPcs were studied in DMF, and the effect of the peripheral substituents on photophysical properties was investigated. Fluorescence quantum yields of the derivatives were lower than those of the standard. The decrease in the fluorescent quantum yields is related to the low degree of symmetry observed in these complexes. Furthermore, the fluorescence of the ZnPc compounds was typically quenched by benzoquinone. The Stern-Volmer kinetics were followed in the fluorescence quenching of zinc phthalocyanines by benzoquinone in DMF.

Disclosure statement

No potential conflict of interest was reported by the authors.

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