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The synthesis and photophysical properties of novel, symmetrical, hexadecasubstituted Zn phthalocyanines and related unsymmetrical derivatives

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Abstract

The synthesis of novel, symmetrical, hexadecasubstituted phthalocyaninatozinc(II) bearing eight, fluorinated phenoxy groups in peripheral positions and eight, non-peripheral hexyloxy groups as well as their related unsymmetrical derivatives is described. The compounds were characterized by ^{1}H NMR, GC–MS, UV–vis and IR. The synthesized ZnPc complexes possess excellent solubility in various organic solvents such as CH_2Cl_2, THF, acetone and ethyl acetate and do not readily aggregate in solution. The new complexes show interesting luminescence properties in different organic solvents.

Keywords: Phthalocyanines; Fluorinated phenoxy; Luminescence; Solubility

1. Introduction

Phthalocyanines (Pcs) are 18, π-electron macrocyclic conjugated systems which attract great interest due to their diverse applications in medicinal and materials chemistry [1]. Such applications are based on their relative stability to air and light, and the delocalized electronic nature of the Pc ring system; the majority of recent uses of phthalocyanines derive from the electronic properties of the π-electrons of the macrocycles. In medicine, phthalocyanines are excellent photosensitizers in photodynamic therapy [1] and have also shown good selectivity toward tumor cell adsorption; their luminescent properties have been utilized in clinical photodiagnosis [2,3].

By varying the peripheral or non-peripheral substituents and/or the central metal of Pcs, their physical properties can be tuned to suit a desired technological application [4]. The nature of the substituents is important not only in terms of the solubility of Pcs but also in the context of the state of their aggregation in solution as well as their physical and photophysical properties [5–7].

Recently, we reported that zinc phthalocyanine derivatives functionalized with substituents such as thiophene and alkyl groups in non-peripheral positions on the benzenoid rings, were moderately soluble in organic solvents, but not in water and the compounds offered potential as photosensitizers due to their interesting photophysical properties [8]. Although considerable interest has been directed toward the synthesis of tetra- and octa-substituted metal phthalocyanines, less attention has been devoted to the synthesis of hexadecasubstituted metal phthalocyanines [9–11].

This paper concerns the preparation of novel, hexadecasubstituted phthalocyanines and unsymmetrical ZnPc dyes through the substitution of Pc with hexyloxy groups in non-peripheral and substituted-phenoxy groups in peripheral positions. The luminescent properties of the synthesized complexes, which are potential photodynamic therapy agents [12], in organic solvents are described.

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2. Experimental

All reagents and solvents used were of reagent-grade quality and were used without further purification unless otherwise stated. Melting points were determined using a Kofler hot-stage melting point apparatus. IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrometer FTIR-400 using KBr disks. ^{1}H NMR spectra (400 MHz) were recorded on a Bruker AVANCE 400 MHz and were obtained using the deuterated solvents specified; microanalyses were performed using a Vario Elemental analyzer CHNS.

Steady-state absorbance measurements were carried out using a 1 cm path length cell housed in a Jasco V570 DS spectrophotometer. Steady-state luminescence measurements were carried out using a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube. Fluorescence lifetime measurements were recorded by a single-photon counting method using the second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser [Spectra-Physics, Tsunami, 1.5 ps full width at half-maximum (fwhm)] and a streak scope (Hamamatsu Photonics) equipped with a polychromator as excitation source and detector, respectively.

2.1. Preparation of 4,5-dichloro-3,6-dihydroxyphthalo nitrile

A mixture of 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (10 g, 0.044 mol) and $Na_2S_2O_4$ (aq) (13.5 g, 0.078 mol in 170 mL water) in toluene was stirred at room temperature for 20 min. The resultant precipitate was filtered and washed with cold water (30 mL) and then hexane. The product was dried under vacuum at 60 °C for 24 h and purified by recrystallization from acetone/water to yield 4,5-dichloro-3,6-dihydroxyphthalonitrile as off-white powder (7.1 g, 70%). IR (KBr): ν_{max}, cm^{-1} 3240 (br), 2225 (m). GC–MS *m/z* (%): 230 (M^+). δ_C (400 MHz, $CDCl_3$): 150.8, 129.1, 113.7, 101.6.

2.2. Preparation of 4,5-dichloro-3, 6-dihexyloxyphthalonitrile

A mixture of 4,5-dichloro-3,6-dihydroxyphthalonitrile (2 g, 8.73 mmol), triphenylphosphine (5.49 g, 20.9 mmol) and 1-hexanol (2.3 g, 22.7 mmol) was dissolved in dry THF (80 mL) and cooled to 0 °C. A solution of diisopropyl azodicarboxylate (4.76 g, 21.5 mmol) in THF (30 mL) was added dropwise over 30 min. The ensuing solution was slowly warmed to room temperature and stirred for an additional 16 h after which time, the solvent was removed under reduced pressure, providing a dark red oil, which was dissolved in diethyl ether (20 mL) and the solution was then filtered to remove the undissolved triphenylphosphine oxide. The solvent was evaporated and the remaining residue was purified using column chromatography (silica gel, eluent: DCM/petroleum ether 40–60 °C, 1:2) to obtain 4,5-dichloro-3,6-dihexyloxyphthalonitrile as white powder (2.8 g, 81%). Found: C, 61.03; H, 6.89; N, 6.95. $C_{20}H_{26}C_{12}N_2O_2$ requires C, 60.46; H, 6.60; N, 7.05%. δ_H (400 MHz, $CDCl_3$): 4.21 (4H, t), 1.88 (4H, quint), 1.47 (4H, m), 1.34 (8H, m), 0.91 (6H, t), δ_C (400 MHz, $CDCl_3$): 155.4, 135.4, 112.2, 108.8, 31.4, 29.9, 25.2, 22.5, 14.02.

2.3. General procedure for the preparation of 4,5-bis-(3,5-disubstitutedphenoxy)-3,6-bis(hexyloxy)phthalonitrile

4,5-Dichloro-3,6-dihexyloxyphthalonitrile (0.5 mmol), **2**, and 3 mmol phenol were heated to 100 °C in dry DMSO with stirring under a nitrogen atmosphere. Dry, finely powdered K_2CO_3 was added in portions (5 × 20 mmol) every 5 min; the mixture was then stirred at 100 °C for 30 min. After cooling to room temperature, the ensuing reaction product was diluted with dichloromethane and the combined organic layers were washed with brine, dried with $MgSO_4$ and filtered. The solvent was evaporated and the resulting product was purified by column chromatography (silica gel, eluent: *n*-hexane/THF 10:1).

*2.3.1. Synthesis of 4,5-bis(3,5-difluorophenoxy)-3, 6-bis-(hexyloxy)phthalonitrile (**4a**)*

Yield (142 mg, 48%) as yellow oil. IR (KBr): ν_{max}, cm^{-1} 2930, 2850 (CH_2), 1590 (Ph), 2224 (C≡N), 1600 (C=C), 1468, 1315, 1263, 1125 (C–O–C), 963, 832. Anal. Calcd. for $C_{32}H_{32}F_4N_2O_4$: C, 65.74; H, 5.52; N, 4.79%. Found: C, 65.58; H, 6.56; N, 4.51. MS (GC–MS): *m/z* (CI) 585. δ_H (400 MHz; $CDCl_3$): δ_H, ppm 6.58 (2H, tt, Ar-*H*), 6.29 (4H, dd, Ar-*H*), 4.17 (4H, t, OCH_2), 1.66 (4H, quint, $-CH_2CH_2(CH_2)_3CH_3$), 1.2–1.48 (12H, m, $-CH_2CH_2(CH_2)_3CH_3$), 0.8 (6H, t, $2CH_3$), δ_C (400 MHz, $CDCl_3$): 164.7, 162.3, 157.6, 157.6, 152.4, 145.1, 112.2, 107.5, 99.6, 31.4, 29.7, 25.1, 22.50, 14.01.

*2.3.2. Synthesis of 4,5-bis(3,5-dimethoxyphenoxy)-3, 6-bis(hexyloxy)phthalonitrile (**4b**)*

Yield (130 mg, 40%) as a brownish powder. IR (KBr): ν_{max}, cm^{-1} 2930, 2850 (CH_2), 1590 (Ph), 2224 (C≡N str), 1600 (C=C), 1468, 1315, 1263, 1125 (C–O–C), 963, 832. Anal. Calcd. for $C_{36}H_{44}N_2O_8$: C, 68.34; H, 7.01; N, 4.43%. Found: C, 67.91; H, 7.17; N, 4.31. MS (GC–MS): *m/z* (CI) 633. δ_H (400 MHz, $CDCl_3$): δ_H, ppm 6.15 (2H, t, 2*Ar-H*), 5.84 (4H, d, 2*Ar-H*), 4.13 (4H, t, $2OCH_2$), 3.69 (6H, s, $2OCH_3$), 1.64 (4H, q), 1.2–1.48 (12H, m), 0.84 (6H, t, $2CH_3$), δ_C (400 MHz, $CDCl_3$): 164.6, 162.2, 157.6, 152.2, 145.1, 112.2, 108.0, 99.5, 31.4, 30.3, 29.7, 25.2, 22.50, 14.4.

2.4. General procedure for the synthesis of zinc phthalocyanine derivatives using DBU

A mixture of 3,6-didecylphthalonitrile (77 mg, 0.191 mmol), 4,5-bis(3,5-difluorophenoxy)-3,6-bis(hexyloxy)-phthalonitrile (112 mg, 0.191 mmol), zinc acetate dihydrate (excess) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry *n*-hexanol (10 mL) was heated at reflux for 12 h with stirring under an argon atmosphere. The reaction mixture was cooled to room temperature and the solvent was

rotary evaporated under reduced pressure. The resulting dark green compound was separated by silica gel column chromatography using the appropriate eluent. Column chromatography using silica gel with *n*-hexane/THF 20:1 as eluent gave five bands. The first fraction was the symmetrical 1,4,8,11,15,18,22,25-octakis (hexyl) phthalocyaninatozinc(II) (16% yield) and the second green fraction was 1,4-dihexyloxy-2,3-bis(3,5-*difluoro*phenoxy)-8,11,15,18,22,25-hexakis(decyl)phthalocyaninato zinc(II), **5a**. Yield (36 mg, 10%) as blue waxy product. IR (KBr): ν_{max}, cm^{-1} 3070 (Ar-CH), 2929 and 2850 (CH_2), 1600 (C=C), 745. δ_H (400 MHz, $CDCl_3$): δ_H, ppm 7.87–7.91 (4H, m, Ar-*H*), 7.71 (2H, d, Ar-*H*), 6.68 (2H, dd, Ar-*H*), 6.57 (4H, tt, Ar-*H*), 4.74 (4H, t, 2Ar-OCH_2–), 4.63 (4H, t, Ar-CH_2), 4.45 (4H, t, Ar-CH_2–), 4.40 (4H, t, Ar-CH_2), 1.96–2.20 (16H, m, 6Ar-CH_2CH_2– and 2Ar-O–CH_2CH_2), 0.72–1.64 (120H, m, 6 $(CH_2)_8CH_3$ and 6O–$(CH_2)_3CH_3$). UV–vis (TN): λ_{max}, nm: 719, 655. MS (GC–FAB): *m/z* (%) 1877 $[M+H]^+$.

The eluent was changed to *n*-hexane/THF 10:1 to collect the third fraction and the solvent was evaporated to provide 2:2 ZnPc, 1,4,8,11-tetrahexyloxy-2,3,9,10-tetra-(3,5-*difluoro*-phenoxy)-15,18,22,25-tetrakis(decyl)phthalocyaninato zinc(II), **5b**. Yield (27 mg, 4%) as green solid product. IR (KBr): ν_{max}, cm^{-1} 3056 (Ar-CH), 2939 and 2850 (CH_2), 1603, 850. δ_H (400 MHz, $CDCl_3$): δ_H, ppm 7.85–7.87 (4H, m, Ar-*H*), 6.45–6.61 (12H, m, Ar-*H*), 4.86 (4H, t, OCH_2), 4.45–4.67 (12H, m), 2.12 (4H, m), 1.91 (4H, m), 1.74 (4H, quint), 1.52 (4H, quint), 1.01–1.29 (80H, m) 0.54–0.87 (24H, m, 8CH_3). UV–vis (TN): λ_{max}, nm: 726, 665. MS (GC–FAB): *m/z* (%) 2050 $[M+H]^+$.

The fourth fraction was collected by changing the eluent to *n*-hexane/THF 9:1 and is expected to be the asymmetrical 1:3 zinc phthalocyanine, 1,4,8,11,15,18-hexahexyloxy-2,3,9,10,16,17-hexa-(3,5-*difluoro*phenoxy)-22,25-di(decyl)phthalocyaninatozinc(II), **5c**. Yield (8 mg, 2.8%) as waxy green product. MS (GC–FAB): *m/z* (%) 2229 $[M+H]^+$.

The final fraction, assigned to the symmetrical phthalocyanine, was collected by changing the eluent to *n*-hexane/THF 4:1. Further purification by column chromatography (silica gel, eluent: petroleum ether 40–60 °C/THF 10:1) secured 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16,17,23,24-octa-(3,5-*difluoro*phenoxy)phthalocyaninatozinc(II), **5d**. Yield (60 mg, 8.4%) as green waxy product. IR (KBr): ν_{max}, cm^{-1} 3050 (Ar-CH), 2943 and 2852 (CH_2). δ_H (400 MHz, CD_3CN): δ_H, ppm 6.70 (16H, m, Ar-H), 6.59 (8H, m, Ar-H), 4.89 (16H, t, 8OCH_2), 1.01–1.8 (64H, m), 0.72 (24H, t, 8CH_3). UV–vis (TN): λ_{max}, nm: 733, 668. MS (GC–FAB): *m/z* (%) 2405 $[M+H]^+$.

3. Results and discussion

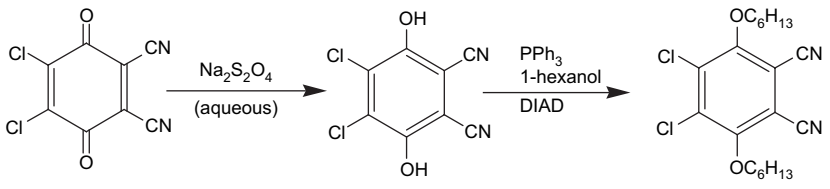
The synthesis of substituted phthalonitrile derivatives is a critical step in phthalocyanine synthesis. Of the different precursors, 4-nitro- and 4,5-dihalo-phthalonitriles are preferred because of the ease with which these compounds can be converted to alkyl/aryl ether or thioether derivatives [13–15]. The use of 4,5-disubstituted phthalonitriles as starting compounds in the synthesis leads to peripherally octa-substituted phthalocyanines. In this synthesis, 4,5-dihalo-phthalonitriles are reacted with *O*- and *S*-nucleophiles to form 4,5-disubstituted phthalonitriles, which are then converted to octa-substituted phthalocyanines [14].

3.1. Synthesis of the phthalonitrile precursors

In this work, the design of the suggested symmetrical hexadecasubstituted Zn phthalocyanine complexes require the phthalonitrile precursors to be fully substituted. Thus, reduction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) **1** with aqueous $Na_2S_2O_4$ results in the corresponding 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (DDHQ) **2** [16]. As a result of this conversion, there are two chloro and two hydroxyl groups which can be used to introduce two different substituents at the 3,6- and 4,5-positions of the phthalonitrile. The *Mitsunobu reaction* was utilized to rapidly alkylate the two alcohols at low temperature to obtain 4,5-dichloro-3,6-dihexyloxyphthalonitrile, **3**. This type of reaction is used to dehydrate aliphatic alcohols and phenols using triphenylphosphine and diisopropyl azodicarboxylate (DIAD) [17]. The ^1H NMR spectrum of **3** showed a triplet at 4.20 ppm assigned to the methylenoxy protons, (Scheme 1).

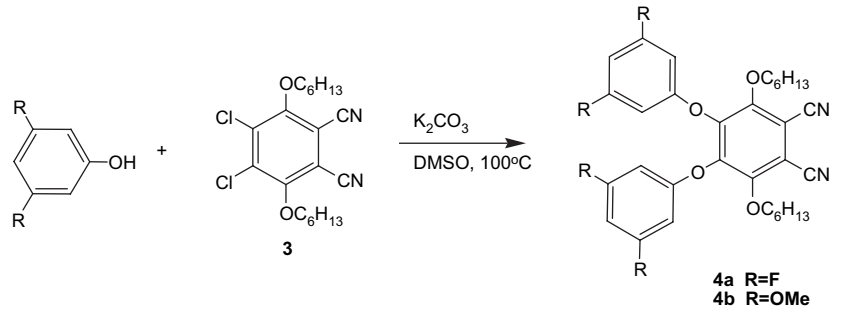
Subsequent nucleophilic displacement reaction was used to introduce the two substituted, aryloxy groups at the 4- and 5-positions in the phthalonitrile derivatives. Compounds **4a–b** were prepared by reaction of 4,5-dichloro-3,6-dihexyloxyphthalonitrile **3** with the appropriate phenol and K_2CO_3 in DMSO, Scheme 2.

For example, the 4,5-bis(3,5-difluorophenoxy)-3,6-dihexyloxyphthalonitrile **4a** was synthesized in 48% yield via treatment of 4,5-dichloro-3,6-dihexyloxyphthalonitrile **3** with 3,5-difluorophenol in presence of K_2CO_3 as a base. Compounds



1 2 3

Scheme 1. Synthesis of 4,5-dichloro-3,6-dihexyloxyphthalonitrile.

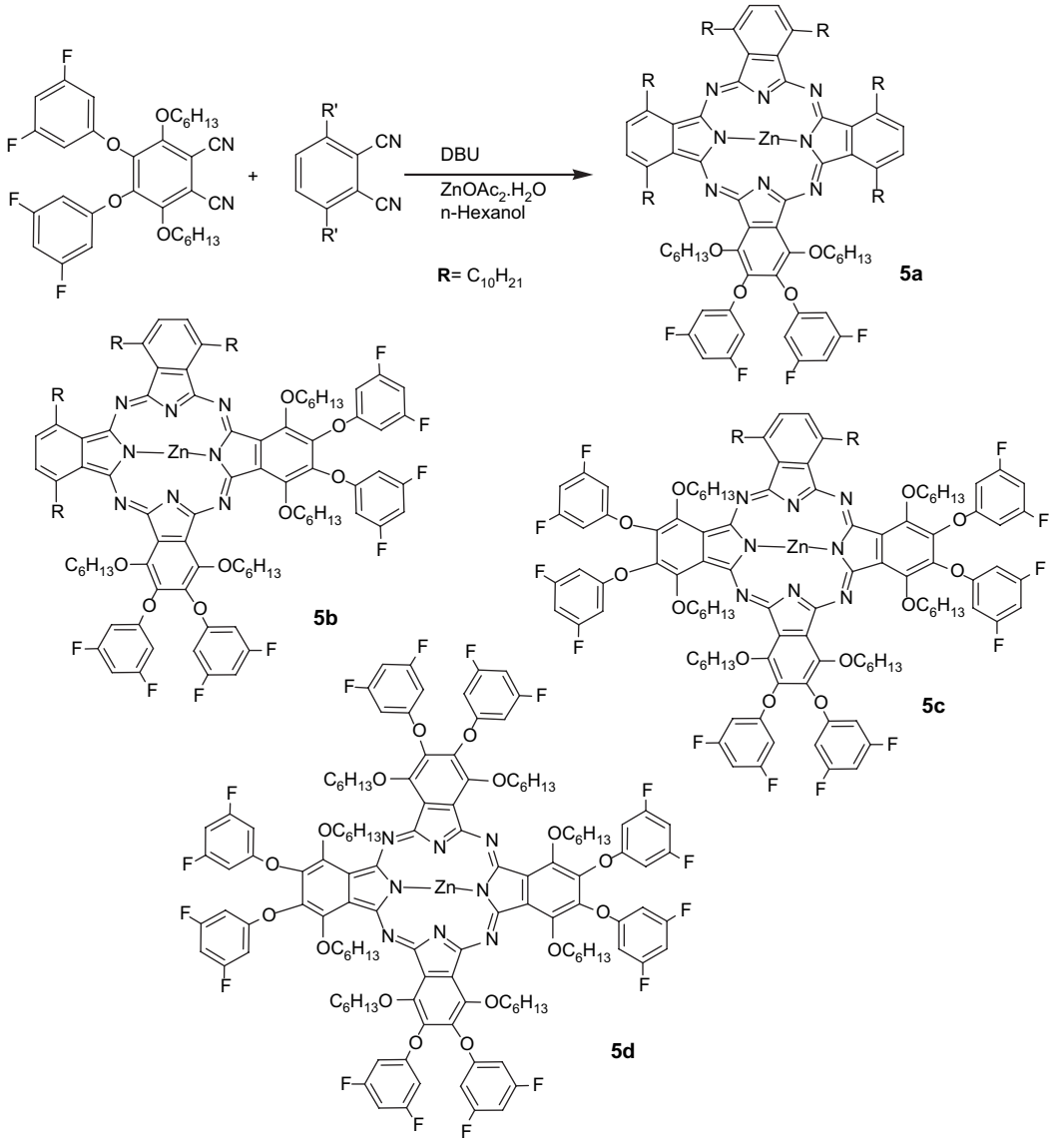


Scheme 2. Synthesis of 4,5-bis(disubstitutedphenoxy)-3,6-dihexyloxyphthalonitrile derivatives.

4a–b were isolated and characterized by ^{1}H NMR, FT-IR, elemental analysis, and GC–MS spectrometry (see Section 2).

3.2. Synthesis of ZnPc derivatives

The 4,5-bis(3,5-difluorophenoxy)-3,6-dihexyloxyphthalonitrile **4a** was condensed with 3,6-didecylphthalonitrile to form the desired ZnPcs, whereas the other precursor **4b** formed unstable products. Thus, the reaction of 4,5-bis(3,5-difluorophenoxy)-3,6-dihexyloxyphthalonitrile **4a** and 3,6-didecylphthalo nitrile (1:1 ratio) was carried out in *n*-hexanol in the presence of a $Zn(OAc)_2 \cdot 2H_2O$ and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 140 °C under an argon atmosphere for 12 h (Scheme 3). These conditions, developed by



Scheme 3. Synthesis of ZnPc derivataives **5a–d**.

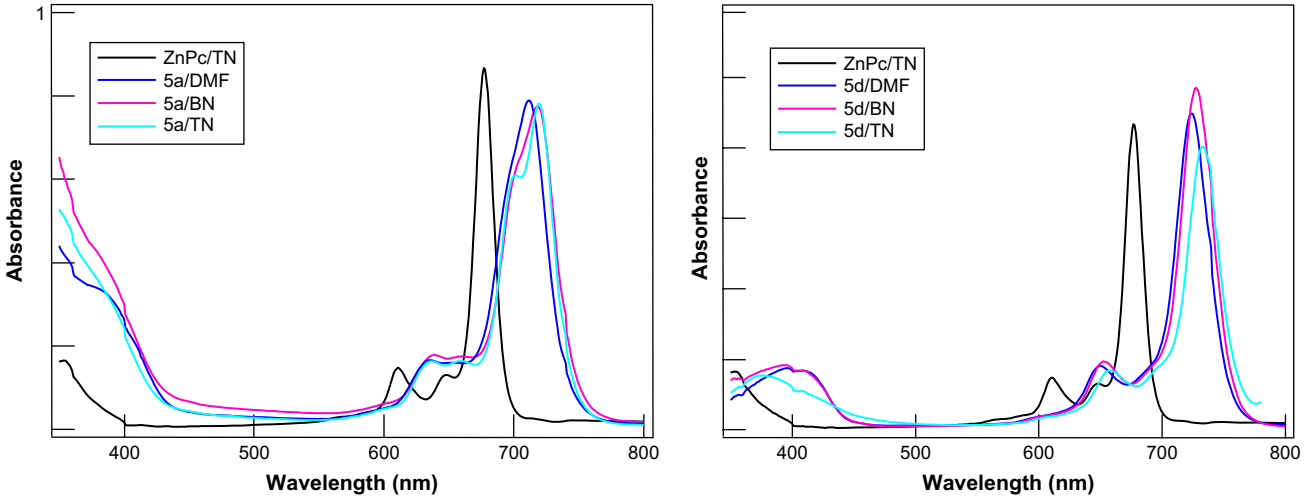


Fig. 1. Steady-state absorption spectra of the isolated Pcs in different organic solvents.

Tomoda et al. [18], have proven to be suitable for the synthesis of a wide variety of phthalocyanines [19]. According to the structure of these compounds (Scheme 3) the optical properties based on the absorption bands are expected to be red shifted due to the increase in the number of the π-conju gated systems. When the resulting crude product was sub jected to TLC analysis using *n*-hexane/THF (20:1) as eluent, it showed five separable spots. Purification by column chroma-tography enabled the separation of these five compounds. The first fraction contained the undesired symmetrical octade-cylphthalocyanine (AAAA) compound and the second fraction contained the required 3:1 ZnPc **5a**, which was collected. ^{1}H NMR revealed the presence of aromatic protons at 6.57–7.91 ppm; the three triplets at 4.63, 4.45, and 4.40 ppm were assigned to the 12 benzylic protons. The four methylenoxy protons appeared as a triplet at 4.74 ppm.

The AABB-isomer **5b** was collected and purified further to afford a waxy green product in 4% yield. This compound has only one plane of symmetry, and the methylene region of the ^{1}H NMR spectrum showed four peaks compared with the ABAB-isomer. The triplet at 4.86 ppm integrating for four protons was assigned to one of the four, methylenoxy protons. The other three peaks integrated for 12 protons appeared as three multiplets. The aromatic region was too complicated to be interpreted due to low symmetry. The expected isotopic cluster at 2050 *m/z* was observed in FAB-MS.

The fourth fraction from the original column was the ABBB product, **5c** which required the increased polarity of *n*-hexane/THF 9:1 as eluent. FAB-MS showed the presence of the characteristic molecular ion peak at 2229 *m/z* which confirmed the proposed structure. Unfortunately, the amount of product obtained from the fourth fraction was insufficient to allow further analysis.

The final fraction collected from the original column separation was the symmetrical phthalocyanine derivative (BBBB) **5d**, which was further purified by using petroleum ether 40–60 °C/THF 10:1 as eluent to yield 60 mg (8.4%) of **5d** as a waxy green product. Owing to the higher symmetry of the product compared with those discussed above, the ^{1}H NMR spectrum was less complex. The aromatic region showed the expected, with two broad signals assignable to the phenoxy substituent ring protons integrating for 24 protons. Only one clear triplet was recorded in the methylene region at 4.89 ppm which was assigned to the 16 methylenoxy protons. FAB-MS showed an isotopic cluster at 2405 *m/z* corresponding to the expected structure.

3.3. Solubility

It was anticipated that the fluorinated phenoxy groups in the peripheral position and hexyloxy groups in the non-peripheral position of phthalocyanines would impart high solubility in organic solvents [20]. This increased solubility might be due to the higher solubility of the substituted dyes in polar organic solvents; also, the steric hindrance of the peripheral 3,5-di-fluorophenoxy substituents makes it impossible to form dimers of **5a** and **5d**. The prepared ZnPcs displayed high solubility in various organic solvents such as benzene, toluene, chloroform, ethyl acetate and tetrahydrofuran.

3.4. Photophysical properties

3.4.1. Steady-state absorption studies

The room temperature absorption spectra of ZnPc **5a** and **5d** in several solvents are shown in Fig. 1. The fluorinated

Table 1
Absorption maxima (λ_{max}^{abs}), fluorescence maxima (λ_{max}^{flu}) and fluorescence quantum yields (Φ_q) of **5a** and **5d**

Compounds	Solvent	λ_{max}^{abs}/nm	λ_{max}^{flu}/nm	Φ_q
ZnPc	TN	677	687	
5a	DMF	711	730	0.032
	BN	718	738	0.027
	TN	719	735	0.033
5d	DMF	723	742	0.026
	BN	729	749	0.023
	TN	733	747	0.021

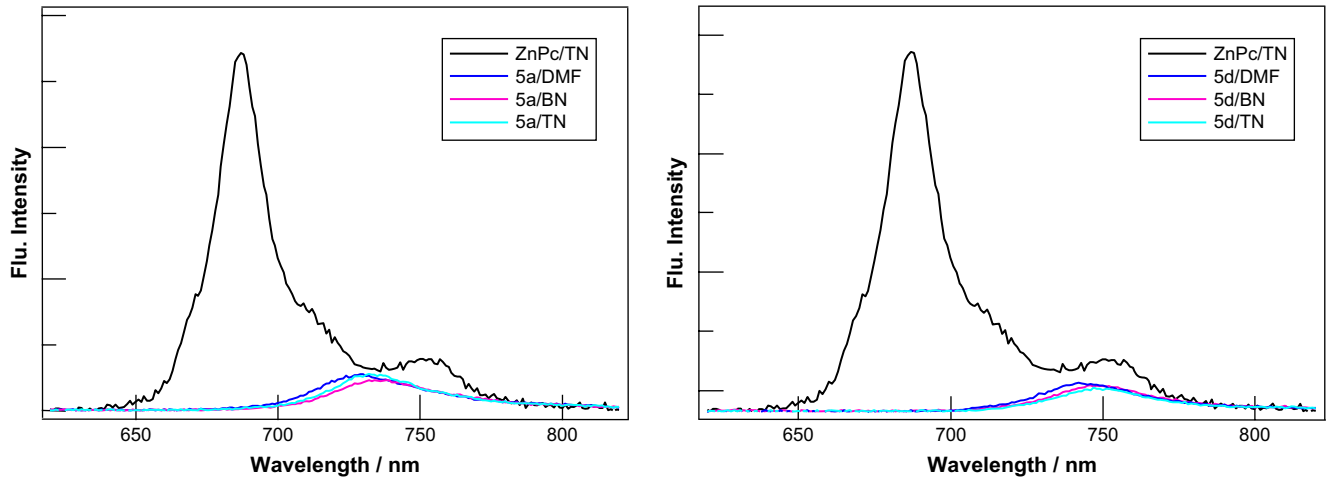


Fig. 2. Steady-state fluorescence spectra of **5a** and **5d** in different organic solvents.

ZnPcs showed typical phthalocyanine spectral features including a soret band and Q-bands. Similar to ZnPc, the absorption spectra of **5a** and **5d** were characterized by strong absorption in the red region and weaker absorption in the blue region. Table 1 lists the absorption peaks of the three species from which it is evident that the absorption bands shifted to longer wavelength as a result of the fluorinated phenoxy group. This shift increased with increasing number of the fluorinated phenoxy groups. For example, **5a** has two fluorinated phenoxy groups and had a Q-band at 719 nm while **5d**, with eight fluorinated phenoxy groups, had a Q-band at 733 nm. The spectral shift is attributable to the distortion of the ZnPc macrocycle. Solvent polarity produced minor spectral shifts.

3.4.2. Emission studies

The luminescent emission maxima of ZnPc, **5a**, and **5d** in different solvents are listed in Table 1. The fluorinated phenoxy species emission maxima were broad and 40–60 nm bathochromic shifted in comparison with ZnPc (Fig. 2). All emission maxima were mirrors of the corresponding absorption spectra, and were solvent-independent. To our surprise, the measured fluorescence quantum yields (Φ_q) for **5a** and **5d** were much lower than those for ZnPc, for which, in chloronaphthalene, a quantum yield of 0.3 at 77 K [21] was obtained, this being ~10 times greater than that of **5a** in DMF at room temperature (Table 1). The non-fluorinated complex, ZnPc, showed a pronounced oxidation wave at 528 mV vs. Ag/AgCl in 0.1 M Bu_4NClO_4/*o*-dichlorobenzene at a 30 mV/s scan rate compared with the fluorinated complex **5d**. It appeared that the fluorine substituents changed the HOMO with a concomitant redistribution of electron density that affected the optical, redox, radical and excited state properties [22,23]. Research is under way to synthesize a series of fluorinated Pcs with various numbers and positions of fluorine substituents. Further experimental work and density functional theory calculations are required to investigate the effects of fluorine substituents on the electrochemistry and luminescence of the reported Pcs.

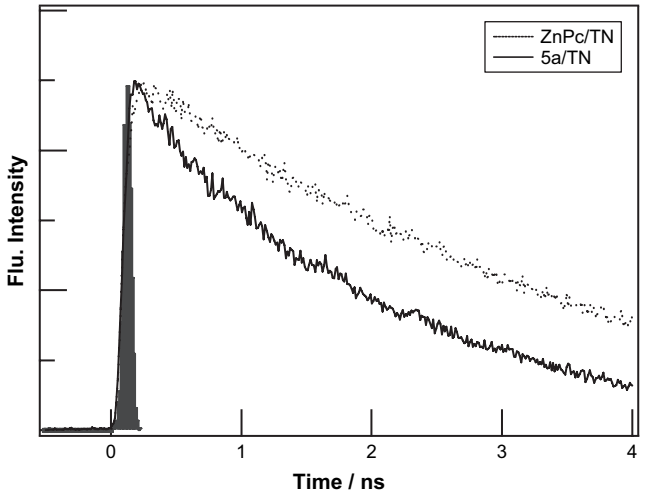


Fig. 3. Time profile of fluorescence intensity of fluorinated phenoxy ZnPc systems **5a** in toluene monitored at 600–800 nm, $\lambda_{ex} = 400$ nm.

3.4.3. Lifetime measurements

Fluorescence decay-times were measured at the luminescence maximum wavelength using excitation with a 400 nm laser pulse. Fig. 3 shows the fluorescence decay of **5a** along with that of the reference, ZnPc. The fluorescence time profile of ZnPc in TN exhibited a single exponential decay with a lifetime (τ_{f0}) of 3.3 ns, which was in agreement with reported values. The lifetimes of the fluorinated, phenoxy ZnPc systems $(\tau_f)_{sample}$ in various solvents, exhibited mono-exponential decay (Table 2). The $(\tau_f)_{sample}$ values of the fluorinated phenoxy ZnPc were 60% shorter than those of ZnPc.

Table 2
Fluorescence lifetime (τ), rate constant (k_q), quantum yield (Φ_q) of quenching of **5a** and **5d** in different solvents, $\lambda_{ex} = 400$ nm

Compounds	Solvent	Lifetime/ns	k_q	Φ_q
ZnPc	TN	3.30		
5a	DMF	1.93	2.18×10^8	0.42
	BN	1.94	2.00×10^8	0.41
	TN	2.00	1.80×10^8	0.34
5d	DMF	1.69	2.90×10^8	0.48
	BN	1.70	2.80×10^8	0.47
	TN	1.90	2.00×10^8	0.42

The rate constant (k_q) and quantum yield (Φ_q) of the fluorinated ZnPc species, with reference to ZnPc, were calculated using Eqs. (1) and (2) and are shown in Table 2.

$$k_q = \left(1/\tau_f\right)_{sample} - \left(1/\tau_{f0}\right)_{reference} \quad (1)$$

$$\Phi_q = \frac{\left(1/\tau_f\right)_{sample} - \left(1/\tau_{f0}\right)_{reference}}{\left(1/\tau_f\right)_{sample}} \quad (2)$$

4. Conclusions

The synthesized, hexadecasubstituted phthalocyaninatozinc(II) complexes possessed excellent solubility in various organic solvents such as CH_2Cl_2, THF, acetone and ethyl acetate. These novel complexes show interesting luminescence in different organic solvents.

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