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Synthesis and photophysical properties of novel hexadeca-substituted phthalocyanines bearing three different groups

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ABSTRACT

The synthesis of novel, hexadeca-substituted metal-free and zinc(II)phthalocyanines bearing naphthoxy groups and chloro groups in peripheral positions and hexyloxy groups in non-peripheral positions is described. These phthalocyanines were characterized with elemental analyses, mass, proton nuclear magnetic resonance (^{1}H NMR), fourier transform infrared spectroscopy (FT-IR) and ultraviolet–visible spectroscopy (UV–vis) techniques. Aggregation properties of these compounds were investigated in the different concentration range. The influences of the substituent on the hexadeca-substituted phthalocyanine framework and metal ion on the spectroscopic and photophysical properties have been investigated. The energy transfer to phthalocyanine core and radiative decays of the naphthol emission and phthalocyanine core were examined.

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1. Introduction

Phthalocyanines (Pcs) are widely investigated organic compounds for many high-technology applications, such as nonlinear optics, photoconductivity, photovoltaic cells, low-dimensional conductors, chemical sensors, optical data storage, Langmuir–Blodgett films, liquid crystals, photodynamic cancer therapy, *etc.* [1]. Improving the solubility of phthalocyanines is an important aspect of their chemistry, as the insolubility of unsubstituted phthalocyanine molecules in common organic solvents causes difficulties for many applications [2]. The introduction of a diverse substituents on peripheral, non-peripheral or axial positions, metal insertion, variation of the main structure of the macrocycle and extension of π-electron density have strong influence on the electronic and absorption characteristics of Pcs [3].

The nature of the substituents is important not only in terms of the solubility of Pcs but also in context of the state of their aggregation. Aggregation causes a drastic decay of Pcs optical properties [4]. For example, aggregation behaviour of Pcs leads to degrade their optical modulating capabilities through reducing the active absorbing excited state lifetime [5]. This has led to a growing interest in designing nonaggregated Pcs and controlling the architecture of these macrocycles tailored to the intended applications in the related fields. Thus many strategies have been investigated to prevent self-association of Pc-based materials [6].

Placing bulky substituents or aryl groups simultaneously at both peripheral and non-peripheral positions of the phthalocyanine core (i.e. hexadeca-substituted phthalocyanines) perfectly prohibit close self-association of the macrocycle even within solid thin film [7] and results in a shift of the Q-band in the visible spectrum into the near-IR region so that the Pc does not display its characteristic blue or green colour [8]. Besides, addition of substituent groups to both peripheral and non-peripheral sides of the phthalocyanine core disrupt π-stacking between macrocycles and therefore increase the solubility of the substituted Pcs even in non-polar solvents such as hexanes [9]. The non-aggregation behaviour, high solubility and red shifted Q-band properties of hexadeca-substituted phthalocyanines make such new chromophore materials to be attractive candidates for several applications such as PDT as photosensitiser, optoelectronics, optical limiters and near-IR devices [10].

Phthalocyanines are ideal photoactive units with outstanding electronic properties, namely strong absorption in the visible region and fine-tunable redox properties, related to their aromatic π-conjugated system. In this regard, many phthalocyanine-based multicomponent systems in which one of these chromophores is covalently or nonconvalently linked to another electro- or photoactive unit have been prepared and their mutual electronic interactions studied [11]. One of the main advantages of using multichromophoric systems is to harvest a wide range of the solar

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spectrum, which is of general interest for optical and photovoltaic applications. The phthalocyanine skeleton permits to attach easily many energy donor arms in the near periphery, and such a light-harvesting system can be expected to show antenna effect [12].

Although non-aggregation and photophysical properties of hexadeca-substituted phthalocyanines are investigated in number of papers [13–15], the light-harvesting phenomena due to additional fluorophore groups has not been studied. This paper concerns with the preparation of novel, hexadeca-substituted phthalocyanines with hexyloxy groups in non-peripheral and chloro and naphthoxy groups in peripheral positions. Aggregation behaviour and photophysical properties of hexadeca-substituted metal-free and zinc(II)phthalocyanine complexes were investigated. The effects of naphthol groups on the efficiency of energy transfer from naphthol group to the phthalocyanine core have been also studied.

2. Experimental

2.1. Equipments and materials

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR (ATR sampling accessory) spectrometer and electronic spectra on a Scinco S-3100 spectrophotometer using 1 cm path length cuvettes at room temperature. ^{1}H NMR spectra were recorded on Agilent VNMRS 500 MHz spectrometer using TMS as internal reference. Mass spectra were performed on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Fluorescence excitation and emission spectra were measured by using Perkin–Elmer LS-55 fluorescence spectrophotometer. Single mode reactor (CEM DISCOVER SP) were used for microwave heating. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC (SiO_2). 4,5-dichloro-3,6-bis(hexyloxy)phthalonitrile (**1**) was prepared according to reported procedures [13–15].

2.2. Synthesis

2.2.1. *4-Chloro-5-bis(2-naphthoxy)-3,6-bis-(hexyloxy) phthalonitrile (**2**)*

4,5-Dichloro-3,6-dihexyloxyphthalonitrile (**1**) (1.2 g, 3 mmol) was dissolved in 10 cm^3 dry dimethylformamide (DMF) at 45 °C and 2-naphthol (0.43 g, 3 mmol) was added to this solution. After stirring for 15 min, 1.26 g of finely ground anhydrous K_2CO_3 (9 mmol) was added portion wise during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 45 °C for further 48 h. After being cooled to room temperature, the mixture was poured into ice/water (100 cm^3). The resulting deep brown solid was extracted with ethylacetate. The organic solution was dried with Na_2SO_4 and the solvent was evaporated to give the crude product. Finally pure product is obtained by recrystallization from ethanol. Yield: 0.635 g (42%) m.p. 52–54 °C ^{1}H NMR (DMSO-d_6): δ 8.03–7.35 (m, H–Ar), 4.29 (t, O–CH_2), 4.16(t, O–CH_2) 1.84 (dd, CH_2), 1.51 (dd, CH_2), 1.36 (dd, CH_2), 1.09 (q, CH_2), 0.73 (t, CH_3); IR (ν, cm^{-1}): 3058 (H–Ar), 2952, 2929, 2854 (H-Alifatik), 2235 (C≡N), 1632 (Ar C=C), 1161 (Ar–O–Ar), MS [m/z]: 507 $[M + H]^+$, 471 $[M - Cl]^+$, 362 $[M - C_{10}H_7O]^+$.

2.2.2. *{1,4,8,11,15,18,22,25-Octahexyloxy-2,3,9,10,16,17,23,24-octachloro-phthalocyaninato}zinc(II) (**3**)*

A mixture of compound **1** (200 mg, 0.5 mmol), anhydrous $Zn(CH_3COO)_2$, (23 mg, 0.125 mmol) and catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in 1.0 cm^3 of *n*-pentanol was irradiated in a microwave oven at 155 °C, 200 W for 15 min. After cooling to room temperature the green suspension was precipitated with methanol–water mixture, filtered, washed with the same solvent, and finally dried *in vacuo*. The purification of the crude product was accomplished by column chromatography on silica gel first with 1:5 Ethyl acetate:*n*-hexane then with ethylacetate as the eluent. Yield: 32 mg (15.5%); m.p. > 200 °C. IR ν (cm^{-1}): 2955–2924 (C–H aliphatic), 1207 (Ar–O–C); UV–Vis (tetrahydrofuran (THF)): λ_{max} nm (log ε) 337 (4.31), 651 (4.4), 725 (4.96); ^{1}H NMR (DMSO-d_6): 4.18 (16H, t, O–CH_2), 2.21 (16H, p, O–C–CH_2), 1.58–1.39 (32H, m, O–C–C–CH_2–CH_2), 0.96 (16H, m, O–C–C–C–C–CH_2), 0.88 (24H, t, –CH_3); MS: m/z 1655.48 $[M + H]^+$.

2.2.3. *{1,4,8,11,15,18,22,25-Octahexyloxy-3,9(10),16(17),23(24)-tetrachloro-2,9(10),16(17), 23(24)-tetrakis(naphth-2-yloxy) phthalocyaninato}zinc(II) (**4**)*

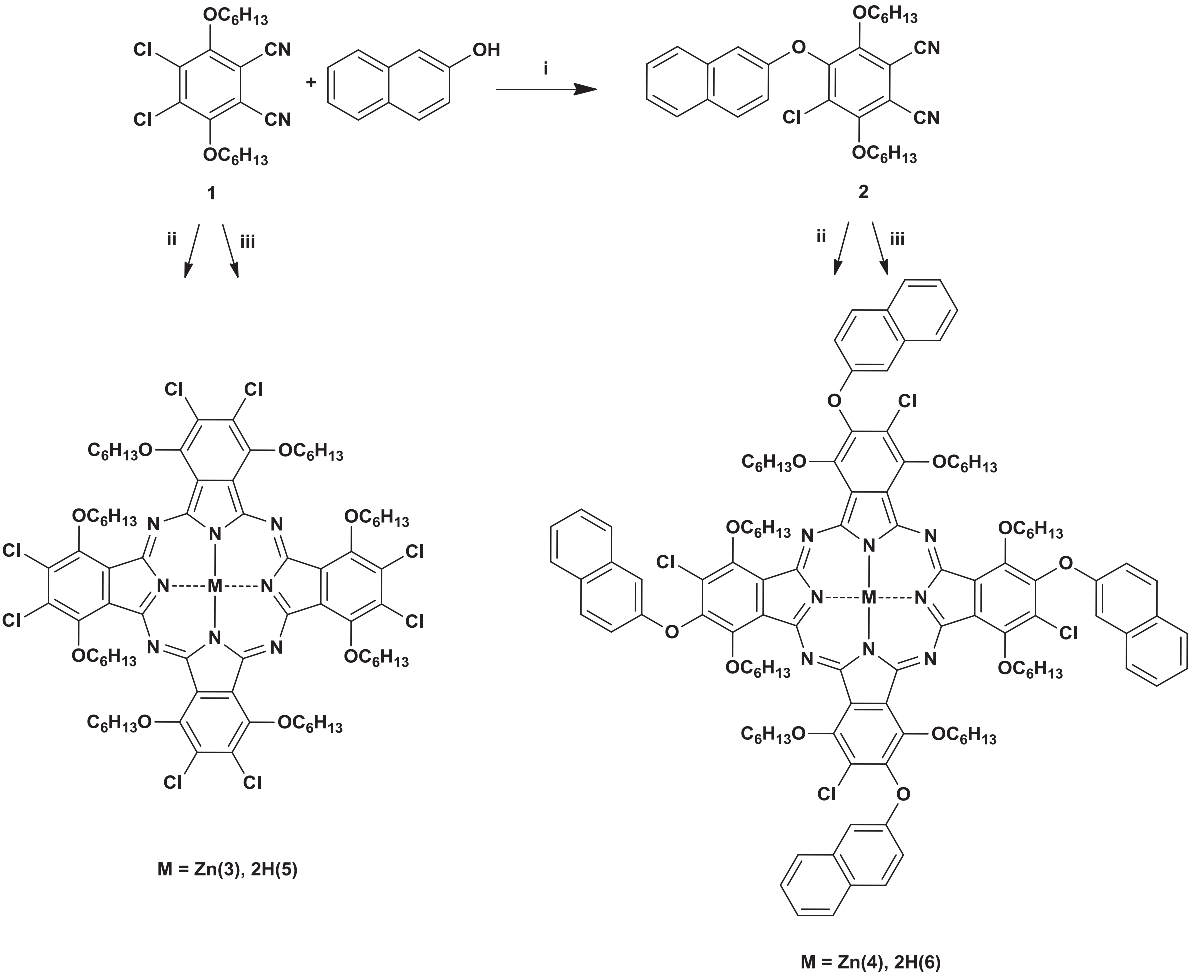
A mixture of compound **2** (101 mg, 0.2 mmol), anhydrous metal salt $Zn(CH_3COO)_2$, (9.2 mg, 0.05 mmol) and catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in 2.0 cm^3 of *n*-pentanol was irradiated in a microwave oven at 155 °C, 200 W for 15 min. After cooling to room temperature the green suspension was precipitated with methanol–water mixture, filtered, washed with the same solvent, and finally dried *in vacuo*. The purification of the crude product was performed by preparative chromatography on silica gel (THF and hexane 1:1 v/v). Pure compound **4** was obtained as an isomeric mixture. Yield: 20 mg, 19%; IR, γ_{max} (cm^{-1}): 3055 (C–H, aromatic), 2953–2924 (C–H aliphatic), 1210 (Ar–O–Ar); UV–Vis (THF): λ_{max} nm (log ε) 328 (4.73), 653 (4.61), 727 (5.37); ^{1}H NMR ($CDCl_3$ δ): 7.86–7.18 (28H, b, Ar–H), 4.93 (16H, b, O–CH_2–), 1.86–0.80 (88H, b, aliphatic–CH); MS [m/z]: 2086 $[M + H]^+$

2.2.4. *{1,4,8,11,15,18,22,25-Octahexyloxy-2,3,9,10,16,17,23,24-octachloro-phthalocyanine} (**5**)*

Lithium metal (20 mg, 2.88 mmol) was heated to dissolve in pentanol (1.5 mL) and allowed to cool to room temperature. Compound **1** (95 mg, 0.24 mmol) was added to the above solution and was heated at 180 °C for 3 h. After cooling to room temperature the green mixture was treated with methanol–water mixture to precipitate the product completely. The green precipitate was collected by centrifuging and then it was washed with methanol–water. It was dissolved in a small amount of methanol and precipitated by diluted hydrochloric acid (HCl) (2 M). In this mixture, the Li_2Pc formed was converted into H_2Pc. The green precipitate was centrifuged and washed successively with water, warm ethanol, warm methanol, and then dried *in vacuo*. This product was then further purified by preparative thin layer chromatography on silica gel using an ethylacetate:hexane (1:5) solvent mixture as the eluting system. Yield: 35 mg, 36%; IR, γ_{max} (cm^{-1}): 3299 (N–H), 2954–2925 (C–H aliphatic), 1242 (Ar–O–C); UV–Vis (THF): λ_{max} nm (log ε) 340 (4.39), 730 (5.04), 752 (5.12); ^{1}H NMR ($CDCl_3$, δ) ppm: 4.93 (16H, t, O–CH_2), 2.19 (16H, p, O–C–CH_2), 1.58–1.39 (32H, m, O–C–C–CH_2–CH_2), 0.96 (16H, m, O–C–C–C–C–CH_2), 0.89 (24H, t, –CH_3); MS [m/z]: 1591 $[M]^+$, 1535 $[M - 3CH_2 - CH_3]^+$

2.2.5. *{1,4,8,11,15,18,22,25-Octahexyloxy-3,9(10),16(17),23(24)-tetrachloro-2,9(10),16(17), 23(24)-tetrakis(naphth-2-yloxy) phthalocyanine)} (**6**)*

Lithium metal (18 mg, 2.6 mmol) was heated to dissolve in pentanol (2 mL) and allowed to cool to room temperature. Compound **2** (130 mg, 0.26 mmol) was added to the above solution and was heated at 180 °C for 3 h. After cooling to room temperature the green mixture was treated with methanol–water mixture to precipitate the product completely. The green precipitate was collected by centrifuging and then it was washed with methanol. It was dissolved in a small amount of THF and precipitated by HCl solution (2 M). In this mixture, the Li_2Pc formed was converted into H_2Pc.



Scheme 1. Structure of hexadeca-substituted metal-free and zinc(II)phthalocyanines (**4**–**6**). **i**: DMF, K_2CO_3, 45 °C, 48 h, **ii**: n-pentanol, $Zn(Ac)_2$, DBU, MW, 15 m (for **3** and **4**), **iii**: *n*-pentanol, lithium, 180 °C, 3 h, HCl (for **5** and **6**).

The green precipitate was centrifuged and washed several times with water, hot ethanol, hot methanol and then dried *in vacuo*. This product was then further purified by preparative thin layer chromatography on silica gel using a THF:hexane (1:10) solvent mixture as the eluting system. Yield: 40 mg, 30%; IR, γ_{max} (cm^{-1}): 3296 (N–H), 3057 (C–H aromatic), 2959–2926 (C–H aliphatic), 1244–1207 (Ar–O–Ar); UV–Vis (THF): λ_{max} nm (log ε) 326 (4.63), 736 (4.90), 759 (4.99); ^1H NMR ($CDCl_3$ δ): 7.95–7.75, 7.70–7.55, 7.50–7.20 (28H, m, Ar–H), 4.80 (16H, m, O–CH2), 1.60–0.47 (88H, m, aliphatic–CH); MS [*m*/*z*]: 2023 $[M]^+$

3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedure as outlined in Scheme 1 started with the synthesis of namely 4-chloro-5-(2-naphthoxy)-3,6-bis-(hexyloxy)phthalonitrile (**2**) by the reaction of 2-naphthol with 4,5-dichloro-3,6-dihexyloxyphthalonitrile (**1**). Cyclotetramerization of the dinitrile **1** and **2** separately to the hexadeca-substituted zinc phthalocyanine (**3**) and (**4**) was accomplished in the presence of anhydrous $Zn(CH_3COO)_2$ in a high-boiling solvent such as *n*-pentanol for 24 h in a sealed tube. Compound **3** and **4** was isolated by preparative chromatography on silica gel using ethylacetate:*n*-hexane (1:5) for **3** and THF:*n*-hexane (5:2) for **4** mixtures as eluent. Conversion of the dinitrile derivatives **1** and **2** into the metal-free Pcs (**5**) and (**6**) was accomplished in a mixture of pentanol in the presence of lithium. Dilithium Pc complexes are unstable towards water and acid, and can easily be converted to the metal-free Pcs. In this study, hexadeca-substituted zinc (**4**) and metal-free (**6**) phthalocyanines were obtained as a mixture of four structural isomers (D_{2h}:C_s:C_{2v}:C_{4h}) owing to the possible positions of the naphthoxy and chloro groups relative to one another. No attempt was made to separate the isomers of complexes **4** and **6**.

All compounds were identified through various spectroscopic techniques such as ^1H NMR, FT-IR, UV–Vis and MALDI-TOF. The spectral data for the newly synthesized compounds were in accordance with the assigned formulations. Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility [15,16]. All studied phthalocyanine complexes (**3**–**6**) exhibited high solubility in organic solvents such as *n*-hexane, acetone, diethyl ether, dichloromethane (DCM), THF, DMF and dimethyl sulfoxide (DMSO).

In the IR spectrum of compound **2**, stretching vibrations of C≡N groups at 2235 cm^{-1}, aliphatic CH groups at 2952–2929–2854 cm^{-1}, aromatic CH groups at 3058 cm^{-1}, and ether (Ar–O–Ar) units at 1161 cm^{-1} appeared at expected frequencies. In the ^1H NMR spectrum of compound **2** in DMSO-d_6, the aromatic protons are present at around δ: 8.03–7.35 ppm. ^1H NMR spectrum of **2** showed two different triplets for Ar–O–CH_2 protons at 4.29 and at 4.16 ppm corresponding to asymmetric configuration. The CH_2 protons of hexyloxy group resonate at δ: 1.84, 1.51, 1.36 and 1.09 ppm as multiplets. For the terminal methyl protons of the side chains exhibited as a triplet at δ: 0.73 ppm. In the mass spectra of **2** the presence of the characteristic molecular ion peaks at m/z 507 $[M]^+$ confirmed the proposed structure.

After conversion into phthalocyanines (**3**, **5**) the characteristic sharp C≡N stretch at 2236 cm^{-1} for phthalonitrile **1** disappeared in the FT-IR spectra of phthalocyanine derivatives. Similarly, cyclotetramerization of **2** to (**4**) and (**6**) can be seen clearly by the absence of the C≡N peaks at 2235 cm^{-1} in the FT-IR spectrum. The FT-IR spectra of zinc (**3**, **4**) and metal-free (**5**, **6**) phthalocyanines are very similar. The significant difference is the presence of N–H vibrations of the inner phthalocyanine core which are assigned to a weak vibration at 3299 cm^{-1} for (**5**) and 3296 cm^{-1} for (**6**).

The ^1H NMR spectrum of zinc (**3**, **4**) and metal-free (**5**, **6**) phthalocyanine derivative was slightly different from the starting compound **1** and dinitrile derivative **2** except for somewhat broad signal and small shifts in the positions of signals. In the H NMR spectrum of **3** and **5**, Ar–O–CH_2 protons of hexyloxy group were observed as triplets at 4.93 ppm and remaining protons of hexyloxy groups were observed between 2.21–1.40 ppm and 0.97–0.91 ppm. In the ^1H NMR spectrum of **4** and **6**, resonances belonging to aromatic protons were observed between 7.90 and 7.06 ppm and integrated for 28 protons. CH_2 and CH_3 protons, integrating for a total of 104, were observed around 4.93–4.80 ppm and 1.86–0.47 ppm. It is probable that the phthalocyanine derivative obtained as positional isomers mixture shows chemical shifts that are similar to each other [17–19].

In the mass spectral results of phthalocyanines (**3**–**6**) obtained by the Maldi-TOF technique, the molecular ion peaks were observed at m/z 1655.48 $[M+H]^+$ for **3** (Fig. 1), 2086 $[M+H]^+$ for **4**, 1591.5 $[M]^+$ for **5** and 2023 $[M]^+$ for **6** (Fig. 2).

The phthalocyanines show typical electronic spectra with two characteristic strong absorption regions, one in the UV region at about 300–400 nm (B-band) and the other one is in the visible region at 600–750 nm (Q-band), both correlate to π–π^* transitions [20–24]. The UV–Vis absorption spectra of zinc phthalocyanines **3** and **4**, in THF exhibited intense Q absorption at 728 and 732, respectively. For the metal-free phthalocyanine **5** and **6** in THF, Q band observed at 751 nm with a shoulder at 730 nm and 752 nm with a shoulder at 732 nm, respectively (Table 1) (Fig. 3) [25]. The Q bands of hexadeca-substituted zinc (**3** and **4**) and metal-free (**5** and **6**) phthalocyanine complexes were red-shifted compared to the peripherally substituted metal-free and zinc phthalocyanine complexes [13,15]. The observed red spectral shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained as being due to a linear combination of the atomic orbital (LCAO) coefficients at the non-peripheral positions of the highest occupied molecular orbital (HOMO) being greater than those at the peripheral positions [26,27]. As a result, the HOMO level is more destabilized upon non-peripheral substitution than peripheral substitution. Besides, simultaneous peripheral and non-peripheral substitution as in the case of hexadeca-substituted phthalocyanine increases this destabilization. Essentially, the energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) becomes smaller, resulting with a ~30–60 nm bathochromic shift [28].

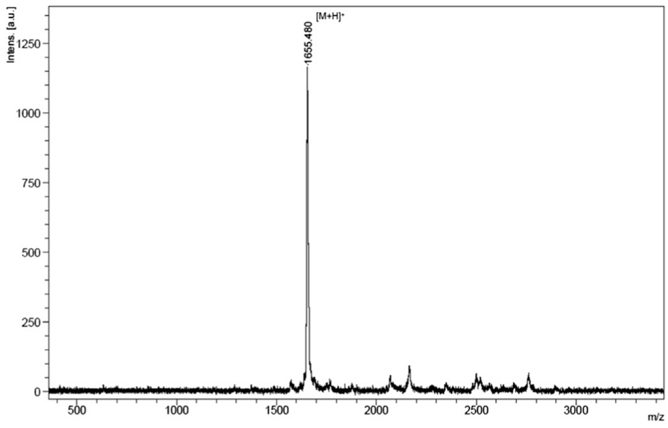


Fig. 1. Maldi-Tof mass spectrum of **3**.

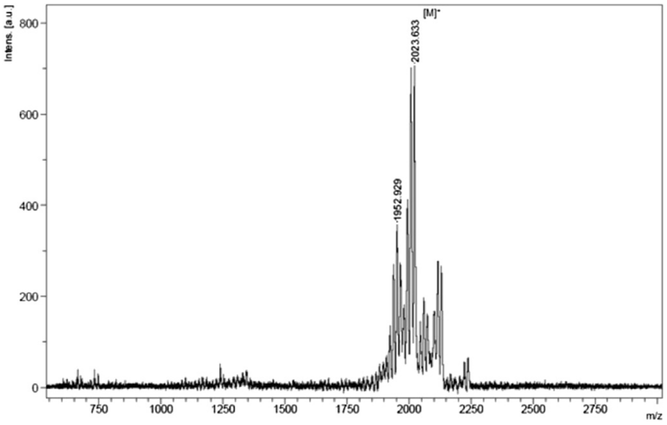


Fig. 2. Maldi-Tof mass spectrum of **6**.

3.2. *Aggregation studies*

The aggregation behaviour was assessed by UV–Vis spectroscopy in THF solution. Usually, the aggregation of the phthalocyanines is indicated by the hypsochromic shift of the Q-band at 700 nm and gradual broadening of this region in a hypochromic fashion [29]. As anticipated, the UV–Vis absorption spectra of hexadeca-substituted phthalocyanine complexes (**3**–**6**) show no evidence of aggregation as shown by the position and the appearance of the intense Q-bands (Fig. 4). Aggregation behaviours of **3**–**6** were examined by UV–vis spectroscopy in different concentrations ranging from 4×10^{-6} to 14×10^{-6} M. As depicted in Fig. 4, the appearance of the Q-band absorption maxima remained unchanged as the concentration increases as well as its apparent molar extinction coefficient remains almost constant indicating purely monomeric form which obeyed the Beer–Lambert Law in the outlined range of concentration (Fig. 5) [30]. By evaluating these observations, it can clearly be concluded that the hexadeca-substituted phthalocyanine derivatives (**3**–**6**) did not show aggregation behaviour in THF at studied concentration range.

3.3. *Fluorescence spectra*

The steady-state fluorescence spectra of the hexadeca-substituted phthalocyanines derivatives were performed in THF, upon excitation at the 660 nm Q-band vibration for **3** and **4** and excitation at the 675 nm Q-band vibration for **5** and **6**. Emission around 739 nm for **3** and 750 nm for **4** (Fig. 6), emission around 772 nm for **5** and 780 nm for **6** (Fig. 7), occurred almost entirely from the phthalocyanine moiety (Table 1). The Q bands of the hexadeca-substituted phthalocyanines' luminescent spectra are red shifted when compared to the corresponding peripheral substituted phthalocyanine complexes. The red shifts observed in

Table 1
Photophysical and photochemical parameters of hexadeca-substituted phthalocyanine complexes (**3**–**6**) in THF.

Comp.	Q band λ_{max}, (nm)	Log ε	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift (nm)	Φ_F	τ_F (ns)	τ_o (ns)	k_F $(s^{-1})(\times 10^8)$[a]
3	728	5.33	724	739	11	0.042	0.16	3.81	2.63
4	732	5.27	730	750	18	0.059	0.05	0.85	11.75
5	730, 751	5.37, 5.44	746	772	21	0.037	0.10	2.89	3.72
6	732, 752	5.25, 5.30	756	780	28	0.057	0.20	3.65	2.85
ZnPc	666[b]	5.19[b]	666[b]	673[b]	7[b]	0.25[b]	2.72[b]	10.9[b]	0.92[b]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Ref. [24].

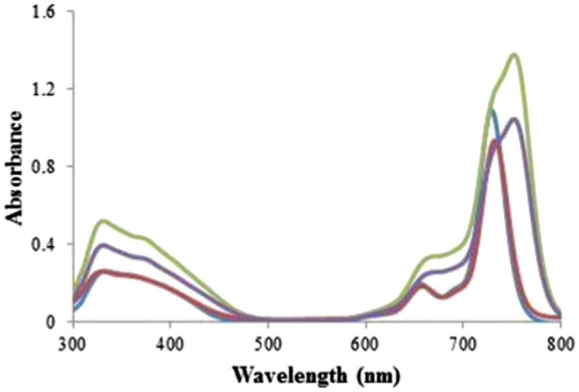


Fig. 3. UV–vis spectra of **3**–**6** in THF. Concentration = 5.0 × 10^{-6} M.

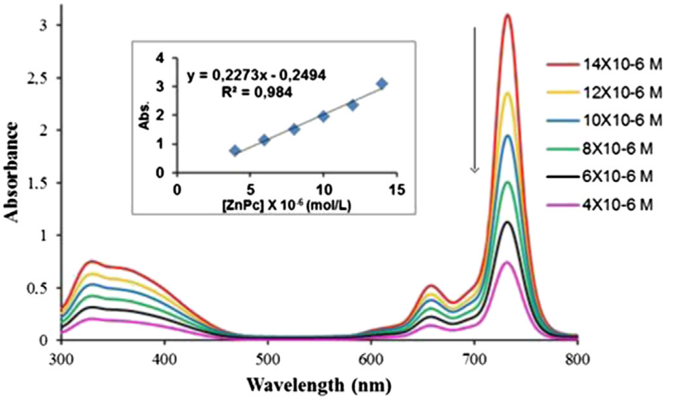


Fig. 4. Aggregation behaviour of **4** in THF at different concentrations.

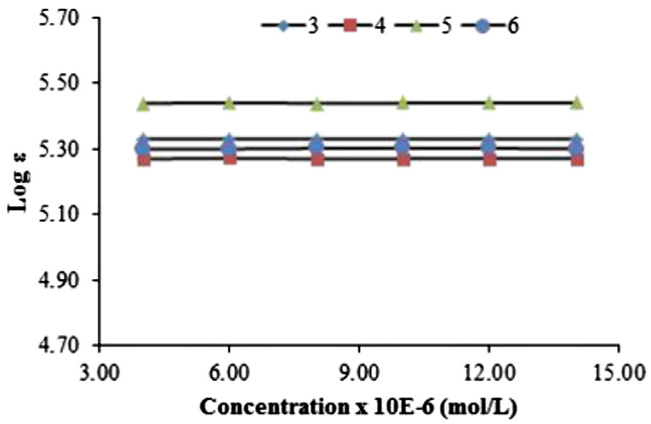


Fig. 5. Plot of the Log ε of **3**–**6** against concentration in THF.

emission maxima are 40–60 nm bathochromic shifted in comparison with peripheral substituted phthalocyanine complexes [10]. The observed red shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained in the literature [25,26].

The excitation spectra of **3** and **4** were similar to absorption spectra and both were mirror images of the fluorescent spectra in THF. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for ZnPc's suggest that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF. Excitation spectrum of hexadeca-substituted H_2Pc's (**5** and **6**) show two shoulder in the red spectral region and emission maxima of hexadeca-substituted H_2Pc's (**5** and **6**) appears at lower energy than those of the corresponding hexadeca-substituted ZnPc's (**3** and **4**). It means that hexadeca-substituted metal-free phthalocyanines shows red shift in emission maxima compared to hexadeca-substituted zinc(II)phthalocyanines because of symmetry lowering [31]. The observed Stokes shifts (Table 1) were typical of phthalocyanine complexes [32].

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [33]:

$$\Phi_F = \Phi_{F(Std)} \left(F A_{Std} \eta^2 / F_{Std} A \eta^2_{Std} \right) \tag{1}$$

where F and F_{Std} are the areas under the fluorescence curves of phthalocyanines derivatives and the standard, respectively. A and A_{Std} are the respective absorbance of the sample and standard at the excitation and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc was employed as a standard in DMF ($\Phi_F = 0.23$) [34]. Both the sample and the standard were excited at the same wavelength. Radiative or natural lifetimes (τ_o) were estimated using PhotochemCAD program which

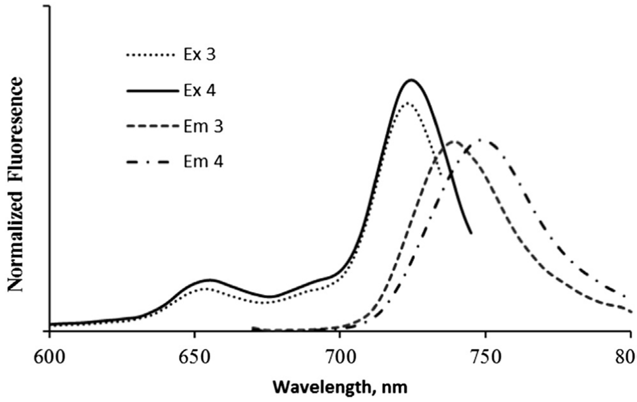


Fig. 6. Excitation and emission spectra of **3** and **4** in THF. Excitation wavelengths: 660 nm. Concentration = 1.0 × 10^{-6} M.

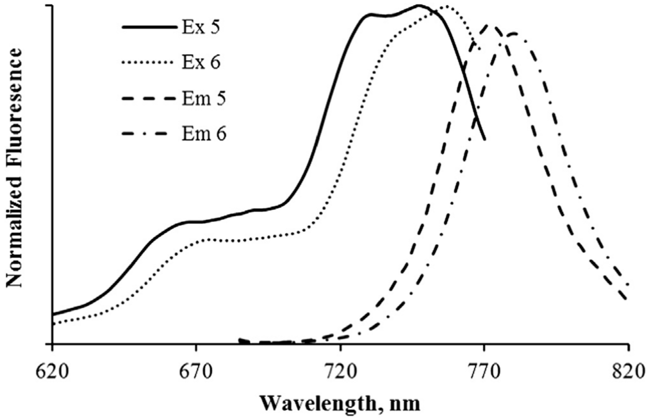


Fig. 7. Excitation and emission spectra of **5** and **6** in THF. Excitation wavelengths: 675 nm. Concentration = 1.0 × 10^{-6} M.

uses the Strickler–Berg equation [35]. Finally, the fluorescence lifetimes (τ_F) were calculated using the following equation (Eq. (2)):

$$\Phi_F = \tau_F/\tau_o \tag{2}$$

The fluorescence quantum yields (Φ_F) of hexadeca-substituted phthalocyanines are given in Table 1. To our surprise, the measured fluorescence quantum yields for hexadeca-substituted phthalocyanines were much lower than those for ZnPc, for which, in DMF and unsubstituted ZnPc in THF [24], both quantum yield of 0.23 and 0.25 respectively at room temperature, this being roughly four times greater than that of hexadeca-substituted phthalocyanines in THF. An apparent reason may be non-peripheral hexyloxy groups enhanced vibrational and rotational motion that may deactivate the excited states [13]. The Φ_F values of the Zn (II) Pc complexes (**3**, **4**) are higher than for the metal-free Pc complexes (**5**, **6**) [36].

The fluorescence lifetime statements to the average time the molecule stays in its excited state before emitting a photon, and its value is directly related to that of fluorescence quantum yield; i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Many factors such as internal conversion and intersystem crossing, shorten the fluorescence lifetime of a molecules and indirectly decreases the value of Φ_F. The τ_F values of the hexadeca-substituted Pc complexes (**3**–**6**) are lower compared to unsubstituted ZnPc in THF (Table 1) [37], suggesting more quenching by substitution. The natural radiative lifetime (τ_o) and the rate constants for fluorescence (k_F) values were also shown in Table 1. The k_F values of studied hexadeca-substituted Pc complexes (**3**–**6**) are higher than unsubstituted ZnPc and have lower natural radiative lifetime (τ_o) values than unsubstituted ZnPc in THF.

3.4. Energy transfer

In this study we examined also the fluorescence and energy transfer properties of the hexadeca substituted metal free and zinc(II)phthalocyanines. This avenue studying excitation energy transfer through donor group has been of much current interest because of its relevance to biological light-harvesting antennae [38]. Excitation and emission spectra of the hexadeca substituted metal free and zinc(II)phthalocyanines were obtained in THF solution. Fig. 8 shows the excitation spectra of 2-naphthol, **3**, **4**, mixture of 2-Naphthol-**3** (4/1) and emission spectra of 2-naphthol. As shown in Fig. 8, the naphthol groups exhibit two absorption bands peaking at 275 and 327 nm and an emission at 356 nm upon excitation at 275 nm. A considerable overlap between the emission spectrum of 2-naphthol and the B-band excitation spectra of **3** and **4** is observed in this figure. This overlap is a clear evidence of the energy transfer from naphthol units to the Pc core of **4** after covalently binding of naphthol as substituents to phthalocyanine core [39,40]. Excitation energy transfer occurred from naphthol units of **4** to ZnPc core of **4**. Fig. 9 shows the excitation spectra of 2-Naphthol, **5**, **6**, a mixture of 2-Naphthol-**5** (4/1) and emission spectra of 2-naphthol. 2-Naphthol groups exhibit broad emission peak at 356 nm upon excitation at 327 nm. The results obtained from the excitation spectrum of **5** and **6** are very similar to the results obtained for **3** and **4**. There are overlap between the emission spectrum of 2-Naphthol and the excitation spectra of **5** and **6** and this overlap is a clear evidence of the energy transfer from naphthol units to the Pc core of **6** after covalently binding of naphthol as substituent to Pc [41].

Upon excitation at 275 nm for **4** (Fig. 10) and 327 nm for **6** (Fig. 11) where the naphthol units absorb and hexadeca-substituted phthalocyanines compounds emit weakly at about 356 nm for **4** and **6** due to the naphthol units, together with an emission at

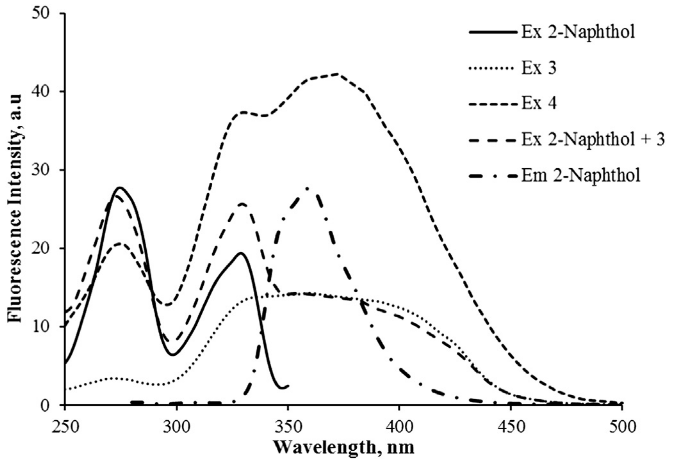


Fig. 8. Excitation spectra of 2-Naphthol (4.0 × 10^{-6} M), **3** (1.0 × 10^{-6} M), **4** (1.0 × 10^{-6} M), mixture of 2-Naphthol + **3** (4:1) (4.0 × 10^{-6} M–1.0 × 10^{-6} M) and emission spectra of 2-Naphthol in THF, emission excited at 275 nm. Excitation spectra were recorded for emission peak at 356 nm. Excitation and emission spectra of 2-Naphthol and mixture of 2-Naphthol + **3** (4:1) were lowered by 10-fold.

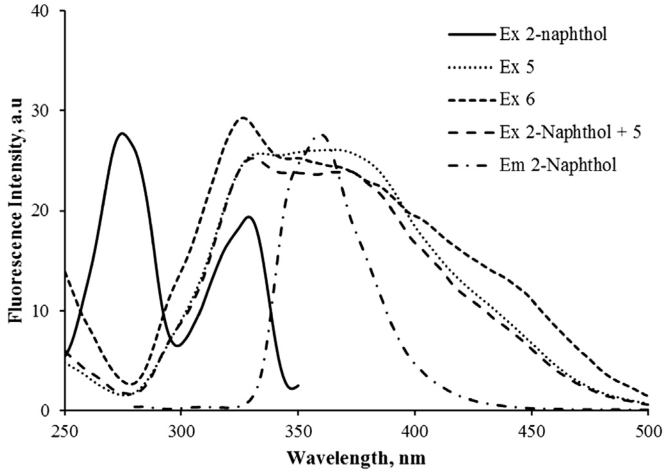


Fig. 9. Excitation spectra of 2-Naphthol (4.0 × 10^{-6} M), **5** (1.0 × 10^{-6} M), **6** (1.0 × 10^{-6} M), mixture of 2-Naphthol + **5** (4:1) (4.0 × 10^{-6} M–1.0 × 10^{-6} M) and emission spectra of 2-Naphthol in THF, emission excited at 327 nm. Excitation spectra were recorded for emission peak at 356 nm. Excitation and emission spectra of 2-Naphthol and mixture of 2-Naphthol + **5** (4:1) were lowered by 10-fold.

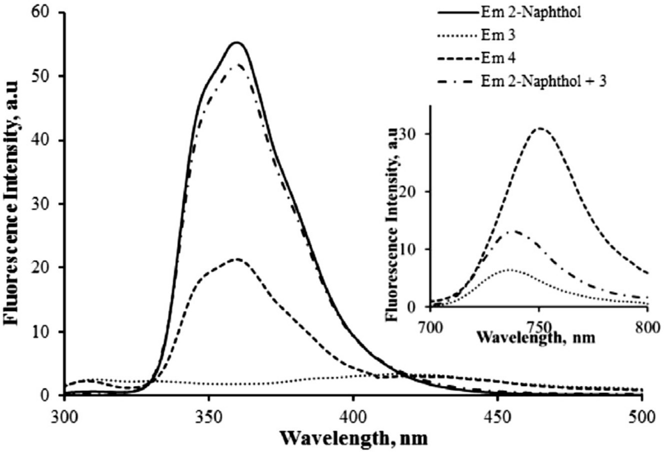


Fig. 10. Emission spectra of 2-Naphthol (4.0×10^{-6} M), **3** (1.0×10^{-6} M), **4** (1.0×10^{-6} M), mixture of 2-Naphthol + **3** (4:1) (4.0×10^{-6} M–1.0×10^{-6} M) in THF, emission excited at 275 nm. Emission spectra of 2-Naphthol and mixture of 2-Naphthol + **3** (4:1) were lowered by 5-fold in B band region.

750 nm for **4** (inset Fig. 10) and at 780 nm for **6** (inset Fig. 11) due to a singlet–singlet energy transfer from the excited arms to the central phthalocyanine cores. The fluorescence of naphthol units was quenched and emission intensity of phthalocyanine part around 750 nm and 780 nm were increased because of the radiative energy transfer resulting from the inner filter effect of the phthalocyanine core [42].

For comparison, fluorescence spectra of the mixture of 2-naphthol-**3** and 2-naphthol-**5** have 4:1 M ratios are represented in Figs. 8–11. It is clearly seen in these figures that the fluorescence emission intensity of the 2-naphthol is bigger than that of the conjugated naphthol units in **4**. Since the distance between 2-naphthol and **3** in the mixture solution is greater, naphthol groups cannot transfer its excitation energy exactly to ZnPc core. But after covalently binding of 2-naphthol to ZnPc to produce **4**, the fluorescence emission intensity of naphthol units of **4** decreased considerably and the fluorescence emission of ZnPc core of **4** increased and a red-shift from 735 nm to 750 nm. These red shifts indicate molecular rearrangement in the excited state originating from intramolecular interactions [43]. The results obtained from the fluorescence spectrum of mixture of 2-naphthol-**5** are very similar to the results obtained for 2-naphthol-**3** (Figs. 8–11). As observed in **4**, after covalently binding of 2-naphthol to H_2Pc to produce **6**, the fluorescence emission intensity of naphthol units of **6** decreased considerably and the fluorescence emission of H_2Pc core of **6** increased and a red-shift from 772 nm to 780 nm occurred. This decrease in the fluorescence emission intensity of naphthol units of **4** and **6** can be considered as an indication of the excitation energy transfer from naphthol units to the phthalocyanine core of **4** and **6** as suggested before due to the overlap between the emission spectrum of 2-naphthol and the excitation spectrum of **4** and **6** in Figs. 6 and 7.

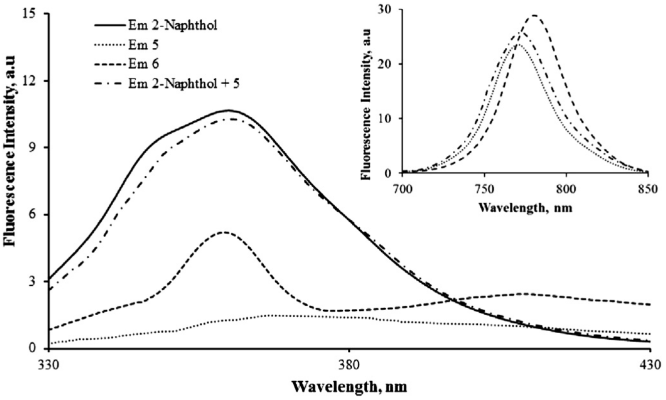


Fig. 11. Emission spectra of 2-Naphthol (4.0×10^{-6} M), **5** (1.0×10^{-6} M), **6** (1.0×10^{-6} M) and mixture of 2-Naphthol + **5** (4:1) (4.0×10^{-6} M–1.0×10^{-6} M) in THF, emission excited at 327 nm. Emission spectra of 2-Naphthol and mixture of 2-Naphthol + **5** (4:1) were lowered by 5-fold in B band region.

These energy transfers from donor (naphthol units) to acceptor (H_2Pc and ZnPc core of 4 and 6) studies were estimated according to the Förster theory by accumulating both the donor and acceptor [44]. Transfer efficiency, ε_T, from donor to acceptor is given by Eq. (3) [12]:

$$\varepsilon_T = \Delta I_A / (I_D * \Phi_A) \tag{3}$$

where ΔI_A is the increase in the integral of the fluorescence emission spectra of the acceptor upon binding of donor to acceptor, I_D is the integral of fluorescence spectrum of the donor before binding to the acceptor and Φ_A is the quantum yield of the acceptor in the absence the acceptor. By using the data in Figs. 10 and 11 and Eq. (3), the energy transfer efficiency from naphthol units to ZnPc core of **4** and H_2Pc core of **6** were calculated as 0.20 and 0.14, respectively.

4. Conclusions

The synthesis, characterization, energy transfer and fluorescence properties of newly synthesized hexadeca-substituted metal-free and zinc(II)phthalocyanines with naphthoxy and chloro groups in peripheral positions and hexyloxy groups in non-peripheral positions have been presented in this work for the first time. All hexadeca-substituted novel phthalocyanine derivatives have not shown any aggregation behaviours in the concentration range from 4×10^{-6} to 14×10^{-6} M. The fluorescence behaviours of the hexadeca-substituted phthalocyanine complexes (**3**–**6**) were studied in THF. Generally, the Φ_F values of the hexadeca-substituted phthalocyanine complexes (**3**–**6**) are lower than unsubstituted ZnPc. These hexadeca-substituted phthalocyanines emit essentially red light after selective ultraviolet or visible irradiation. In the case of ultraviolet irradiation, these systems comprising central phthalocyanines linked to peripheral photon-harvesting naphthol moieties have been shown to act as antennas.

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