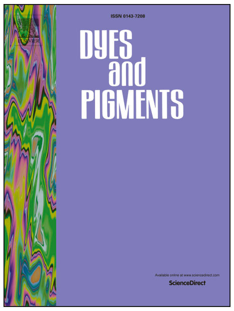

Synthesis, photophysical and electrochemical properties of novel hexadeca-substituted phthalocyanines bearing naphthoxy groups

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Graphical abstract Synopsis

Synthesis, photophysical and electrochemical properties of novel hexadeca-substituted phthalocyanines bearing naphthoxy groups

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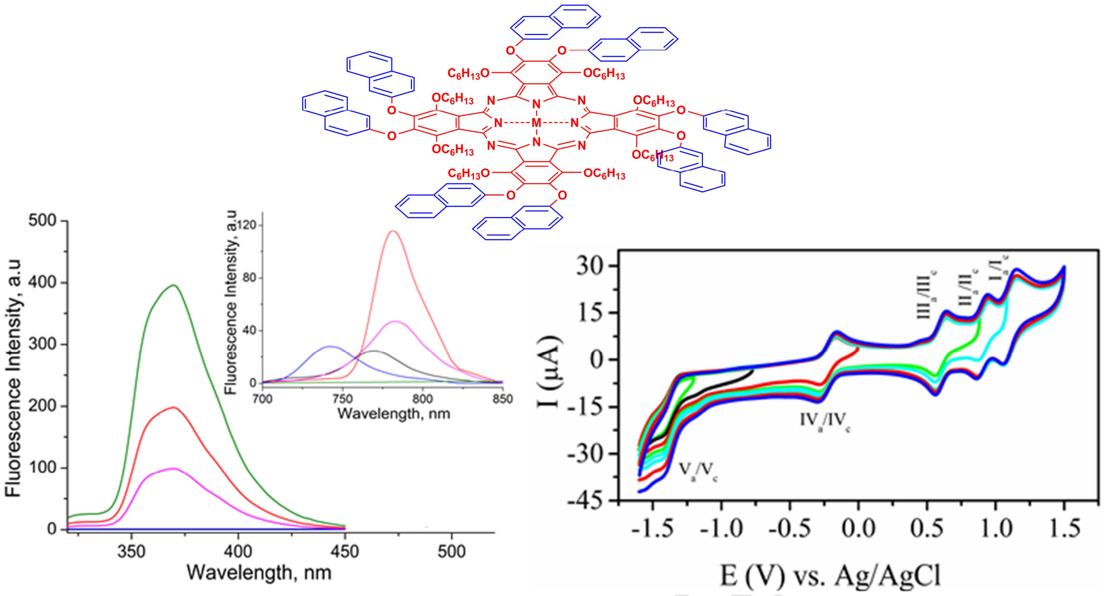
Graphical Abstract

The synthesis of novel tetra-substituted phthalonitrile and hexadeca-substituted phthalocyanines are described. Aggregation properties of phthalocyanine compounds were investigated. The energy transfer to phthalocyanine core and radiative decays of the naphthol emission and phthalocyanine core were examined. Besides, electrochemistries of the complexes were studied with cyclic voltammetry and square wave voltammetry techniques.

Graphical abstract



Synthesis and photophysical and electrochemical properties of novel hexadeca-substituted phthalocyanines bearing naphthoxy groups

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Abstract

The synthesis and characterization of a novel tetra-substituted phthalonitrile together with hexadeca-substituted metal-free and metallo phthalocyanines bearing naphthoxy groups in peripheral positions and hexyloxy groups in non-peripheral positions were described. Aggregation properties of phthalocyanine compounds were investigated in a concentration range of 1.4×10^{-5}M to 4×10^{-6} M. The energy transfer to phthalocyanine core and radiative decays of the naphthoxy emission and phthalocyanine core were examined. Electrochemistry of the complexes was studied with cyclic voltammetry and square wave voltammetry techniques. While zinc phthalocyanine (ZnPc) showed two phthalocyanine-based oxidation and two phthalocyanine-based reduction processes, cobalt phthalocyanine (CoPc) illustrated a metal-based and a phthalocyanine-based reductions and one metal-based and two phthalocyanine-based oxidation processes. Redox reactions of CoPcs are electrochemically and chemically reversible, while the reduction processes of ZnPc are reversible and the oxidation processes of ZnPc are quasi-reversible processes.

Keywords: Phthalocyanine, hexadeca-substitution, energy transfer, naphthol, electrochemistry.

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Introduction

Phthalocyanines (Pcs) are versatile and stable compounds. Structurally, Pcs are similar to porphyrins, but they are synthetic macrocyclic derivatives. Pcs have found numerous applications in materials science such as gas and chemical sensors, molecular solar cells, industrial catalytic systems, electrochromic display devices, optical switching, nanotechnology and light-emitting devices in recent years [1]. Unsubstituted Pc compounds are insoluble in water and organic solvents. For this reason, an important object of research in Pc chemistry has been to obtain soluble products. Addition of various substituents at different positions on the Pc cores makes solvation easier and enables the production of new materials having the desired functions for different applications [2].

The nature of the substituents is important for the solubility of Pcs and also for reducing the aggregation tendency. Aggregation causes an intense decay on optical properties of Pcs. A great number of strategies have been investigated to prevent aggregation of Pc-based materials [3]. The insertion of bulky or aryl groups at both peripheral and non-peripheral positions of the Pc core (*i.e.* hexadeca-substituted Pcs) highly prevents the aggregation of the macrocycle [4, 5] and results in a shift of the Q-band in the visible spectrum into the near-IR region [6]. Besides, hexadeca-substition on the Pc core disrupts π stacking between Pc structures and increases the solubility of the Pcs even in non-polar solvents such as hexane, benzene, and cyclohexane [7].

The high solubility in many solvents, non-aggregation behavior and red-shifted Q-band properties of hexadeca-substituted Pcs make them excellent candidates for specific high-tech applications such as photosensitizer for photodynamic therapy, optoelectronics, optical limiters and near-IR devices. Synthesis of peripheral or non-peripheral tetra- and octa-substituted Pcs has attracted a great deal of interest, but hexadeca-substituted Pcs are relatively less studied [8]. Therefore, recently our group has focused on synthesizing and examining the properties of hexadeca-substituted Pcs [9, 10].

In our current study, novel metal-free and metallo (zinc (II), cobalt (II) and copper (II)) hexadeca-substituted Pcs with hexyloxy groups in non-peripheral and naphthoxy groups in peripheral positions were synthesized and characterized. Aggregation behaviors of these Pcs and the effects of naphthol groups on the efficiency of energy transfer from naphthol group to the Pc core were investigated. Besides, electrochemistry of MPcs was examined in order to support the proposed structure and possible usage of the complexes. Electrochemical behaviors of functional materials are used at various technological applications. Evaluation of the electrochemical behaviors of the complexes will enable us to find out the possible usage of the complexes in different electrochemical fields such as electrocatalysis and electro-sensing.

2. Experimental

2.1 Materials and equipment

FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrometer and electronic spectra was obtained on a Scinco S-3100 spectrophotometer using 1cm path length cuvettes at room temperature. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Agilent VNMRS 500 MHz spectrometer using TMS as internal reference. Mass spectra were performed on a Bruker Microflex LT MALDI-TOF MS spectrometer. Single mode reactor (CEM Discover SP) was used for microwave heating. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. Anhydrous metal salts were finely ground and dried at 100 ^{o}C. The purity of the products was tested in each step by thin-layer chromatography (TLC). The solvents were stored over molecular sieves. 4,5-dichloro-3,6-bis(hexyloxy)phthalonitrile (**1**) was prepared according to the literature [6]. Metal-free (**3**) and zinc (**4**) phthalocyanine were prepared according to reported procedure (Scheme 1) [4].

2.2 Synthesis

2.2.1. Synthesis of 3,6-bis-(hexyloxy)-4,5-bis(naphthalen-2-yloxy)phthalonitrile (2)

4,5-dichloro-3,6-bis(hexyloxy)phthalonitrile (**1**) (1.2 g, 3 mmol) was dissolved in 10 cm^{3} of dry DMF and 2-naphthol (1.728 g, 12 mmol) was added to this solution. After stirring for 15 min, finely ground anhydrous K_2CO_3 (2.88 g, 20 mmol) was added portion wise during 1 h with efficient stirring. The reaction mixture was stirred under nitrogen at 110 ºC for further 8 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 ethyl acetate. The organic solution was dried with Na_2SO_4 and the solvent was evaporated to give the crude product. Finally, the pure product is obtained by recrystallization from ethanol. Yield: 0.936 g (51%) m.p. 55-56 °C ^{1}H NMR (DMSO-d6): 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); FTIR (ν, cm^{-1}): 3058 (H– Ar), 2952, 2929, 2854 (H-Aliphatic), 2235 (C≡N), 1632 (Ar C=C), 1161 (Ar–O–Ar), MS [m/z]: 507 $[M+H]^+$, 362 $[M-C_{10}H_7O]^+$.

2.2.2. Synthesis of metal-free phthalocyanine (5)

Lithium metal (10 mg, 2.6 mmol) was dissolved in n-hexanol (2 mL) by heating and it was allowed to cool to room temperature. Compound **2** (100 mg, 0.26 mmol) was added to the above solution and was heated at 150 ºC for 2 h. After cooling to room temperature, the green mixture was treated with acetone to precipitate the product completely. The green precipitate was collected by centrifuging and then it was washed with acetone. It was dissolved in a small amount of methanol and precipitated by diluted HCl (2 M). In this mixture, the Li_2Pc formed was converted into H_2Pc with the action of the mineral acid. The green precipitate was centrifuged and washed several times with water, hot ethanol, hot methanol, ethyl acetate, acetone and diethyl ether, and then dried in vacuum. This product was then further purified by preparative thin layer chromatography (silica gel) using a tetrahydrofuran (THF):n-hexane (1:10) solvent mixture as the eluting system. Yield: 25 mg, 22%; FTIR, γ_{max} (cm^{-1}): 3296 (N-H), 3058 (C-H aromatic), 2927-2857 (C-H aliphatic), 1256-1236 (Ar-O-Ar); ^{1}H NMR ($CDCl_3$ δ): 7.77-7.65, 7.50-7.30, 7.12-7.05 (m, Ar-H, 56H), 4.24 (m, O-CH_2, 16H), 1.80-1.55, 1.20-1.07, 0.80-0.56 (m, Alip-H, 88H) ppm; UV-Vis (THF): λ_{max} (nm) (log ε) = 324 (5.19), 711 (5.22), 771 (4.98); MS [m/z]: 2451.05 $[M]^+$

2.3. General procedures for metallophthalocyanine derivatives (6-8)

Reaction: A mixture of compound **2** (120 mg, 0.2 mmol), 0.08 mmol anhydrous metal salt [$Zn(CH_3COO)_2$, 13 mg; $CoCl_2$, 10 mg; $Cu(CH_3COO)_2$, 13 mg] and a catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in 1.0 cm^3 of n-hexanol was irradiated in a microwave oven at 160 °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*. Pure complexes were obtained by chromatography.

2.3.1. 1,4,8,11,15,18,22,25-octakis-hexyloxy-2,3,9,10,16,17,23,24-octakis(naphthalen-2-yloxy)phthalocyaninato zinc(II)(6).

The purification of the crude product was performed by preparative chromatography on silica gel (THF and n-hexane 1:1 v/v). *Color:* Dark green. *Solubility*: Extremely soluble in acetone, toluene, diethyl ether, dichloromethane (DCM), chloroform ($CHCl_3$), THF, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Yield: 40 mg, 32%; FTIR, γ_{max} (cm^{-1}): 3058 (C-H aromatic), 2927-2857 (C-H aliphatic), 1256-1236 (Ar-O-Ar); ^1H NMR ($CDCl_3$ δ): 7.82-7.52, 7.50-7.24, 7.12-6.93 (m, Ar-H, 56H), 4.27 (m, O-CH_2, 16H), 1.68-1.55, 1.40-0.60 (m, Alip-H, 88H) ppm; UV-Vis (THF): λ_{max} (nm) (log ε) = 305 (4.77), 670 (4.41), 742 (5.03); MS [m/z]: 2516.21 $[M+2H]^+$

2.3.2. 1,4,8,11,15,18,22,25-octakishexyloxy-2,3,9,10,16,17,23,24-octakis(naphthalen-2-yloxy)phthalocyaninato cobalt(II)(7).

The purification of the crude product was performed by preparative chromatography on silica gel ($CHCl_3$ and Hexane 1:2 v/v). *Color:* Dark green. *Solubility*: Extremely soluble in acetone, toluene, diethyl ether, DCM, $CHCl_3$, THF, DMF and DMSO. Yield: 34 mg, 26%; FTIR, γ_{max} (cm^{-1}): 3057.09 (C-H aromatic), 2953-2855 (C-H aliphatic), 1243-1162 (Ar-O-Ar); UV-Vis (THF): λ_{max} (nm) (log ε) = 318 (4.97), 652 (4.61), 722 (5.20); MS [m/z]: 2509.73 $[M]^+$

2.3.3. 1,4,8,11,15,18,22,25-octakishexyloxy-2,3,9,10,16,17,23,24-octakis(naphthalen-2-yloxy)phthalocyaninato copper(II)(8)

The purification of the crude product was performed by column chromatography on silica gel ($CHCl_3$ and Hexane 2:5 v/v). *Color:* Dark green. *Solubility*: Extremely soluble in acetone, toluene, diethyl ether, DCM, $CHCl_3$, THF, DMF and DMSO. Yield: 40 mg, 30%; FTIR, γ_{max} (cm^{-1}): 3057.32 (C-H aromatic), 2924-2855 (C-H aliphatic), 1256-1236 (Ar-O-Ar); UV-Vis (THF): λ_{max} (nm) (log ε) = 328 (4.78), 664 (4.61), 740 (5.29); MS [m/z]: 2515.00 $[M+2H]^+$

2.4 Electrochemical and in situ spectroelectrochemical measurements

The cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 ˚C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

UV-Vis absorption spectra and chromaticity diagrams were measured with an Ocean Optics QE65000 diode array spectrophotometer. *In situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25˚C. The working electrode was a Pt gauze electrode. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

3. Results and Discussion

3.1. Synthesis and characterization

Scheme 2 shows the synthetic procedures for the synthesis of the target Pcs (**5-8**). As a first step, the novel phthalonitrile derivative, namely 3,6-bis-(hexyloxy)-4,5-bis(naphthalen-2-yloxy)phthalonitrile (**2**) was carried out by using the procedure previously described [4]. In normal conditions, one or two chlorine atoms are displaced by the nucleophile according to the basicity [11, 12], the bulkiness of the nucleophile, or the temperature of the reaction medium. We, in this study, preferred to control the temperature to displace one or two chlorine atoms. In case of high temperature, 3,6-bis-(hexyloxy)-4,5-bis(2-naphthoxy)phthalonitrile **2** was obtained as the major product and a small amount of 3,6-bis-(hexyloxy)-4-chloro-5-(2-naphthoxy)phthalonitrile, which was the starting material of the previous study [4], was also produced. Depending on the ambient temperature, different ratios were obtained. The symmetrical hexadeca-substituted MPcs (Zn(II), Co(II), Cu(II)) (**6-8**) were obtained from the phthalonitrile derivative **2** and corresponding anhydrous metal salts ($Zn(CH_3COO)_2$, $CoCl_2$ and $Cu(CH_3COO)_2$) catalyzed by DBU in n-hexanol using microwave irradiation. Metal-free derivative (**5**) was accomplished in a mixture of n-hexanol in the presence of lithium and then acidification with HCl (Scheme 2). The newly synthesized Pcs were obtained purely after column and/or preparative chromatography on silica gel by using THF/n-hexane, $CHCl_3$, and $CHCl_3$/n-hexane mixture as the eluents. The dark green products are extremely soluble in polar and nonpolar solvents such as diethyl ether, acetone, $CHCl_3$, DCM, THF, DMF and DMSO.

Phthalonitrile **2** was obtained by base-catalyzed nucleophilic aromatic displacement reaction between 4,5-dichloro-3,6-bis(hexyloxy)phthalonitrile (**1**) and 2-naphthol in dry DMF using potassium carbonate as the base at 110 ^{o}C for 8 h under N_2 atmosphere (Scheme 2). The product was purified by column chromatography on silica gel by using dichloromethane/petroleum ether mixture as the eluent and obtained as dark yellow solid in 51% yield.

The FT-IR spectra of Pcs **5-8** confirmed the structures of target compounds by exhibiting the disappearance of C≡N band at 2231 cm^{-1} and the presence of aromatic CH stretching bands at 3058 cm^{-1}. Intense stretching bands of inner core NH groups appeared at 3296 cm^{-1} in the FT-IR spectrum of **5**. MALDI-TOF mass spectra of the Pcs show the presence of the characteristic peaks at m/z = 2451.05 $[M]^+$ (**5**), 2516.21 $[M+2H]^+$ (**6**), 2509.73 $[M]^+$ (**7**) and 2515.00 $[M+2H]^+$

(**8**) confirming the proposed structures. The signals that occurred in the ^{1}H NMR spectra of MPcs **5** and **6** are in agreement with the proposed structure for those compounds.

In the UV-Vis spectra of complexes at the same concentration ($8x10^{-6}$ M) in THF, the absorption peaks belonging to Q band of ZnPc, CoPc and CuPc (**6-8**) were observed at 742, 722, and 740 nm and B band at 305, 318 and 328 nm, respectively (Fig. 1). Naturally, hexadeca-substituted Pcs, with substituents at both non-peripheral and peripheral positions produced larger bathocromic shifts, 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 [13, 14]. The spectrum of compounds **5** was somewhat different with a split Q band (around 711 and 771 nm) indicating the lower symmetry (D_{2h}) of the metal-free derivative [15, 16].

The concentration dependence of the UV-Vis spectra of CuPc **8** was further assessed in order to prove the absence of aggregation [17-20]. Therefore, in this study, we investigated the aggregation behavior of **8** in a concentration range of $1.4x10^{-5}$M to $4x10^{-6}$ M in THF (Fig. 2). As the concentration was increased, the intensity of the absorption of the Q band at 740 nm also increased and there were no new bands (normally blue shifted) due to the aggregated species [7, 21].

3.2 Fluorescence Spectra

The steady-state fluorescence spectra of the hexadeca-substituted Pcs (**5**, **6**) were investigated together with similar compounds having chloro substituents (**3**, **4**) instead of naphthoxy groups in order to see the contribution of naphthoxy units. The measurements were performed in THF, upon excitation at the 675 nm Q-band vibrations for **3**, **5** and **6** and excitation at the 660 nm for **4**. Emission between 742 nm and 782 nm for hexadeca-substituted Pcs (**3** - **6**) (Fig.3) occurred almost entirely from the Pc moiety (Table 1) [22]. The luminescent spectra of the Q bands of the hexadeca-substituted Pcs are red-shifted when compared to the corresponding peripherally substituted Pc complexes. The observed red shifts are typical of Pcs with substituents at the non-peripheral positions and have been explained in the literatures [4, 23]. Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [24]:

$$\Phi_F = \Phi_{F(\mathrm{Std})} \, (F A_{\mathrm{Std}} \eta^2 / F_{\mathrm{Std}} A \eta^2_{\mathrm{Std}}) \quad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of studied Pcs and the standard, respectively. A and A_{Std} are the respective absorbance's 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. Octakis(hexylthio)phthalocyaninatozinc(II) was employed as a standard in DMSO ($\Phi_F = 0.10$) [25]. Both the sample and the standard were excited at the same wavelength.

The fluorescence quantum yields (Φ_F) of the hexadeca-substituted Pcs (**3-6**) are given in Table 1. The measured fluorescence quantum yields for hexadeca-substituted Pcs were much lower than those for ZnPc, for which, in DMSO and unsubstituted ZnPc in THF [26], both quantum yield of 0.10 and 0.25 respectively at room temperature. It implies that non-peripheral hexyloxy groups enhanced vibrational and rotational motion that results in fluorescence quenching, due to enhancement of intersystem crossing (ISC) [27]. The Φ_F values of the Zn (II) Pc complexes (**4, 6**) are higher than for the metal-free Pc complexes (**3, 5**) [4, 28].

3.3 Energy Transfer

In this part of the current study we examined the energy transfer properties of the hexadeca-substituted metal-free and zinc(II) Pcs (**3-6**) in THF. Excitation energy transfer from the acceptor group to the donor group has been of much current interest because of its relevance to biological light-harvesting antennae [29, 30]. Fig. 4 shows the excitation spectra of 2-naphthol and (**3-6)** and emission spectra of 2-naphthol. As shown in Fig. 4, the naphthol groups exhibit two absorption band peaks between 260 and 330 nm and an emission at 360 nm upon excitation at 260 nm [4, 31]. A considerable overlap between the emission spectrum of 2-naphthol and the B-band excitation spectra of **5** and **6** is observed in this figure. This overlap is a clear evidence of the energy transfer from naphthol units to the Pc core of **5** and **6** after covalent binding of naphthol as substituents to Pc core [32-34]. Excitation energy transfer occurred from naphthol units of **5** and **6** to Pc cores of these compounds. This overlap is first evidence of the energy transfer from naphthol units to the Pc core of **5** and **6** after covalent binding of naphthol as substituent to Pc cores [4, 32].

Upon excitation at 260 nm for **5** and **6** (Fig. 5) where the naphthol units absorb and Pc derivatives emit weakly at about 360 nm for **5** and **6** due to the naphthol units, together with an emission at 781 nm for **5** (insert Fig. 5) and at 783 nm for **6** (insert Fig. 5) because of the singlet-singlet energy transfer from the excited arms to the central Pc cores. The fluorescence of naphthol units was quenched and emission intensity of Pcs part around 780 nm was increased because of the radiative energy transfer resulting from the inner filter effect of the Pc core [35]. Another excitation at 260 nm was applied for **3** and **4** but no emission band observed at 360 nm, due to the lack of substituted naphthol groups (Fig. 5).

This decrease in the fluorescence emission intensity of naphthol units of **5** and **6** is the second evidence of the energy transfer and it can be considered as an indication of the excitation energy transfer suggested before due to the overlap between the emission spectrum of naphthol units and the excitation spectrum of **5** and **6** in Figs. 4 and 5 [32, 33]. The energy transfer efficiency estimated from the fluorescence quenching is not naturally 100%, probably due to the presence of ethereal oxygen atom between the naphthol units and the Pc core [36].

3.4 Voltammetric Measurements

Redox responses of ZnPc (**6**) and CoPc (**7**) were determined with CV and SWV in DCM/TBAP electrolyte at GCE. ZnPc illustrates two reductions III_a/III_c couple at -0.75 V and IV_a/IV_c couple at -1.07 V vs SCE at 0.100 Vs^{-1} scan rate (Fig. 6). These couples have reversible peak characters with respect to ΔE_p, $I_{p,a}/I_{p,c}$, and [I_p *vs.* $\nu^{1/2}$] data [37]. The oxidation processes, II_a/II_c couple at 0.83 V and I_a/I_c couple at 1.09 V, are quasi-reversible processes, since values ΔE_p of these couples are out of reversible range (145 mV for II_a/II_c couple and 175 mV for I_a/I_c couple at 0.100 Vs^{-1} scan rate). $I_{p,a}/I_{p,c}$ values are smaller than unity at all scan rates for both couples. I_p *vs.* $\nu^{1/2}$ graphs did not give straight lines [37]. These analyses illustrate presence of a chemical reaction succeeding the I_a/I_c couple. Small wave observed at around 1.30 V at slow scan rates may results from the oxidation of the chemical reaction product. CV responses of the complexes recorded with different vertex potentials support these peak analyses. As shown in Fig. 7, while the quasi-reversible characters of the reduction processes were not affected from the vertex potential, the reverse wave current significantly affected from the vertex potential due to the succeeding chemical reaction. Peak positions, peak to peak separations (0.32 V for III_a/III_c and IV_a/IV_c couples, and 0.26 V for I_a/I_c and II_a/II_c couples) and the differences between the first oxidation and first reduction processes (1.58 V, HOMO-LUMO gap) show that these processes are Pc based electron transfer reactions. It is well documented that Zn^{II} metal ion in the core of

Pc ring is redox-inactive within the potential range of DCM/TBAP electrolyte potential window. Therefore, the electrochemical responses of ZnPc are in harmony with the electrochemistry of similar ZnPc complexes in the literature [38-40]. Consequently, the CV and SWV responses illustrated here support the proposed structure of ZnPc complex.

CoPc (7) represents two reductions IV_a/IV_c couple at -0.22 V and V_a/V_c couple at -1.35 V and three oxidations III_a/III_c couple at 0.61 V, II_a/II_c couple at 0.90 V, and I_a/I_c couple at 1.11 V vs SCE at 0.100 Vs^{-1} scan rate (Fig. 8). All couples have electrochemically reversible peak characters with respect to ΔE_p, $I_{p,a}/I_{p,c}$, and [I_p *vs.* $\nu^{1/2}$] data. While the second reduction process is chemically irreversible, all other processes are also chemically reversible. Due to the presence of the chemical reaction succeeding the first reduction process, two small waves are observed at -1.11 V and 1.51 V. The CV responses recorded with different vertex potentials supports the reversible characters of the electron transfer processes (Fig. 9). Peak positions, and ΔE_p, $I_{p,a}/I_{p,c}$, and [I_p *vs.* $\nu^{1/2}$] data of the processes do not changes when the vertex potential is altered. It is well known that MPcs, such as CoPc having metal centers whose d orbitals located between HOMO and LUMO orbitals of Pc ring gives electron transfer reactions before Pc based processes [41-47]. With respect to these data it is easy to assign the first reduction couple IV_a/IV_c couple at -0.22 V to $[Co^{II}Pc^{2-}]/[Co^{II}Pc^{2-}]^{1-}$ process. It is well illustrated that MPcs having redox active metal centre can give metal-based oxidation process before the Pc based one in polar coordinating solvents such as DMSO. However, in the nonpolar and non-coordinating solvents, such as DCM, the d orbital of the metal centre is not located between HOMO and LUMO of Pc ring [41-47]. Thus, the first oxidation process is assigned to the Pc ring, while the second one to the metal centred process. To support the assignments of the redox processes of both of ZnPc (**6**) and CoPc (**7**), in situ spectroelectrochemical responses were tested. Unfortunately, these measurements did not give reasonable spectral changes for the redox processes due to the fast decomposition of the complexes under light illumination. With respect to the CV and SWV responses, the following mechanism is proposed for the redox reactions of CoPc.

$$[Co^{II}Pc^{2-}] \overset{IV_a/IV_c\, E_{1/2}=-0.21\,V}{\Longleftrightarrow} [Co^{I}Pc^{2-}]^{1-} \overset{V_a/V_c\, E_{1/2}=-1.31\,V}{\Longleftrightarrow} [Co^{I}Pc^{3-}]^{2-}$$

$$[Co^{II}Pc^{2-}] \overset{III_a/III_c\, E_{1/2}=-1.31\,V}{\Longleftrightarrow} [Co^{I}Pc^{1-}]^{2+}[Co^{II}Pc^{1-}]^{1+} \overset{II_a/II_c\, E_{1/2}=-1.31\,V}{\Longleftrightarrow} [Co^{III}Pc^{1-}]^{2+}$$

$$\overset{I_a/I_c\, E_{1/2}=-1.31\,V}{\Longleftrightarrow} [Co^{III}Pc^{0}]^{3+}$$

Conclusions

In this study, the synthesis of hexadeca-substituted metal-free and metallo Pcs bearing naphthoxy groups in peripheral positions and hexyloxy groups in non-peripheral positions were synthesized and characterized. Synthesized phthalocyanines are extremely soluble in polar and nonpolar solvents such as diethyl ether, acetone, $CHCl_3$, DCM, THF, DMF and DMSO. All Pcs derivatives have not shown any aggregation behavior in the studied concentration range. The fluorescence behaviors of the synthesized Pcs (**3-6**) were studied in THF. Generally, the Φ_F values of these Pcs are lower than unsubstituted ZnPc. Here, we have shown that peripheral naphthol units are acting as efficient antennae for photon-harvesting to central Pc cores. Besides, electrochemistry of these Pcs supported the proposed structure of the complexes. Electrochemical analysis showed that Co^{II} shows five reversible redox processes, two metal based and three Pc based processes. Redox richness of CoPc illustrated its worthy for the practical use in various electrochemical technologies.

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References

[1] Leznoff CC, Lever ABP. Phthalocyanines: Properties and Applications, vols.3. New York: VCH; 1993.

[] McKeown N, Phthalocyanine Materials Synthesis, Structure and Function, Cambridge University Press, 1998.

[3] Selçukoğlu M, Hamuryudan E, Novel phthalocyanines with pentafluorobenzyloxy-substituents. Dyes. Pigm. 2007; 74: 17-20

[4] Kurt Ö, Özçesmeci İ, Gül A, Koçak MB, Synthesis and photophysical properties of novel hexadeca-substituted phthalocyanines bearing three different groups, J. Organomet. Chem. 2014; 754: 8-15.

[5] Atsay A, Gül A, Koçak MB, A new hexadeca substituted non-aggregating zinc phthalocyanine, Dyes Pigm. 2014 ;100: 177-183.

[6] Güzel E, Atsay A, Nalbantoglu NS, Dogan L, Gül A, Koçak MB, Synthesis, characterization and photodynamic activity of a new amphiphilic zinc phthalocyanine, Dyes Pigm. 2013; 97: 238-243.

[7] Snow AW, Kadish KM, Smith KM, Guilard R, The Porphyrin Handbook, Vol. 17, Phthalocyanine Aggregation, Elsevier Science, Amsterdam, 2003, pp. 129-173.

[8] Güzel E, Koca A, Gül A, Koçak MB, Microwave-assisted synthesis, electrochemistry and spectroelectrochemistry of amphiphilic phthalocyanines, Synth. Met. 2015; 199: 372–380.

[9] Kurt Ö, Özçesmeci İ, Sesalan BS, Koçak MB, The synthesis and investigation of binding properties of a new water soluble hexadeca zinc(II)phthalocyanine with bovine serum albumin and DNA, New J. Chem. 2015; 39(7): 5767-5775.

[10] Kurt Ö, Koca A, Gül A, Koçak MB, Synthesis, electrochemistry and in situ spectroelectrochemistry of novel hexadeca-substituted phthalocyanines with three different groups, Synth. Met. 2015; 206: 72-83.

[11] Karaoğlu HBP, Koca A, Koçak MB, Synthesis, electrochemical and spectroelectrochemical characterization of novel soluble phthalocyanines bearing chloro and quaternizable bulky substituents on peripheral positions, Dyes Pigm. 2012; 92: 1005-1017.

[12] Karaoğlu HBP, Koca A, Koçak MB, The synthesis and electrochemistry of novel, symmetrical,octasubstituted phthalocyanines, Synth. Met. 2013; 182: 1– 8.

[13] McKeown NB, Li H, Helliwell M, A non-planar, hexadeca-substituted, metal-free phthalocyanine, J. Porphyrins Phthalocyanines, 2005; 9: 841–845.

[14] Konami M, Hatano M, Tajiri A, Inter-ring overlap integrals in dimer complexes of phthalocyanines and porphyrins, Chem. Phys. Lett. 1990; 166: 605-608.

[15] Özçeşmeci M, Synthesis, photophysical and photochemical properties of metal-free and zinc(II) phthalocyanines bearing α-naphtholbenzein units, J. Organomet. Chem 2014; 767: 16-21.

[16] Özçeşmeci İ, Burat AK, Bayır ZA, Synthesis and photophysical properties of novel unsymmetrical metal-free and metallophthalocyanines, J. Organomet. Chem 2014; 750: 125-131.

[17] Atsay A, Koca A, Koçak MB, Synthesis, electrochemistry and in situ spectroelectrochemistry of water-soluble phthalocyanines, Transition Met. Chem. 2009; 34: 877-890.

[18] Koçak MB, Gürek A, Gül A, Bekaroglu Ö. Synthesis and characterization of phthalocyanines containing 4 14-membered tetraaza macrocycles, Chem. Ber. 1994; 127: 355-8.

[19] Dinçer HA, Gül A, Koçak MB, Tuning of phthalocyanine absorption ranges by additional substituents, Dyes Pigm. 2007; 74: 545-550.

[20] Burat AK, Bayır ZA, Phthalocyanines with rigid carboxylic acid containing pendant arms, Polyhedron 2006; 25: 39-42.

[21] Özçesmeci İ, Tekin A, Gül A, Synthesis and aggregation behavior of zinc phthalocyaninessubstituted with bulky naphthoxy and phenylazonaphthoxy groups:An experimental and theoretical study, Synth. Met. 2014; 189: 100-110.

[22] Özçesmeci İ, Synthesis and fluorescence properties of phthalocyanines with dibromo- and tribromo-phenoxy functionalities, Synth. Met. 2013; 176: 128-33.

[23] Makhseed S, Al-Sawah M, Samuel J Manaa H, Synthesis, characterization and nonlinear optical properties of nonaggregating hexadeca-substituted phthalocyaninesi, Tetrahedron Lett. 2009; 50: 165-168.

[24] Ogunsipe A, Nyokong T, Photophysical and photochemical studies of sulphonated non-transition metal phthalocyanines in aqueous and non-aqueous media, J. Photochem. Photobiol., A 2005; 173: 211-220.

[25] Çamlıca M, Nyokong T, Synthesis and photophysical properties of metal free, titanium, magnesium and zinc phthalocyanines substituted with a single carboxyl and hexylthio groups, Polyhedron 2011; 30: 1975–1981.

[26] Saka ET, Durmuş M, Kantekin H, Solvent and central metal effect on photophysical and photochemical properties of 4-benzyloxy-benzoxy substituted phthalocyanines, J Organomet. Chem. 2011; 696: 913-924.

[27] Al-Raqa SY, The synthesis and photophysical properties of novel, symmetrical, hexadecasubstituted Zn phthalocyanines and related unsymmetrical derivatives, Dyes Pigm. 2008; 77: 259–265.

[28] Çamur M, Durmuş M, Bulut M, Synthesis, characterization, and comparative studies on photophysical and photochemical properties of metal-free and zinc (II) phthalocyanines with phenyloxyacetic acid functionalities, Polyhedron 2011; 30: 1935-1945.

[29] Özçeşmeci M, Özçeşmeci İ, Hamuryudan E. Synthesis and characterization of new polyfluorinated dendrimeric phthalocyanines. Polyhedron 2010; 29(13): 2710-5.

[30] Jiang DL, Aida T, Morphology-Dependent Photochemical Events in Aryl Ether Dendrimer Porphyrins: Cooperation of Dendron Subunits for Singlet Energy Transduction, J. Am. Chem. Soc. 1998; 120: 10895-10901.

[31] Özçeşmeci İ, Gelir A, Gül A, Synthesis and photophysical properties phthalocyanine–pyrene dyads, Dyes Pigm. 2012; 92: 954-960.

[32] Valeur B, Molecular Fluorescence Principles and Applications, Wiley-VCH, Germany, Weinheim, 2002.

[33] Lakowicz JR, Principles of Fluorescence Spectroscopy, 3rd edition, Springer, Berlin, 2006.

[34] Özçeşmeci İ, Gelir A, Gül A, Synthesis and photophysical properties of indium(III) phthalocyanine derivatives, J. Lumin., 147 (2014) 141–146.

[35] Ng DKP, Dendritic phthalocyanines: synthesis, photophysical properties, and aggregation behaviour, C. R. Chim. 2003; 6: 903-910.

[36] Drouet S, Paul-Roth CO, Simonneaux G, Synthesis and photophysical properties of porphyrins with fluorenyl pendant arms, Tetrahedron 2009; 65: 2975-2981.

[37] Kissinger P, Heinemann WR, Laboratory Techniques in Electroanalytical Chemistry, revised and expanded, CRC press, 1996.

[38] Li R, Zhang X, Zhu P, Ng DK, Kobayashi N, Jiang J, Electron-donating or -withdrawing nature of substituents revealed by the electrochemistry of metal-free phthalocyanines, Inorg. Chem. 2006; 45: 2327-2334.

[39] L'her M, Pondaven A, The Porphyrin Handbook: Phthalocyanines: Spectroscopic and Electrochemical Characterization, (2003) 117.

[40] Özçeşmeci İ, Kalkan AK, İpek Y, Koca A, Bayır ZA, Synthesis, electrochemical and spectroelectrochemical properties of phthalocyanines having extended π-electrons conjugation, Electrochim. Acta 2013; 89: 270-7.

[41] Koca A, Özçeşmeci M, Hamuryudan E, Substituents effects to the electrochemical, and in situ spectroelectrochemical behavior of metallophthalocyanines: electrocatalytic application for hydrogen evolution reaction, Electroanalysis, 2010; 22: 1623-1633.

[42] Nevin WA, Hempstead MR, Liu W, Leznoff CC, Lever A, Electrochemistry and spectroelectrochemistry of mononuclear and binuclear cobalt phthalocyanines, Inorg. Chem. 1987; 26: 570-577.

[43] Sakamoto K, Ohno E, Electrochemical characterization of soluble cobalt phthalocyanine derivatives, Dyes Pigm. 1998; 37: 291-306.

[44] Obirai J, Nyokong T, Synthesis, spectral and electrochemical characterization of mercaptopyrimidine-substituted cobalt, manganese and Zn (II) phthalocyanine complexes, Electrochim. Acta, 2005; 50: 3296-3304.

[45] Obirai J, Rodrigues NP, Bedioui F, Nyokong T, Synthesis, spectral and electrochemical properties of a new family of pyrrole substituted cobalt, iron, manganese, nickel and zinc phthalocyanine complexes, J Porphyr Phthalocya, 2003; 7: 508-520.

[46] Şener MK, Koca A, Gül A, Koçak MB, Synthesis and electrochemical characterization of biphenyl-malonic ester substituted cobalt, copper, and palladium phthalocyanines, Polyhedron 2007; 26: 1070-1076.

[47] Arıcı M, Arıcan D, Uğur AL, Erdoğmuş A, Koca A, Electrochemical and spectroelectrochemical characterization of newly synthesized manganese, cobalt, iron and copper phthalocyanines, Electrochim. Acta 2013; 87: 554-566.

Table

Table 1 Photophysical parameters of hexadeca-substituted phthalocyanine complexes (**3-8**) in THF.

Comp.	**Q band** λ_{max}, **(nm)**	**log ε**	**Excitation** λ_{Ex}, **(nm)**	**Emission** λ_{Em},**(nm)**	**Stokes shift** Δ_{Stokes}, **(x10^5 cm^{-1})**	Φ_F
3	730, 751	5.37, 5.44	746	770	5.26	0.034
4	728	5.33	724	742	7.14	0.039
5	711, 771	5.22, 4.98	765	782	9.09	0.041
6	742	5.03	759	783	2.44	0.050
7	722	5.20	-	-	-	-
8	7.40	5.29	-	-	-	-
ZnPc	666[a]	5.19[a]	666[a]	673[a]	14.28[a]	0.25[a]

[a] Ref. [26].

Figures

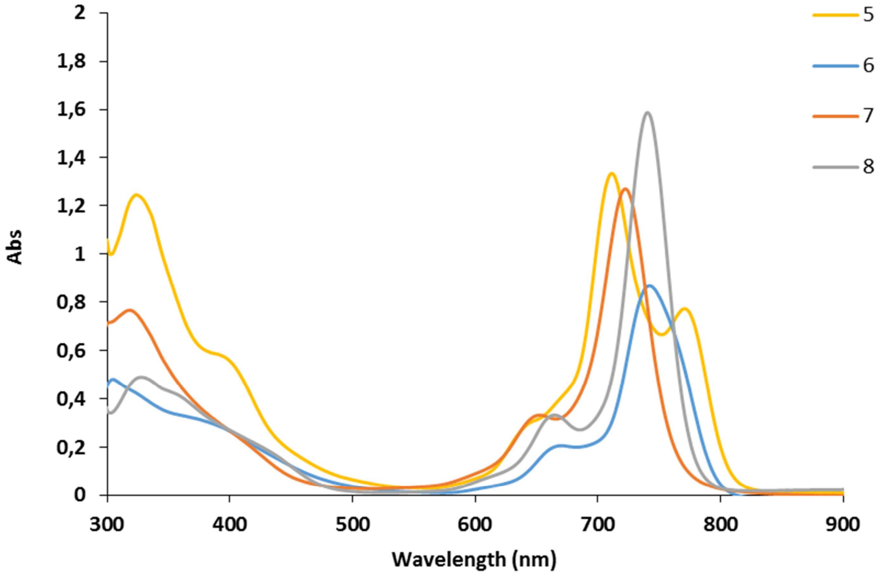


Figure 1 Absorption spectra of metal-free (**5**) and metallophthalocyanines (**6-8**) in THF.

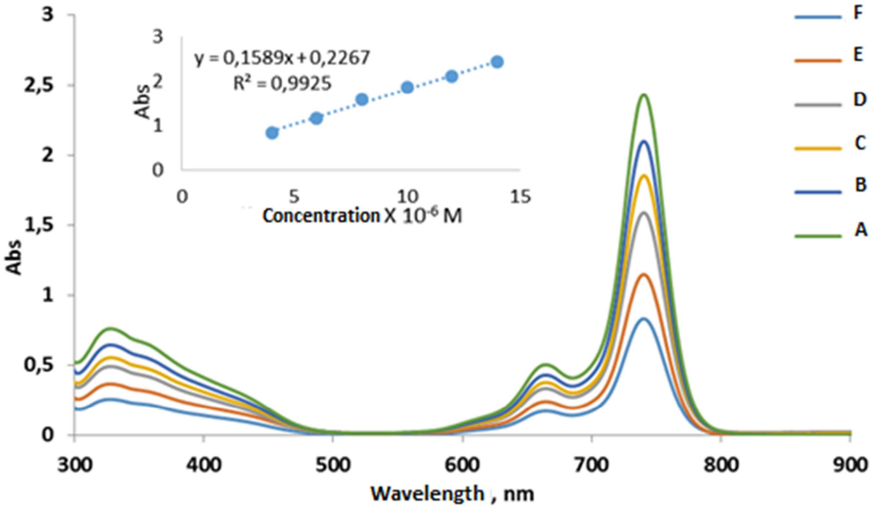


Figure 2 Absorption spectra of CuPc (**8**) in THF at different concentrations: 1.4x10^{-5} M(A), 1.2x10^{-5} M (B), 1.0x10^{-5} M (C), 8x10^{-6} M (D), 6x10^{-6} M (E) and 4x10^{-6} M (F).

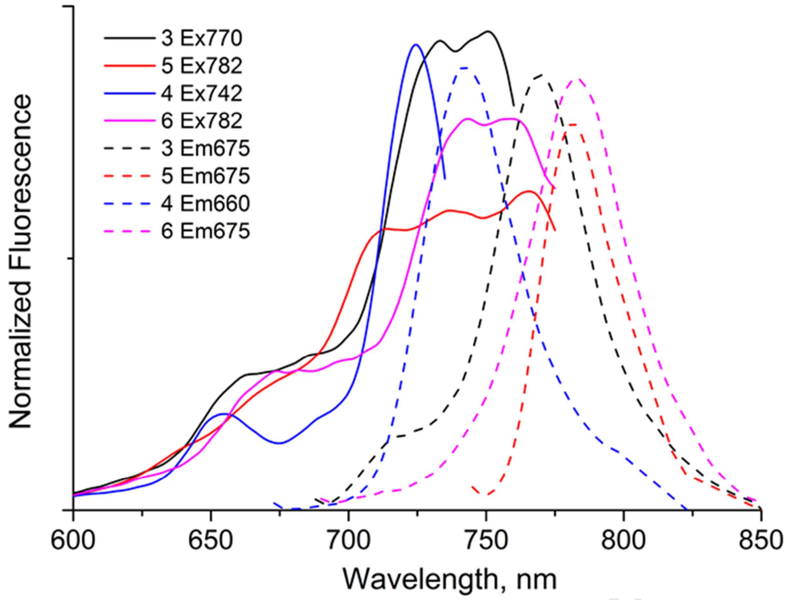


Figure 3 Excitation and emission spectra of **(3-6)** in THF. Concentration = 1.0×10^{-6} M

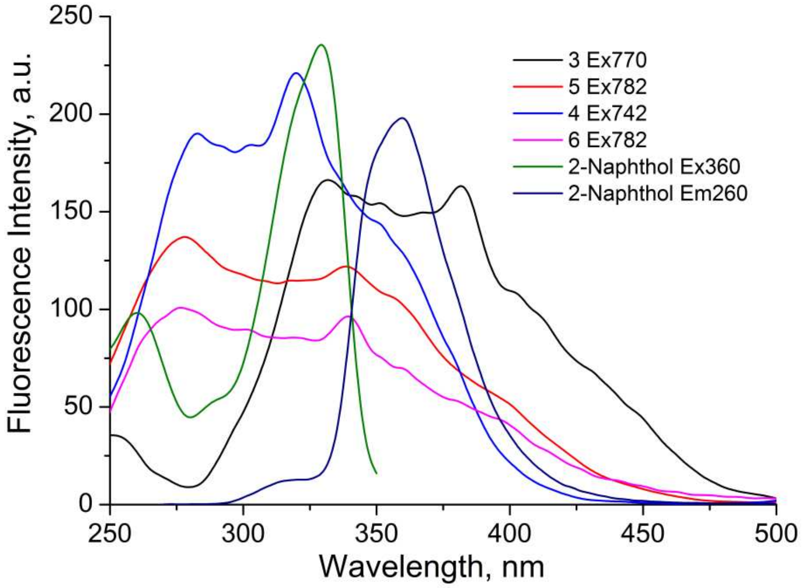


Figure 4 Excitation spectra of 2-naphthol (4.0×10^{-6} M), (**3-6**) (1.0×10^{-6} M) and emission spectra of 2-naphthol in THF, emission excited at 260 nm. Excitation and emission spectra of 2-naphthol were lowered by 3-fold.

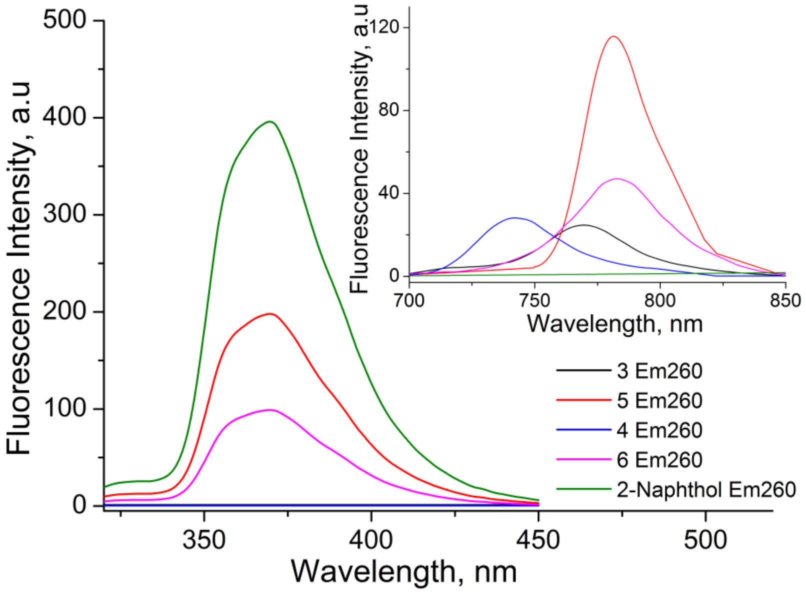


Figure 5 Emission spectra of 2-naphthol (4.0x10^{-6} M) and **(3-6)** (1.0x10^{-6} M) in THF, emission excited at 260 nm in B band and Q band (insert figure). Emission spectra of 2-naphthol were lowered by 3-fold in B band region.

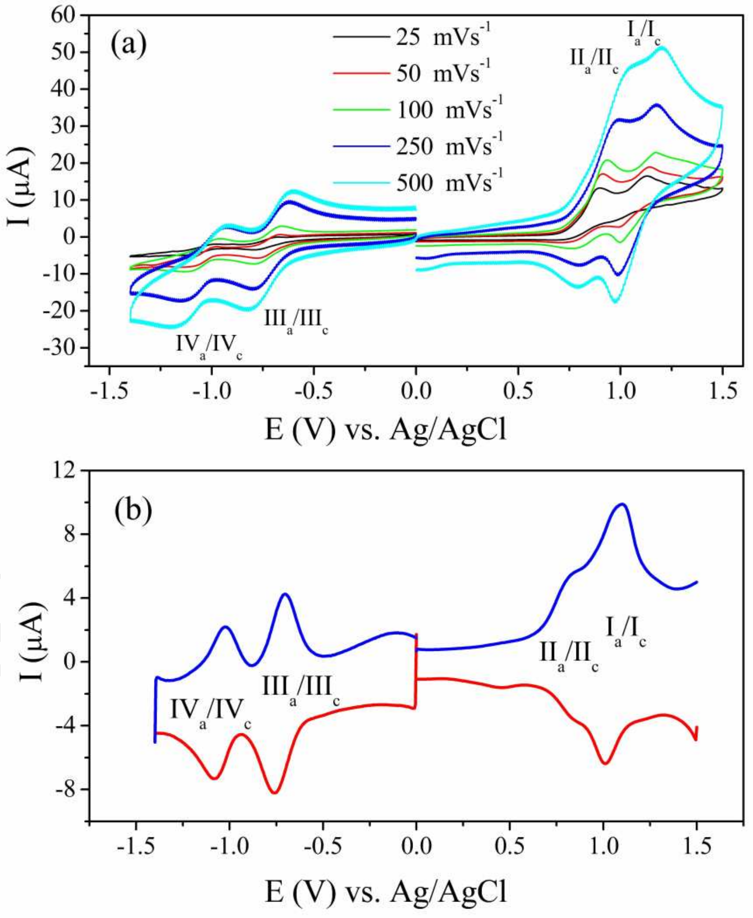


Figure 6 CVs and SWVs of ZnPc (**6**) (5.0 x10^{-4} mol.dm^{-3}) recorded at various scan rates on a GCE working electrode in DCM /TBAP.

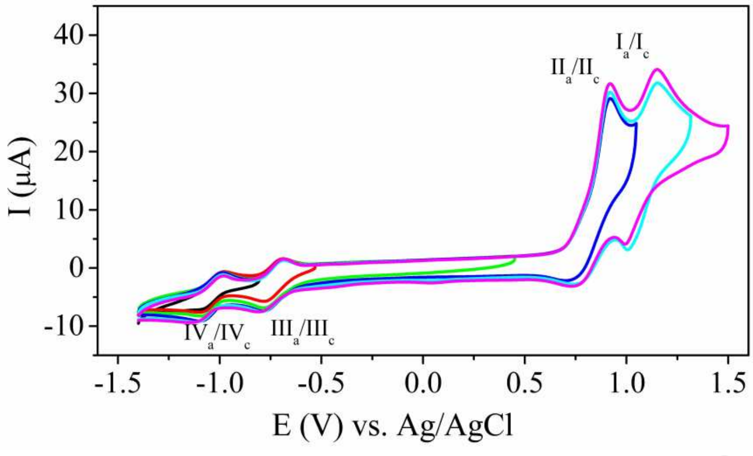


Figure 7 CVs of ZnPc (**6**) (5.0 x10^{-4} mol.dm^{-3}) recorded with different vertex potentials at 0.100 Vs^{-1} scan rates on a GCE working electrode in DCM /TBAP.

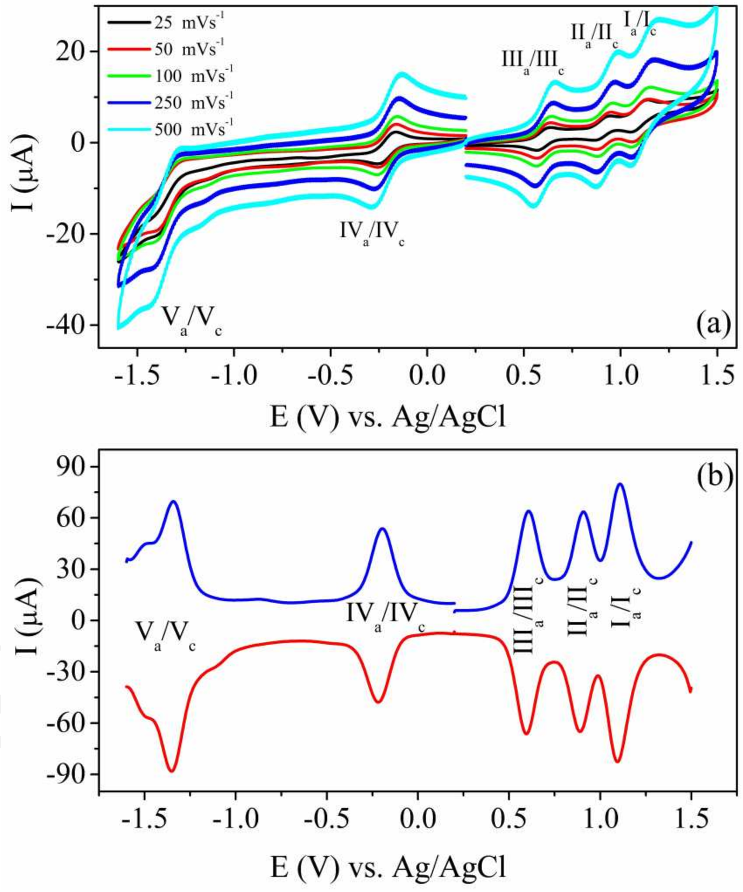


Figure 8 CVs and SWVs of CoPc (**7**) (5.0 x10^{-4} mol.dm^{-3}) recorded at various scan rates on a GCE working electrode in DCM /TBAP.

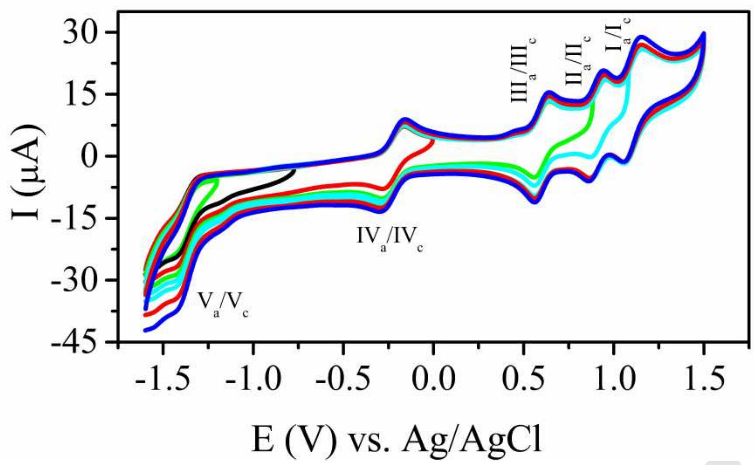
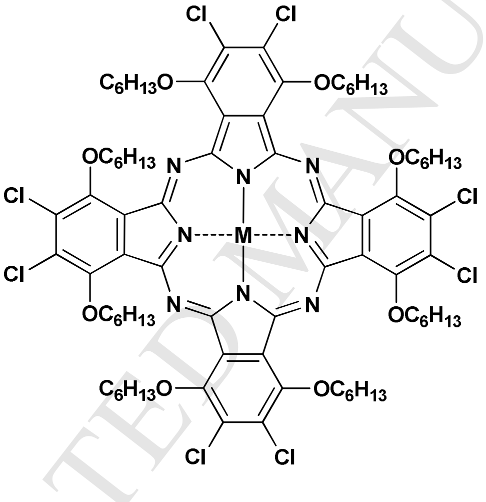
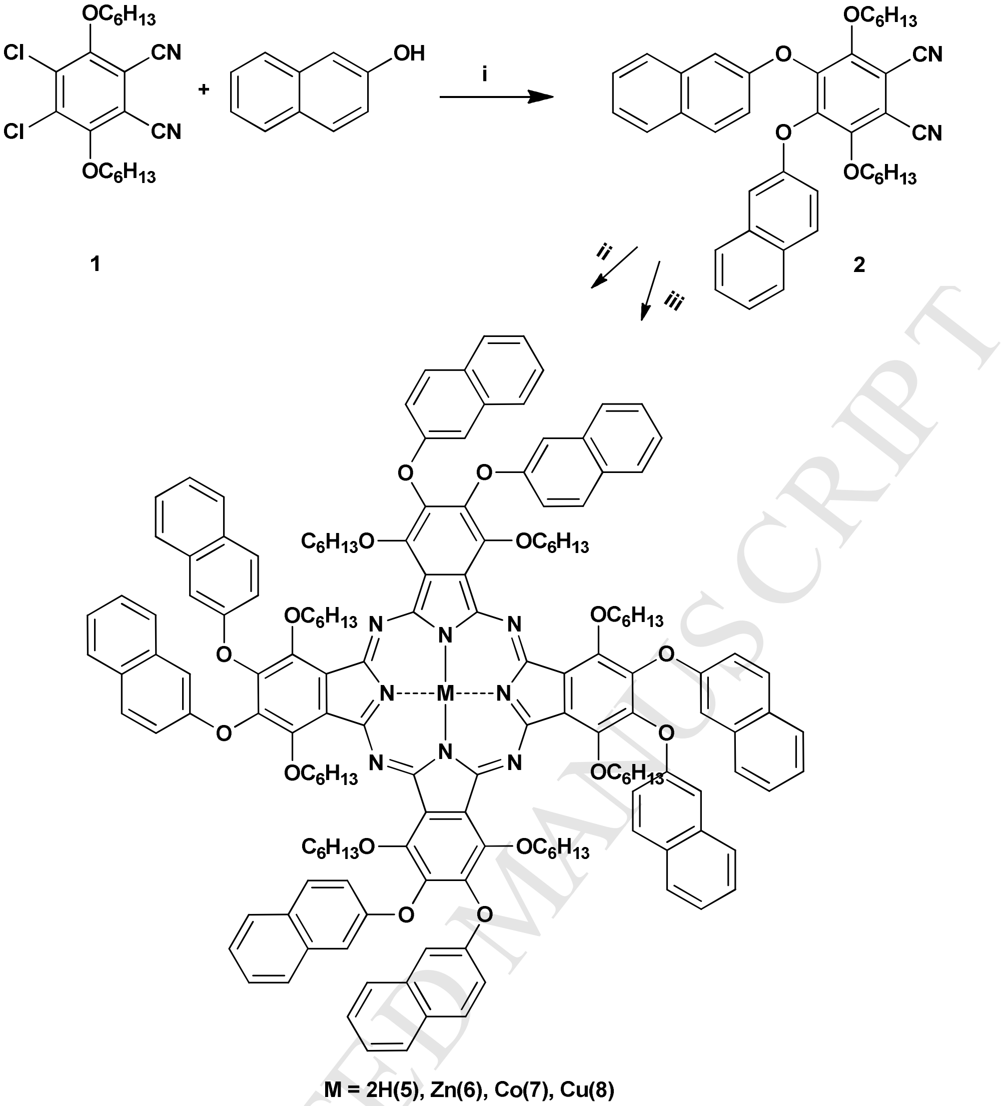


Figure 9 CVs of CoPc (**7**) (5.0 x10^{-4} mol.dm^{-3}) recorded with different vertex potentials at 0.100 Vs^{-1} scan rates on a GCE working electrode in DCM /TBAP.



M = 2H(3), Zn(4)

Scheme 1 Structures of metal-free (**3**) and zinc (**4**) phthalocyanines



Scheme 2 Synthetic route **i:** DMF, K_2CO_3, 100 ^oC, 8h **ii:** n-hexanol, lithium metal, 150 ^oC, 2h, then 2 M HCl (for M=2H), **iii:** n-hexanol, metal salts ($Zn(OAc)_2$, $CoCl_2$, $Cu(OAc)_2$), DBU, MW, 200 W, 15 m.

Research Highlights

- Hexadeca-substituted phthalocyanines were prepared and characterized.
- Aggregation properties of these compounds were investigated.
- The energy transfer efficiency between Pc core and naphthoxy units was examined.
- Electrochemistries of these phthalocyanines have been investigated.