Research Article

JOTCSA, volume 2, issue 4 (2015), pp. 32-41

http://dergipark.ulakbim.gov.tr/jotcsa

Synthesis and characterization of near-IR absorbing metal-free and zinc(II) phthalocyanines modified with aromatic azo groups

Mukaddes Özçeşmeci[a]

[a]Department of Chemistry, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey

Corresponding author. E-mail: selcukoglu@itu.edu.tr. Tel: +90 212 285 7308; Fax: +90 212 285 6386

Abstract: Metal-free and zinc(II) phthalocyanine complexes bearing peripheral (E)-4-((2-hydroxynaphthalen-1-yl)diazenyl) units have been synthesized. Novel phthalonitrile derivative required for the preparation of phthalocyanine complexes was prepared by coupling 4-aminophthalonitrile and 2-naphthol. The structures of these new compounds were characterized by using elemental analyses, proton and carbon nuclear magnetic resonance, fourier transform infrared spectroscopy, ultraviolet–visible spectrophotometry, fluorescence spectrophotometry, and mass spectrometry. In the UV-Vis spectra a broad absorption band appears for phthalocyanine complexes at around 450–500 nm resulting from the azo-group introduced onto the phthalocyanine ring. The photophysical properties of metal-free and zinc(II) phthalocyanines were studied in tetrahydrofuran.

Submitted: April 9, 2015. **Revised:** May 1, 2015. **Accepted:** May 5, 2015.

Keywords: Phthalocyanines; synthesis; 2-naphthol; azobenzene; fluorescence.

Introduction

Organic colorants are being extensively studied because of numerous advantageous properties with many areas of possible applications. Phthalocyanines (Pcs) are important classes of these organics which have a highly conjugated pi-electron system. Interest of the Pcs still arises due to their excellent chemical and physical properties which give potential application in many fields of science and technology such as non-linear optics, gas sensors, electrocatalysis, solar cells, and sensitizers for photodynamic cancer therapy [1-6]. Pcs have high photosensitivity in the near-infrared region (650–850 nm). However, they exhibit a low optical absorption in the visible region (450–650 nm), and cannot be used in white light imaging processes. These properties of Pcs may be modulated by introducing substituent groups on peripheral, non-peripheral or axial positions, changing the symmetry of the Pc molecule, or introducing different metal cations into the cavity of the Pc ring [7-10].

Another class of organic colorants is azo compounds, are used in various areas, such as textiles, electro-optical devices, lasers, and ink-jet printers. They consist of one or more conjugated chromophore azo (–N=N–) groups in their structures. Due to their conjugated structures, azo compounds show intense absorptions in the visible region (450–650 nm) [11-13].

Although many kinds of Pcs and azo compounds have been widely used in many fields, azo group substituted Pcs are still scarce [14-17]. When Pcs and azo groups are included in the same framework, the components bring along their useful properties to the whole molecule. We therefore initiated a study on the mixed arrays of Pcs and azo compounds. In this study, we have reported synthesis and characterization of azo group modified Pcs containing naphthyl groups on the periphery.

Materials and Methods

All chemicals and reagents were purchased from major suppliers and used without any further purification. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent VNMRS 500 MHz spectrometer. Chemical shifts (δ, ppm) were determined with TMS as the internal reference. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrometer, electronic spectra were recorded on a Scinco LabProPlus UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. Mass spectra were measured on a Bruker microflex LT MALDI–TOF MS spectrometer and Perkin Elmer Clarus 500 mass spectrometer in positive electron impact mode. The isotopic patterns for all assigned signals are in agreement with the calculated natural abundance. Data have been given for the most abundant isotope only. Melting points were determined on a Büchi Melting Point B-540 apparatus. Elemental analyses were performed on a Thermo Flash EA 1112. The homogeneity of the products was tested in each step by TLC (SiO_2). 4-Aminophthalonitrile was prepared according to the reported procedure [16].

Synthesis

Synthesis of (E)-4-((2-hydroxynaphthalen-1-yl)diazenyl)phthalonitrile (1)

4-Aminophthalonitrile (0.715 g, 5.0 mmol) was stirred and dissolved in a mixture of 10 mL of deionized water and 16 mL of concentrated hydrochloric acid until a clear solution was obtained. This solution was cooled to 0–5 °C, and then a solution of $NaNO_2$ (0.552 g, 8.0 mmol) in 10 mL of deionized water was added dropwise to the first solution. On the other hand, 2-naphthol (0.720 g, 5.0 mmol) was dissolved in 5 mL of 10% NaOH, cooled to 0–5 °C and then added to the solution of 3,4-dicyanobenzenediazonium chloride in small portions. Solid product immediately precipitated. The resulting mixture was stirred for further an hour at room temperature. The precipitate was filtered off, washed several times with water. The product was purified by crystallization with from ethanol. Yield: 0.641 g (43%); mp > 200 °C; anal. calcd. for $C_{18}H_{10}N_4O$: C, 72.48; H, 3.38; N, 18.78%. Found: 72.59; H, 3.39; N, 18.76%. IR: ν_{max}, cm^{-1} 3182 (OH), 3056 (Ar-CH), 2226 (C≡N), 1597 (C=C), 1479 (N=N). ^{1}H NMR (DMSO-d_6): δ, ppm 10.28 (s, H, -OH) 8.58 (d, H, Ar-H), 8.28 (s, H, Ar-H), 8.02 (m, 4H, Ar-H), 7.59 (t, H, Ar-H), 7.11 (d, H, Ar-H), 7.05 (d, H, Ar-H). ^{13}C NMR (DMSO-d_6): δ, ppm 158.53 (aromatic C), 153.49 (aromatic C-OH), 146.53 (aromatic C-H), 135.11 (aromatic C-H), 130.37 (aromatic C-H), 129.48 (aromatic C), 129.01 (aromatic C-H), 128.38 (aromatic CH), 128.33 (aromatic C-H), 127.87 (aromatic C), 126.51 (aromatic C-H), 126.11 (aromatic C), 123.50 (aromatic C), 123.16 (aromatic C-H), 120.22 (aromatic C), 116.35 (aromatic C), 115.72 (C≡N), 114.87 (C≡N). UV-Vis (THF): λ_{max}, nm (log ε) 310 (4.43), 447 (4.62). MS (EI^+): m/z 298.0 $[M]^+$.

Metal-free phthalocyanine (2)

Metallic lithium (0.134 g, 19.291 mmol) was suspended in 2 mL of n-pentanol and heated at 90 °C with stirring until a homogeneous mixture containing lithium pentanolate was formed. Then phthalonitrile derivative 1 (0.200 g, 0.671 mmol) was added to the reaction mixture and temperature was raised to 140 °C. The mixture was stirred for additional two hours. After cooling to room temperature the green crude product was precipitated with water and then 2 mL of concentrated hydrochloric acid was added to this mixture. In this mixture, the Li_2Pc was converted into H_2Pc. The precipitate was filtered off and washed with methanol, ethanol, hexane, chloroform, and acetone then dried *in vacuo*.

Yield: 0.022 g (11%); mp > 200 °C; anal. calcd. for $C_{72}H_{42}N_{16}O_4$: C, 72.35; H, 3.54; N, 18.75%. Found: 72.45; H, 3.55; N, 18.71%. FT-IR: v_{max}, cm-1 3257 (NH), 3182 (OH), 3056 (Ar-CH), 1597 (C=C), 1479 (N=N). 1H NMR (DMSO-d6): δ, ppm 11.24 (s, 4H, OH), 8.37–6.65 (br, 36H, Ar-H), -4.03 (bs, 2H,-NH). UV-Vis (THF): λ_{max}, nm (log ε) 330 (4.50), 525 (4.63), 658 (4.51), 727 (4.54). MS (MALDI-TOF): m/z 1233.5 $[M+K]^+$.

Zinc(II) phthalocyanine (3)

A mixture of compound 1 (0.200 g, 0.671 mmol), $Zn(CH_3COO)_2$ (0.035 g, 0.190 mmol) and two drops of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2 mL of n-pentanol were heated and stirred at 140 °C in a glass sealed tube for 24 h under nitrogen atmosphere. The mixture was cooled down to room temperature and the solid product was precipitated by adding water. The precipitate was filtered off and washed with methanol, ethanol, hexane, chloroform, and acetone then dried *in vacuo*. Yield: 0.027 g (13%); mp > 200 °C; anal. calcd. for $C_{72}H_{40}N_{16}O_4Zn$: C, 68.71; H, 3.20; N, 17.81%. Found: C, 81.33; H, 3.90; N, 5.42%. IR: v_{max}, cm^{-1} 3183 (OH), 3056 (Ar-CH), 1598 (C=C), 1479 (N=N). ^{1}H NMR (DMSO-d_6): δ, ppm 11.38 (s, 4H, OH), 8.52–6.66 (br, 36H, Ar-H). UV-Vis (THF): λ_{max}, nm (log ε) 345 (4.87), 440 (4.87), 734 (5.07). MS (MALDI-TOF): m/z 1260.7 $[M+2]^+$.

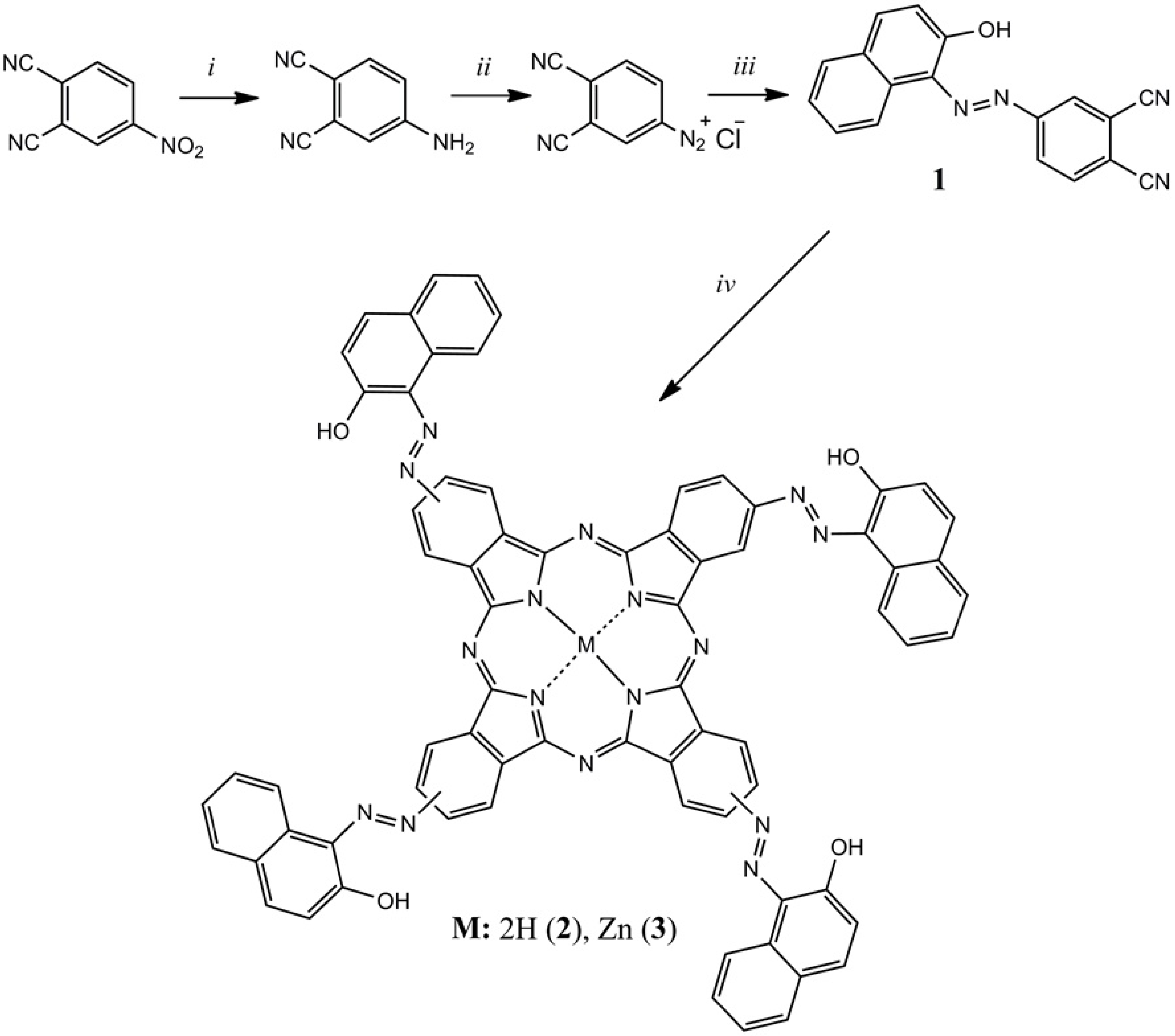
Results and Discussion

Synthesis and Characterization

In this study, the synthesis of (E)-4-((2-hydroxynaphthalen-1-yl)diazenyl)phthalonitrile (**1**) obtained by diazotization of 4-aminophthalonitrile and coupling with 2-naphthol in 10% NaOH solution. Diazonium cation was produced by treating the 4-aminophthalonitrile with nitrous acid ($NaNO_2$/HCl) at 0–5 °C for two hours. All spectroscopic data of newly synthesized phthalonitrile derivative (**1**) show a good agreement with proposed structures.

Cyclotetramerization of the phthalonitrile derivative (**1**) to the metal-free phthalocyanine (**2**) was accomplished by "Li method" in pentanol at reflux temperature in a sealed tube. The direct conversion of Li_2Pc to the metal-free complex **2** was achieved by addition of concentrated HCl to the solution of Li_2Pc. Compound **1** reacted with anhydrous $Zn(CH_3COO)_2$ in the presence of a catalytic amount of DBU via a template-oriented reaction in pentanol at refluxed temperature to obtain the zinc(II) phthalocyanine derivative (**3**) (Scheme 1). In this study, synthesized tetra-substituted phthalocyanine compounds (**2** and **3**) were obtained as mixture of four region-isomers of D_{2h}, C_s, C_{2v} and C_{4v} symmetries for similar physical and chemical properties. Both of synthesized phthalocyanines were soluble in DMF and DMSO, but insoluble in common organic solvents such as methanol, ethanol, hexane, chloroform, and acetone. The purification of complexes **2** and **3** was carried out by washing with methanol, ethanol, hexane, chloroform, and acetone. FT-IR, ^{1}H NMR, UV-Vis, elemental analysis, and mass characterization techniques were used to shed light into the structure of the novel Pcs (**2** and **3**). Spectral data of the novel compounds were in very good agreement with expected structures.

In the FT-IR spectrum of phthalonitrile derivative **1**, aromatic CH, aromatic C=C, azo group (N=N) stretching vibrations appeared at 3056, 1597, and 1479 cm^{-1}, respectively. The presence of the OH group was confirmed by the observation of broad OH stretching at 3182 cm^{-1}. In addition, the characteristic vibration of the C≡N appears at 2226 cm^{-1}, after conversion of the dinitrile into the phthalocyanine, the sharp peak for the C≡N vibration completely disappeared. The FT-IR spectra of the phthalocyanines **2** and **3** are very similar, except NH stretching band at 3257 cm^{-1} in the inner core of metal-free phthalocyanine **3**.



Scheme 1. Synthetic route for phthalonitrile (**1**) and phthalocyanines (**2** and **3**) (i: HCl, Fe, CH_3OH; ii: HCl, $NaNO_2$, 0 °C; iii: 2-naphthol, 10% NaOH, 0–5 °C; iv: a) Metallic lithium, n-pentanol, reflux; b) $Zn(CH_3COO)_2$, DBU, n-pentanol, reflux).

In the ^1H NMR analysis of **1** in DMSO-d_6, aromatic protons appear at 8.58, 8.28, 8.02, 7.59, 7.11, 7.05 ppm as a doublet, singlet, multiplet, triplet, doublet and doublet, respectively. The OH proton appeared at 10.28 ppm as singlet. The ^1H NMR spectra of the compounds **2** and **3** are somewhat broader than corresponding signals in the compound **1** due to aggregation of the phthalocyanine isomers which is frequently encountered at the concentrations used for NMR spectroscopy. The inner NH protons of **2** were also identified in the ^1H NMR spectra with a broad chemical shift at -4.03 ppm.

In ^{13}C NMR analysis of **1** in DMSO-d_6, aromatic carbons appear at 158.53, 146.53, 135.11, 130.37, 129.48, 129.01, 128.38, 128.33, 127.87, 126.51, 126.11, 123.50, 123.16, 120.22, and 116.35 ppm, C-OH group appeared at 153.49 ppm, nitrile carbons appeared at 115.72 and 114.87 ppm, respectively.

In the EI$^+$ mass spectrum of **1**, the presence of the characteristic molecular ion peak at m/z 298.0 [M]$^+$ confirmed the proposed structure. In the case of **2**, the molecular ion peak was found at m/z 1233.5 [M+K]$^+$ according to MALDI-TOF spectrum (Fig. 1). Also, the molecular ion peak for compound **3** found at m/z = 1260.7 [M+2]$^+$. The elemental analyses were satisfactory.

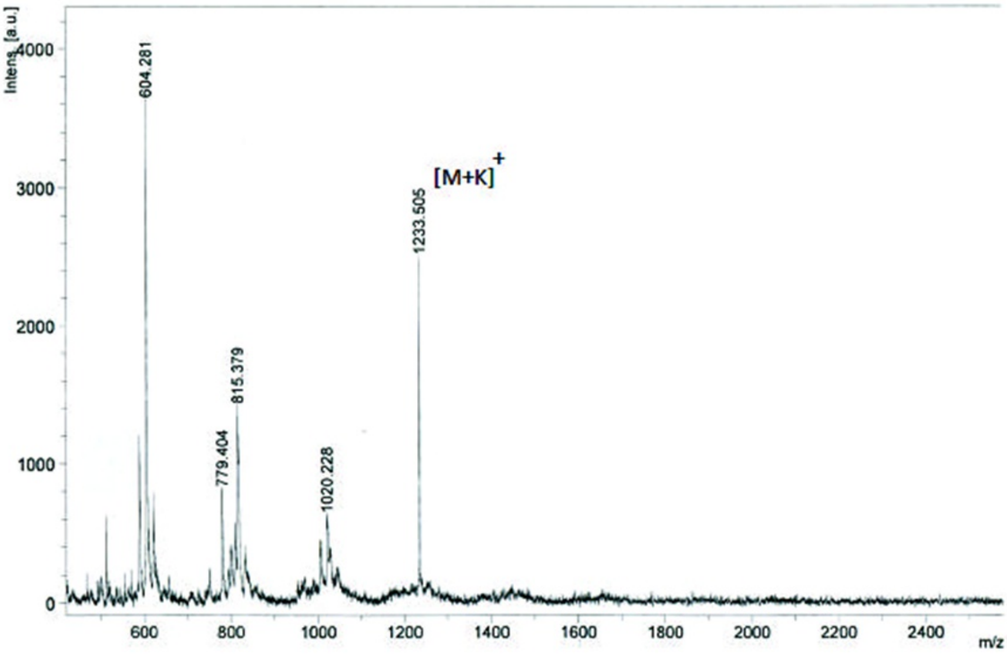


Figure 1. MALDI-TOF MS spectrum of compound **2**.

Ground state electronic absorption spectra

The simplest Pc unit is a 18-π electron system giving rise to electronic spectra with two strong absorption regions, one of them is in the UV region at about 300–400 nm (B band) and the other one is in the visible region at about 600–700 nm (Q band), both correlating to π-π* transitions. The absorption spectra of **2** and **3** in THF were shown in Figs. 3 and 4. The Soret bands are observed at 330 nm for complex **2** and 345 nm for complex **3**. The Q band, of complex **2**, is somewhat different from complex **3**, with a split Q band indicating lower symmetry (D_{2h}) of the metal-free derivative. The Q-band regions of the UV-Vis spectra are red-shifted into the near-IR region at 658 and 727 nm for complex **2** and at 734 nm for complex **3**. Due to the great extension of π-conjugation by four peripheral azo-dye moieties, the Q-bands of **2** and **3** are significantly red-shifted as compared to tetra-*tert*-butylphthalocyanines [4]. In addition, the extension of π-conjugation as well as aggregation in solution also leads to peak broadening. The precursor **1** and phthalocyanine complexes (**2** and **3**) produce intense absorptions from 450 to 550 nm (Figs. 2-4). This kind of additional absorptions is really uncommon, and might suggest some novel opto-electronic properties to the Pcs.

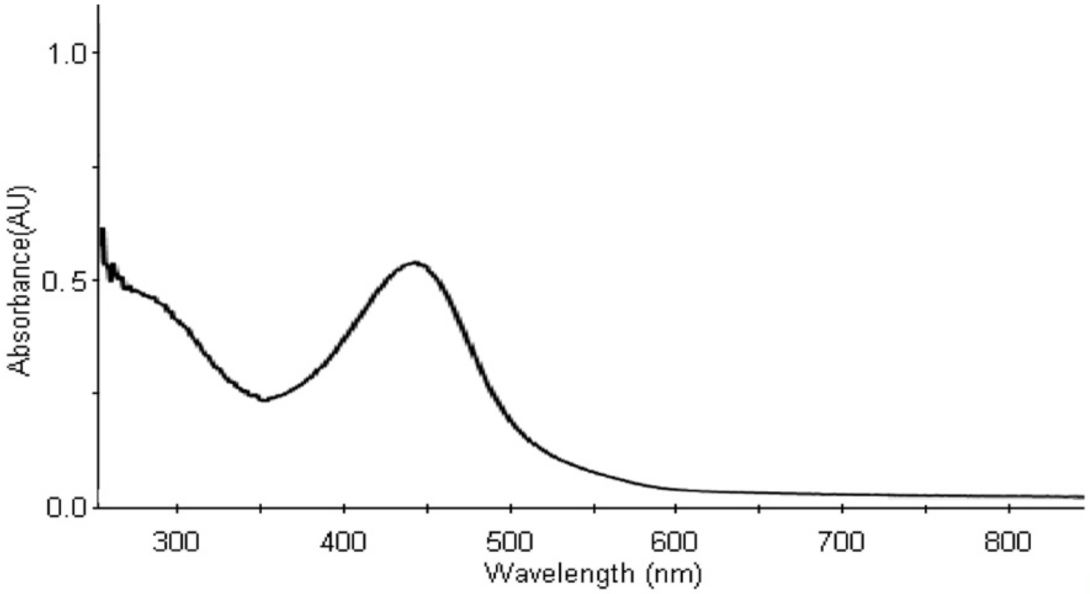


Figure 2. UV spectrum of **1** in THF.

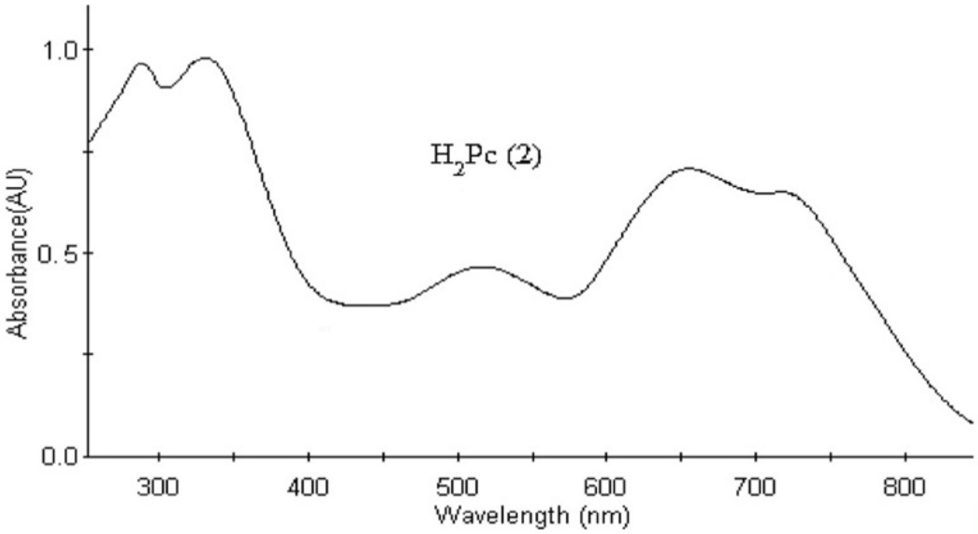


Figure 3. UV spectrum of **2** in THF.

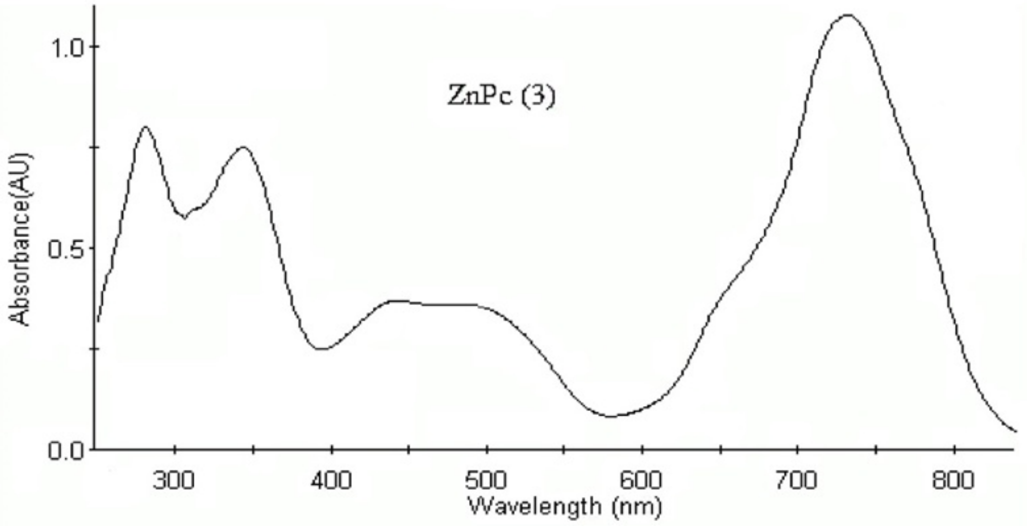


Figure 4. UV spectrum of **3** in THF.

Fluorescence spectra

The steady-state fluorescence spectra of phthalocyanine derivatives (**2** and **3**) were performed in THF, upon excitation at the 650 nm Q-band vibration for **2** and excitation at the 670 nm Q-band vibration for **3**. Emission around 744 nm for **2** and 755 nm for **3** (Fig. 5), occurred almost entirely from the phthalocyanine moiety. The Q bands of phthalocyanine derivatives' (**2** and **3**) luminescent spectra are red-shifted when compared to the corresponding peripherally substituted phthalocyanine complexes. The red-shifts observed in emission maxima are 40-60 nm bathochromically shifted in comparison with peripherally substituted phthalocyanine complexes [19]. Essentially, the energy gap (ΔE) between the S_0 and S_1 becomes smaller, resulting a bathochromic shift [19].

The excitation spectra of **2** and **3** were similar to absorption spectra and both were mirror images of the fluorescent spectra in THF. The proximity of the wavelength of the Q-band absorption to the Q-band maxima of the excitation spectra for ZnPcs suggest that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in THF [20-22]. Excitation spectra of H_2Pc (**2**) show two shoulders in the red spectral region because of the lowering of symmetry [23].

Comparative method [Eq. (1)] was used to determine the quantum yields of the compounds (**2** and **3**) as described in [24, 25]. In this method, the quantum yield of a compound is determined by using a standard which has similar fluorescence properties as the tested compound has. All measurements of the standard and the compound must be performed at the same environmental conditions with the same instrumental settings.

$$\Phi_F = \Phi(Std)\,\frac{F A_{Std} \eta^2}{F_{Std} A \eta^2_{Std}} \qquad (1)$$

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 (Φ_F = 0.23) [26]. The fluorescence quantum yield (Φ_F) values for the complexes were found to 0.14 for H_2Pc (2) and 0.19 for ZnPc (3). The Φ_F values of all the studied Pc complexes are lower than unsubstituted ZnPc. It implies that the presence of the substituents (azo group) certainly results in fluorescence quenching, due to enhancement of intersystem crossing (ISC) by the presence of a heavier azo-naphthol groups in these complexes [27]. The Stokes' shifts ranged from 15 to 20 nm, typical of Pc complexes [28-29].

Conclusion

In this study, modified phthalocyanines having azo group and bearing naphthol units on the periphery were successfully prepared. The new compounds were characterized by using elemental analyses, ^{1}H NMR, UV-Vis and FT-IR spectroscopy and mass spectrometry. The results confirmed their proposed structures. The complexes (**2** and **3**) have good solubility in THF, DMF and DMSO. The Q bands of the phthalocyanine complexes (**2** and **3**) were red-shifted compared to the peripherally substituted metal-free and zinc phthalocyanine complexes. These complexes (**2** and **3**) produce an intense absorption from 450 to 500 nm and might suggest for some novel opto-electronic devices.

The fluorescence behaviors of the phthalocyanine complexes (**2** and **3**) were studied in THF. Generally, the Φ_F values of these complexes are lower than unsubstituted ZnPc.

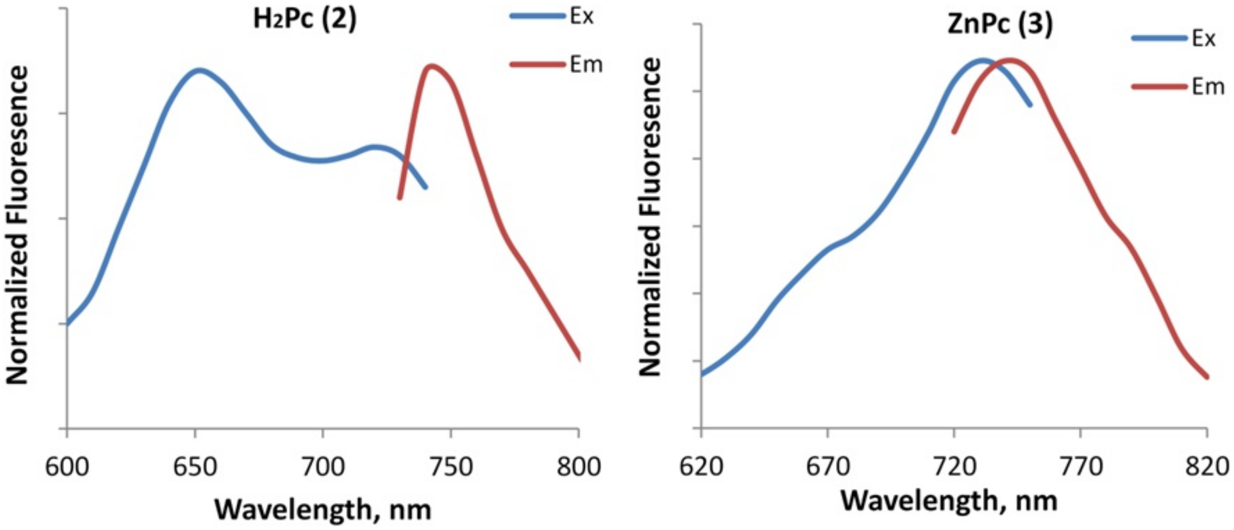


Figure 5. Excitation and emission spectra of **2** and **3** in THF. Excitation wavelengths: 650 nm for **2** and 670 nm for **3**.

Acknowledgments

This work was supported by the Research Fund of the Istanbul Technical University.

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