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The effect of p-tolyl-sulfonylamido units on thermal stability, mesogenic, photophysical properties and base sensitivity of unsymmetrical Zn(II) phthalocyanines

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Two unsymmetrically substituted phthalocyanines bearing six alkoxy moieties (**3a**) and six alkoxy facing two p-tolyl-sulfonyl(tosyl)amido moieties (**3b**) were synthesized by cyclotetramerization reactions of corresponding two different phthalonitrile derivatives in the presence of an anhydrous $Zn(AcO)_2$ and strong base. These novel compounds were fully characterized by elemental analyses, IR, ^1H and ^{13}C NMR and Mass spectra. The thermal stabilities of the phthalocyanine compounds were determined by thermogravimetric analysis (TGA). The mesogenic properties of these new materials were studied by differential scanning calorimeter (DSC) and optical microscopy. Absorption and emission based spectral characterization were done in THF. The base sensitivity of both compounds was examined with absorbance and fluorescence spectrophotometer in THF. The effect of tosylamido units on thermal stability, and mesogenic, photophysical and base sensitivity properties were discussed by comparing two compounds.

1. Introduction

The designing and synthesis of phthalocyanines (Pcs) have aroused extensive interest in the past decades because of their potential applications in various high technological areas such as sensors [1], catalysts [2], liquid crystals [3], nonlinear optics [4], photovoltaic solar cells [5,6] and photodynamic therapy [7–9]. The poor solubility of unsubstituted Pcs in common organic solvents causes to difficulties for most of these applications. The controlling of the solubility and also other properties of Pcs can be accomplished with designing of molecular composition with the number, position and nature of substituents and type of central metal.

In previous studies, we focused on the *p*-tolyl-sulfonylamido (tosylamido) substituted phthalocyanines [10–14]. The hydrogen bonding and deprotonation abilities of tosylamido unit bring interesting spectroscopic properties to Pc core such as solvatochromism and acidochromism [10]. Owing to these properties, the *octa*-tosylamido substituted Pcs were found as pH [11] and pentachlorophenol [12] sensitive optical sensors in solution and film. It is well known that the ordered films obtained from liquid crystalline Pcs are more sensitive than those of disordered films [15,16]. The sensor ability of *octa*-tosylamido substituted Pcs might be developed in ordered films but they do not exhibit liquid crystalline properties.

Recently, we reported the synthesis and mesogenic properties of unsymmetrically substituted Ni(II) Pcs bearing two tosylamido and six alkylthio moieties [14]. It was found that the phase transition temperature of these Pc derivatives are higher but clearing temperatures are lower than their symmetric analogous substituted with eight alkylthio groups. Nevertheless, this comparison was not sufficient to understand the effect of tosylamido groups on mesogenic properties of Pcs. Because unsymmetrical and symmetrical derivatives have different number (six and eight) of alkyl chains which is very effective in the phase transition and clearing temperatures.

Therefore, we designed two novel unsymmetrical Zn(II)Pcs which were substituted with six dodecylalkoxy groups (**3a**) and with six dodecylalkoxy and tosylamido groups (**3b**) in order to determine the effect of the tosylamido groups on thermal stability, and mesogenic, photophysical and base sensitivity properties. Zn(II) central metal was preferred to improve photophysical properties of Pc unit. The mesogenic and photophysical properties of both compounds were compared as well.

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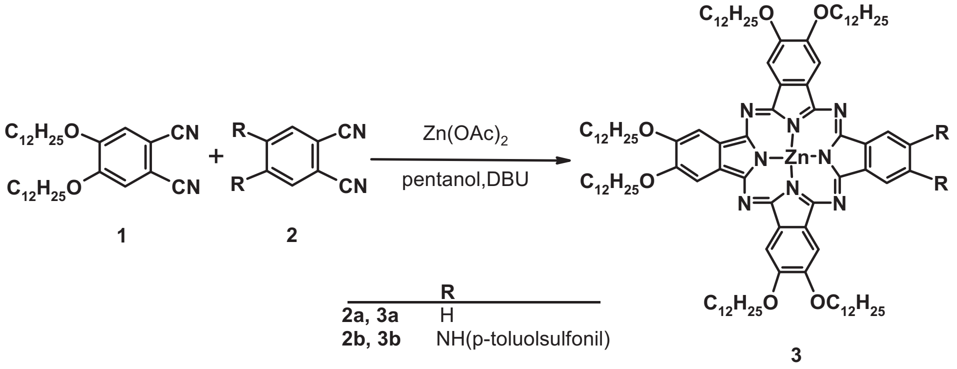

Scheme 1. Synthesis routes of novel asymmetric phthalocyanine complexes.

2. Experimental

2.1. Materials

$Zn(OAc)_2$, 1,5-diazabicylo[4.3.0]non-5-ene (DBU), THF-d_8, phthalonitrile and all solvents were purchased from commercial suppliers. Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 P F_{254}.

2.2. Measurements

Elemental analyses were obtained from Thermo Finnigan Flash 1112. Infrared spectra in KBr pellets were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. Optical spectra in UV–Visible region were recorded with a Shimadzu 2001 UV spectrophotometer and fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer. The mass spectra were recorded on a MALDI (Matrix Assisted Laser Desorption Ionization) BRUKER Microflex LT using a 2,5-dihydroxybenzoic acid as matrix. ^{1}H and ^{13}C NMR spectra were recorded in THF-d_8 solutions on a Varian 500 MHz spectrometer. The phase transition behavior of phthalocyanine complexes were observed by means of polarizing microscope (Leitz Wetzler Orthoplan-pol.) equipped with the hot stage (Linkam TMS 93) and temperature-controller (Linkam LNP). Thermogravimetric analyses and the determination of transition temperatures were carried out on Mettler Toledo Star^e Thermal Analysis System/DSC 822^e with scan rate of 10 °C min^{-1}. Differential scanning calorimeter system was calibrated with indium from 4 to 7 mg samples under nitrogen atmosphere.

2.2.1. Spectroscopic studies

Absorption and fluorescence spectra were recorded at room temperature using 1 cm path length quartz cells. The fluorescence quantum yields (Φ_F) of Pcs were determined by comparative method [17] in THF with that of Zn(II) phthalocyanine (ZnPc) as a reference ($\Phi_F = 0.20$) [18]. The samples and standard were excited at the same wavelength, at 616 nm for **3a** and 621 nm for **3b**. Natural radiative (τ_0) lifetimes were determined using Photochem CAD program which uses the Strickler–Berg equation [19]. The fluorescence lifetimes (τ_F) were evaluated using Equation $\Phi_F = \tau_F/\tau_0$.

Acid-base titrations of Pcs were performed by addition of increasing amounts of KOH or HCl solutions in MeOH to the fixed concentrations of Pcs (3 ml; 7.5×10^{-6} mol dm^{-3}). Blank tests were applied to eliminate the possibility of any effect of MeOH, but no appreciable change was observed.

2.3. Syntheses

The 1,2-di(dodecylalkoxy)-4,5-dicyanobenzene (**1**) [20] and 4,5-dicyano-N,N′-ditosyl-o-phenylenediamine (**2b**) [10] were synthesized according to published procedures.

2.3.1. 2,3,9,10,16,17-Hexakis(dodecylalkoxy)phthalocyaninato zinc(II) (*3a*)

A mixture of 1,2-di(dodecylalkoxy)-4,5-dicyanobenzene (**1**) (3.88 g, 7.81 mmol), phthalonitrile (**2a**) (0.2 g, 1.56 mmol), anhydrous $Zn(OAc)_2$ (0.85 g, 4.68 mmol), DBU (1 mL) (1.018 g, 6.68 mmol) and freshly dried n-pentanol (7 mL) were heated to reflux for 18 h under argon atmosphere. After cooling to room temperature, the reaction mixture was treated with ethanol (50 mL) and occurring green precipitate was filtered then washed several times with ethanol. The dark green product was purified by preparative thin layer chromatography (TLC) using silica gel, and 50/1 dichloromethane/ethanol solvent system as eluent. Yield: 0.17 g, 6.5%. FT-IR ν_{max}/cm^{-1}(KBr pellet): 3078 (CH_{ar}), 2919-2850 (CH), 1606, 1494, 1464, 1385, 1277, 1204, 1115, 1098, 1073, 1048, 854,

Table 1
Phase transition temperatures and enthalpies (kj/mol) for the compound **3a** and **3b** as determined by DSC and microscope. Heating and cooling rates in DSC: 10 °C, heating range:0–350 °C for **3a**; 0–220 °C for **3b**; C = crystal, LC = liquid crystal, I = isotropic phase.

Sample	Heating		Cooling	
	C ⟶ LC	⟶ I	I ⟶ LC	⟶ C
3a	82 (8.97)	390 (mic.; Decomp.)	-------	38(5.89)
3b	183 (18.80)	295 (mic.; Decomp.)	-------	169(12.11)

739. ^{1}H NMR (THF-d_8) δ(ppm): 0.80 (t, 18H, CH_3), 1.47 (m, 12H, CH_2), 1.42–1.22 (m, 84H, CH_2), 1.68 (m, 12H, CH_2), 2.07 (m, 12H, CH_2), 4.38 (t, 12H, O–CH_2), 7.92 (b, 2H, CH_{ar}), 8.32, 8.41 and 8.46 (s, 6H, CH_{ar}), 9.07 (b, 2H, CH_{ar}). ^{13}C NMR (THF-d_8) δ(ppm): 13.50 (CH_3), 22.62 (CH_2), 26.50 (CH_2), 26.53 (CH_2), 29.44 (CH_2), 29.78 (CH_2), 29.83 (CH_2), 29.87 (CH_2) 29.94 (CH_2), 29.96 (CH_2), 31.96 (O–CH_2), 105.45 ($C_{ar}H$), 122.08 ($C_{ar}H$), 127.78 ($C_{ar}H$), 131.94 (C_{ar}), 132.29 (C_{ar}), 138.20 ($C_{ar}O$), 151.37 ($NC_{ar}N$), 152.46 ($NC_{ar}N$). Calc. for $C_{104}H_{160}N_8O_4Zn$: %C 74.18, %H 9.58, %N 6.65; Found: %C 74.06, %H 9.69, %N 6.57. MS (MALDI) *m*/*z*: Calc. 1683; Found: 1683 $[M]^+$

2.3.2. 2,3,9,10,16,17-Hexakis(dodecylalkoxy)-23,24-bis(tosylamido) phthalocyaninato zinc(II) (*3b*)

A mixture of 1,2-di(dodecylalkoxy)-4,5-dicyanobenzene (**1**) (0.42 g, 0.86 mmol), 4,5-dicyano-N,N′-ditosyl-*o*-phenylenediamine (**2b**) (0.2 g, 0.43 mmol), anhydrous $Zn(OAc)_2$ (0.11 g, 0.64 mmol), DBU (1 mL) (1.018 g, 6.68 mmol) and freshly dried n-pentanol (7 mL) were heated to reflux for 18 h under argon atmosphere. After cooling to room temperature, the reaction mixture was treated with ethanol (50 mL) and occurring green precipitate was filtered then washed several times with ethanol. The crude product was dissolved in a mixture of 1/5 acetic acid/dichloromethane (100 mL). After extracting with distilled water (4 × 100 mL), the organic phase was dried over anhydrous Na_2SO_4 and solvent was removed. The dark green desired product was purified by preparative thin layer chromatography (TLC) using silica gel, and 50/1 dichloromethane/ethanol solvent system as eluent. Yield: 0.12 g, 13.8%. FT-IR ν_{max}/cm^{-1} (KBr pellet): 3347–3278 (NH), 3076 (CH_{ar}), 2922–2852 (CH), 1604, 1347-1166 (SO_2) 1494, 1457, 1418, 1381, 1278, 1201, 1090, 1042, 915813, 743, 707, 667. ^{1}H NMR (THF-d_8) δ(ppm): 0.79 (t, 18H, CH_3), 1.18–1.51 (m, 72H, CH_2), 1.61 (m, 24H, CH_2), 1.69 (p, 12H, CH_2), 1.92–2.06 (m, 12H, CH_2), 2.21 (s, 6H, CH_3), 4.39 and 4.47 (t, 12H, O–CH_2), 7.22 (d, 4H, $CH_{ar(tosyl)}$), 7.80 (d, 4H, $CH_{ar(tosyl)}$), 8.66 (s, 2H, CH_{ar}), 870 and 8.71 (s, 6H, CH_{ar}), 8.96 (s, 2H, NH). ^{13}C NMR (THF-d_8) δ(ppm): 13.46 (CH_3), 20.55 ($CH_{3(tosyl)}$), 22.59 (CH_2), 26.39 (CH_2), 26.47 (CH_2), 29.39 (CH_2), 29.61 (CH_2), 29.68 (CH_2), 29.72 (CH_2), 29.82 (CH_2), 29.84 (CH_2), 29.87 (CH_2), 31.93 (O–CH_2), 105.99 ($C_{ar}H$), 118.39 ($C_{ar}H$), 127.66 ($C_{ar}H_{(tosyl)}$), 129.40 ($C_{ar}H_{(tosyl)}$), 132.21 (C_{ar}), 132.46 (C_{ar}), 132.53 (C_{ar}), 135.78 ($C_{ar}O$), 137.37 ($C_{ar(tosyl)}$–SO_2), 143.40 ($C_{ar(tosyl)}$–CH_3), 152.66 ($NC_{ar}N$), 153.67 ($NC_{ar}N$). Calc. for $C_{118}H_{174}N_{10}O_{10}S_2Zn$: %C 70.08, %H 8.67, %N 6.93; Found: %C 70.01, %H 8.90, %N 6.78. MS (MALDI) *m*/*z*: Calc. 2022; Found: 2022 $[M]^+$.

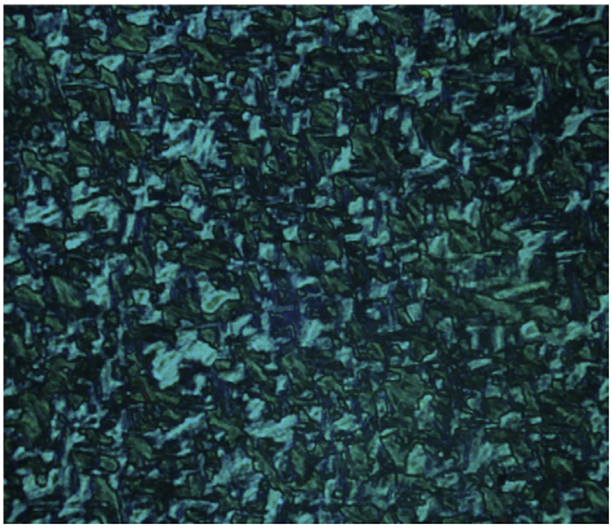

Fig. 1. Photomicrograph of the texture of **3a** at 100 °C.

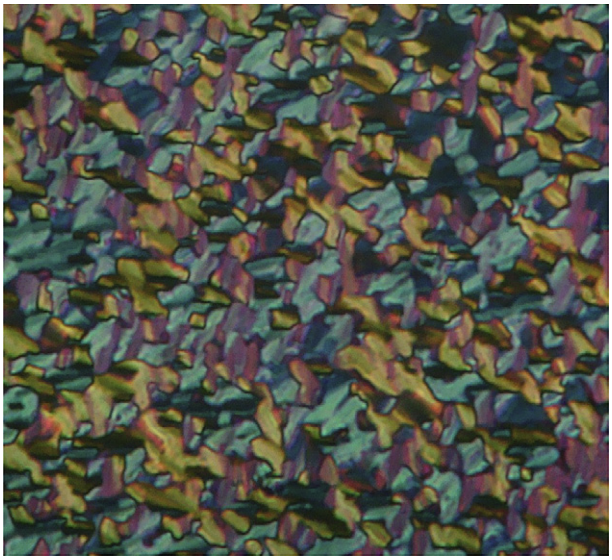

Fig. 2. Photomicrograph of the texture of **3b** at 200 °C.

3. Results and discussion

3.1. Synthesis and characterizations

The synthesis of 1,2-di(dodecylalkoxy)-4,5-dicyanobenzene (**1**) [20] and 4,5-dicyano-*N,N′*-ditosyl-o-phenylenediamine (**2b**) [10] starting materials were achieved as reported. The unsymmetrical Zn(II)Pcs (**3a**, **3b**) were synthesized by statistical condensation reactions of 5:1 mixture of 1,2-di(dodecylalkoxy)-4,5-dicyanobenzene (**1**) and phthalonitrile (**2a**) or 2:1 mixture of 1,2-di(dodecylalkoxy)-4,5-dicyanobenzene (**1**) and 4,5-dicyano-N,N′-ditosyl-o-phenylenediamine (**2b**) in the presence of anhydrous $Zn(OAc)_2$ and DBU in n-pentanol as outlined in Scheme 1. In both reactions, the symmetrical *octa*-(dodecyloxy) substituted Zn(II)Pc was formed in major amount. Desired compound (**3a** or **3b**) was isolated from reaction mixture by preparative thin layer chromatography (TLC) using silica gel, and 50/1 dichloromethane/ethanol solvent system as eluent. Both compounds were soluble in dichloromethane, chloroform, tetrahydrofuran and hexane. Compound **3b** was also soluble in hot polar solvents such as ethyl acetate, DMF and DMSO.

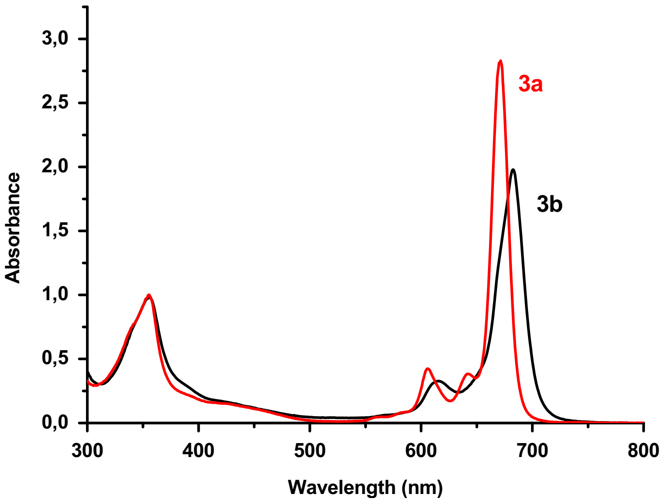

Fig. 3. Absorption spectra of compounds **3a** and **3b** (1×10^{-5} M in THF).

Table 2
Absorption and fluorescence spectra related data of compounds **3a** and **3b** in THF.

Comp	λ^1_{abs} (logε)	λ^2_{abs} (logε)	λ^{ex}_{max}	λ^{em}_{max}	$\Delta\lambda_{ST}$	Φ_F	τ_F
3a	672 (5.46)	352 (4.97)	671	686	17	0.237	1.474
3b	683 (5.29)	353 (4.99)	684	696	15	0.195	1.161

The novel unsymmetrical Zn(II) Pcs (**3a**, **3b**) were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, and mass spectra and the results were given in experimental section. The mass spectra which were obtained by MALDI (2,5-dihydroxybenzoic acid was used as matrix) were consistent with assigned formulations. The ^{1}H and ^{13}C NMR spectra of compounds **3a** and **3b** were achieved in deuterated THF and all protons and carbons were observed in their respective regions and results were given in experimental section.

3.2. Thermotropic behaviors

It is well known that the substitution with long flexible hydrocarbon chains provides phthalocyanine compounds with thermotropic liquid crystalline behavior showing discotic mesophase. The mesogenic properties of the unsymmetrical Zn(II) Pcs which were bearing with only six dodecylalkoxy groups (**3a**) or with six dodecylalkoxy and tosylamido groups (**3b**) were investigated and compared to determine the effect of tosylamido groups on mesogenic properties.

Thermal stability of compounds **3a** and **3b**, evaluated by thermal gravimetric analysis (TGA), was the first investigated parameter to determine the beginning of the thermal degradation. This is helpful to guide further phase transition investigations. The TGA thermograms of compounds **3a** and **3b** were recorded at a heating rate of 10 °C/min. The decomposition of compound **3a** was determined around 390 °C with 60% weight loosing which can be attributed to breaking off the alkyl chains. The compound **3b** showed two decompositions around 295 °C with 18% weight loosing and 390 °C with 45% weight loosing which were assigned as breaking of two tosylamido units and then alkyl chains.

The phase transition behaviors of novel unsymmetrical Zn(II)Pcs (**3a**, **3b**) were determined by polarized optical microscopy (POM) observations and differential scanning calorimeter (DSC): Results are summarized in Table 1. In DSC measurements, the heating cycles (0–350 °C for **3a**; 0–220 °C for **3b**) were interrupted before reaching a clearing point to avoid decomposition. The DSC diagrams of both compounds showed one endothermic peak in the heating cycle and one exothermic peak in the cooling cycle (Table 1). All these peaks were assumed to transition from crystalline to liquid crystalline or from liquid crystalline to crystalline phases. In the microscopic investigations, only one type of mesophase were detected for compounds **3a** and **3b** and they conserved the liquid crystalline phases until decomposition points, 390 °C and 295 °C, respectively (Table 1). The optical textures, shown in the Fig. 1 and Fig. 2, were typical mosaic of that of a hexagonal columnar mesophase Col$_h$ which is often observed on thermotropic phthalocyanine liquid crystals [14,21–26].

3.3. Spectroscopic investigations based on absorption and emission Spectra

Our previous studies exposed that the hydrogen bonding and deprotonation abilities of tosylamido unit bring solvatochromic and acidochromic properties to Pc core: In basic medium, the absorbance and fluorescence spectra of Zn(II), Ni(II) and metal free derivatives of *octa*-tosylamido substituted Pcs showed bathochromic shifting [10,11]. However, in acidic medium only Zn(II) derivative showed new band in the longer wavelength. Here we present the investigation and comparison of photophysical properties of two novel unsymmetrical Zn(II) Pcs which contain only six dodecylalkoxy (**3a**) or with six dodecylalkoxy and tosylamido (**3b**) moieties.

The absorption spectra of both compounds showed two main bands which are typical for metallo Pcs; the Q band was observed at 672 nm for compound **3a** and 683 nm for compound **3b** and the B band was observed around 350 nm for both compounds (Fig. 3). The Q band is a major π–π* transition from the HOMO to the LUMO [27–32] and it corresponds to an electronic charge transfer from the pyrrole carbon skeleton to the other atoms of molecule [27]. It is well documented that the size and symmetry of the π–conjugated system [30], the central metal atom [31], and the type, number and

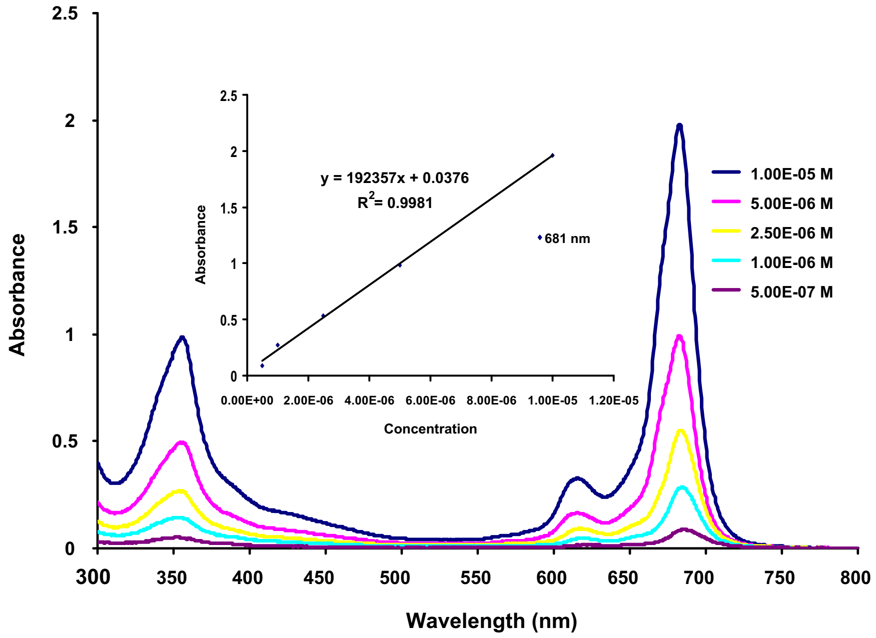

Fig. 4. Aggregation behavior of **3b** in THF at different concentrations.

positions of the substituents [28,29,31,32] can affect the energy gap (ΔE) between HOMO and LUMO as the position and bandwidth of bands in absorption spectra. Generally, the bearing of electron-releasing groups on Pc core causes to red shifts of Q and B band, while electron-withdrawing groups (except halogens) causes to shift to blue shifts, oppositely [29,32]. In our case, the bearing of tosylamido groups which is unique difference between two structures caused to red shifted and less intense Q band in compound **3b** compared to compound **3a** (Table 2). A result of the absorption maximum of the Q bands indicate that the tosylamido groups should not be considered as electron-withdrawing substituents despite electron-withdrawing tosyl units. However, as mentioned by Shaposhnikov *et al.*, detailed interpretation of the substitution pattern effect of Pcs to their electronic absorption spectra may be difficult, as the geometry of the molecule plays a role as well [31]. With this viewpoint, the effect of tosylamido groups on the geometry of compound **3b** must be taken account.

Aggregation causes to several problems for almost all applications of Pcs and it is usually dependent of concentration, nature of substituent, central metal ions, and temperature [33,34]. Aggregation changes the shapes of UV–Vis. spectra in lowering the extinction coefficients in the Q band at high concentrations. We studied the effect of concentration on the absorption spectra for both compounds (Fig. 4 for compound **3b**, Fig. S1 for compound **3a**). Beer–Lambert law was obeyed at maximum absorption (Q band) in the concentration ranging from 1×10^{-7} to 1×10^{-5} mol dm^{-3}. As the concentration was increased, the absorption maxima of Q band also increased and the blue shift of band was not observed. This fact confirms that both compounds show no aggregation in the concentration range of our spectral investigations.

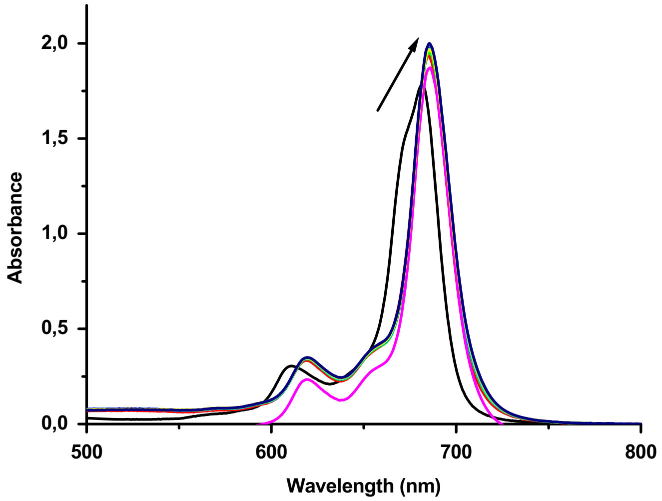

Fig. 6. Spectral changes in Q band of compound **3b** (3 ml, 7.5×10^{-6} M in THF) upon addition of increasing amounts of KOH in EtOH (2.25×10^{-3} M): 0, 10, 20, 30, 40, 50, 60, 70, 80 μl.

Compound **3a** and **3b** show similar fluorescence behavior in THF. Their absorption, excitation and emission spectra were given in Fig. 5. And all spectral data including excitation and emission spectra related emission (λ_{max}^{em}) and excitation (λ_{max}^{ex}) maxima, Stoke's shift ($\Delta\lambda_{ST}$), fluorescence quantum yields (φ_F) and lifetimes (τ_F) are summarized in Table 2. The proximity of the wavelength of the Q band absorption to the Q band maxima of the excitation

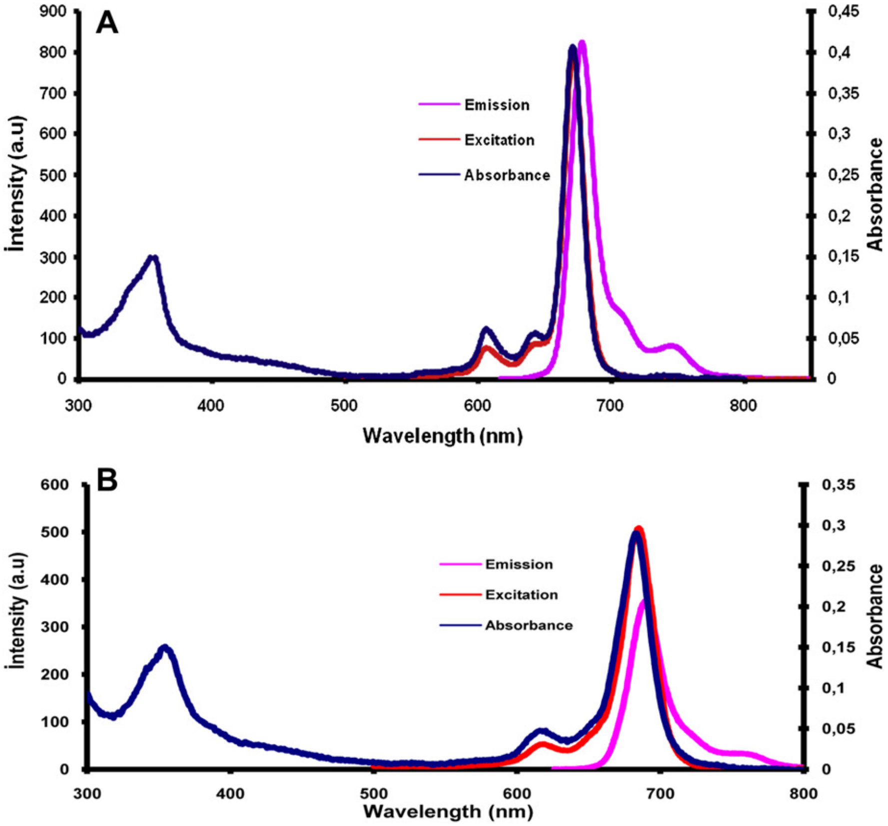

Fig. 5. Absorption, excitation and emission spectra for A) compound **3a** and B) compound **3b** in THF. Excitation wavelength 616 nm for **3a** and 621 nm for **3b**.

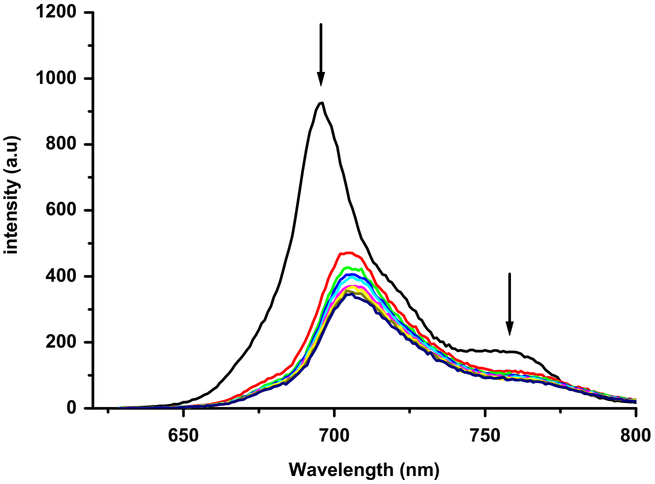

Fig. 7. Spectral changes in emission band of compound **3b** (3 ml, 7.5 × 10^{-6} M in THF) upon addition of increasing amounts of KOH in EtOH (2.25 × 10^{-3} M): 0, 10, 20, 30, 40, 50, 60, 70, 80 μl.

spectra for both compounds confirms that the nuclear configurations of the ground and excited states are similar and not affected by excitation in THF. Compounds **3a** and **3b** show one emission band centered at 686 and 696 nm, respectively. Comparison of compounds **3a** and **3b** shows that the bearing of tosylamido unit in compound **3b** causes to tolerable decreasing in quantum yield and fluorescence lifetime (Table 2). The lower fluorescence quantum yield and lifetime may be a result of intra-molecular quenching of the excited singlet state by tosylamido groups.

We have preliminary investigated and compared the spectral changing of with or without *octa*-tosylamido substituted asymmetrically Pc compounds (**3a** and **3b**) in acidic or basic medium on absorbance and fluorescence spectra. Acidic medium was obtained by portional addition of HCl solution to THF solutions of compounds, while KOH solution was used for basic medium.

The addition of increasing concentrations of KOH to THF solution of compound **3a** did not caused to any changing on absorbance and fluorescence spectra (Figs. S2 and S3 in supplementary file). Although, it caused to small bathochromic shifting in Q absorbance band and noticeable decreasing in emission band of compound **3b** as shown in Fig. 6 and Fig. 7, respectively. On the successive addition of HCl to this basic solution of compound **3b**, the absorbance and florescence spectra turned back to the original states. These reversible spectral changing which are caused by deprotonation

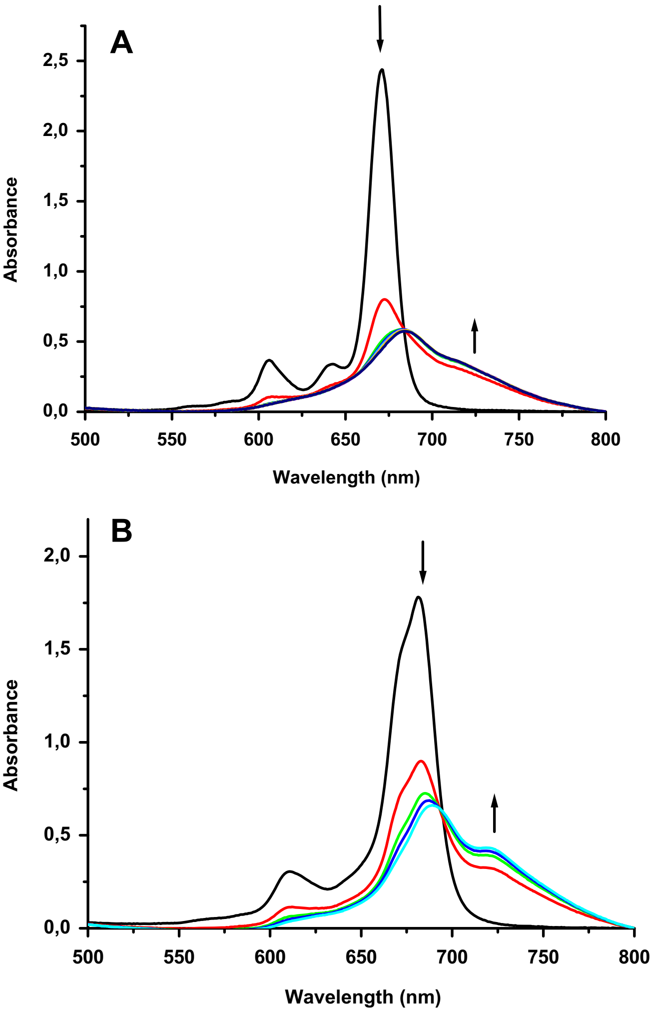

Fig. 8. Spectral changes in Q bands of A) compound **3a** (3 ml, 7.5 × 10^{-6} M in THF) B) compound **3b** (3 ml, 7.5 × 10^{-6} M in THF) upon addition of increasing amounts of HCl in EtOH (2.25 × 10^{-3} M): 0, 10, 20, 30, 40, 50, 60, 70, 80 μl.

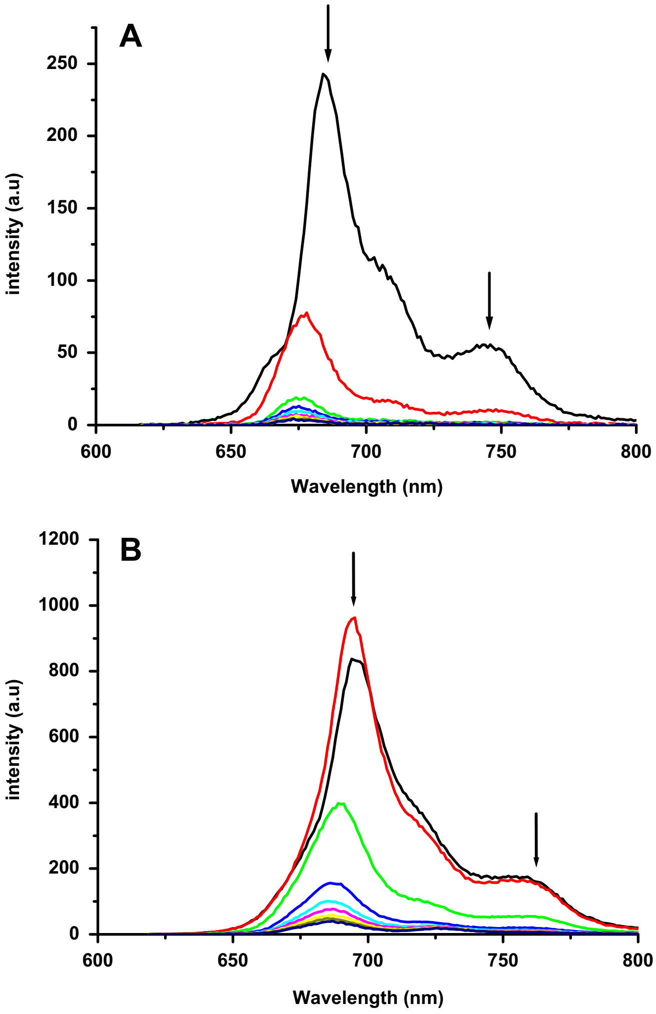

Fig. 9. Spectral changes in emission bands of A) compound **3a** (3 ml, 7.5 × 10^{-6} M in THF) B) compound **3b** (3 ml, 7.5 × 10^{-6} M in THF) upon addition of increasing amounts of HCl in EtOH (2.25 × 10^{-3} M): 0, 10, 20, 30, 40, 50, 60, 70, 80 μl.

abilities of tosylamido units were compatible to our expectation. Although, change on signal wavelength on absorbance band was found less than *octa*-tosylamido substituted Pcs [10,11] because of the less number of tosylamido groups in molecule. Fortunately, the spectral change on emission band was found noticeable even less number of tosylamido groups.

With addition of increasing concentrations of HCl to THF solutions of compounds **3a** and **3b** showed very similar behaviors on absorbance and fluorescence spectra. In the absorbance spectra of both compounds, the intensity of Q band decreased and new band appeared in the longer wavelength (Fig. 8). In the fluorescence spectra, acid addition was caused to quenching of emission bands as seen Fig. 9. Sequential addition of KOH to these acidic solutions gave corresponding original spectra. This reversible acid response was exactly same for both compounds with and without tosylamido moiety. It is clear that the weak acidic [35] tosylamido moiety cannot bring any spectral changing with acid titration. This changing can be attributed to protonation of meso nitrogen atoms of Pc rings. Because four meso nitrogen atoms of metalated azaporphyrins and phthalocyanines, especially Zn(II)Pcs, exhibit basic character and able to give acid–base interaction with an acid which causes to spectral changing on absorbance and emission bands [10,36–39].

4. Conclusions

In this study, we synthesized and characterized two novel unsymmetrical Zn(II) Pcs which are substituted with only six dodecylalkoxy groups (**3a**) or with six dodecylalkoxy and tosylamido groups (**3b**) in order to determine the effect of tosylamido units on thermal stability, and mesogenic, photophysical and base sensitivity properties by comparing two compounds. The results were found: **1**) In thermogravimetric analysis, both compounds gave main decomposition in 390 °C with breaking off the alkyl chains but compound **3b** began to decompose at 295 °C with breaking off tosylamido units. **2**) Both compounds showed one type mesophase which was detected by polarized microscopy and also differential scanning calorimeter (DSC). The presence of tosylamido units in compound **3b** caused to increase of clearing temperature and decrease of melting point because of the lower decomposition temperature then compound **3a**. **3**) The comparison of the absorption and fluorescence spectra of both compounds showed that the presence of tosylamido units in compound **3b** gave rise to red shifted, less intense Q band and also red shifted excitation band with slightly lower quantum yield and fluorescence lifetime. **4**) The preliminary spectral investigations of both compounds in acidic or basic medium showed that only compound **3b** sensitive to base which is caused by tosylamido units but they both are sensitive to acid like as almost all Zn(II)Pcs. All spectral changes are found reversible and reproducible even after several assays.

It is well known that the ordered films obtained from liquid crystalline Pcs are more sensitive than those of disordered films. With this respect, it was expected that the acid and base sensitivity of compounds **3a** and **3b** might be improved by ordered liquid crystalline films. Unfortunately, these compounds are not liquid crystal in ambient temperature, therefore the spectral investigations have been completed in solution and expected hints have been obtained. Later studies should focused on obtaining similar tosylamido substituted phthalocyanine compounds being liquid crystalline at room temperature.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2011.10.019.

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