



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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ABSTRACT

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 ¹³C 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.

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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.

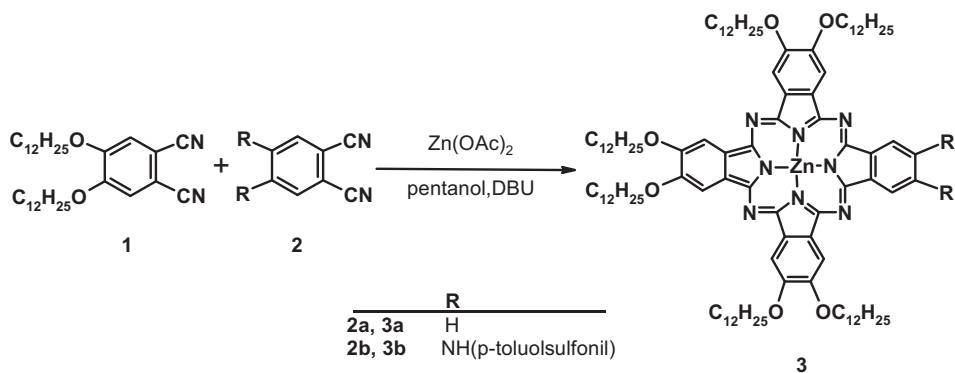
In previous studies, we focused on the *p*-tolyl-sulfonylamido (tosylamido) substituted phthalocyanines [10–14]. The hydrogen bonding and deprotonation abilities of tosylamido unit bring interesting spectroscopic properties to Pc core such as solvatochromism and acidochromism [10]. Owing to these properties, 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-diazabicyclo[4.3.0]non-5-ene (DBU), THF-d₈, 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 F₂₅₄.

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. ¹H and ¹³C NMR spectra were recorded in THF-d₈ 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 $\nu_{\text{max}}/\text{cm}^{-1}$ (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	LC → I	I → LC	LC → C
3a	82 (8.97)	390 (mic.; Decomp.)	-----	38(5.89)
3b	183 (18.80)	295 (mic.; Decomp.)	-----	169(12.11)

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