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# Preparation and optical properties of novel symmetrical hexadecachlorinatedphthalocyaninato zinc(II) spin coated thin films

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#### Abstract

Novel symmetrical 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16,17,23,24-octa-(3,5- dichlorophenoxy)phthalocyaninato zinc(II) was synthesized and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, UV-Vis, XRD, and IR spectrometry. The synthesized ZnPc complex is soluble in various organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, THF, acetone, and ethyl acetate. This property helped to obtain thin films of the new ZnPc complex by spin coating method. The surface morphology of the thin films was investigated by atomic force microscopy, AFM, and showed that the molecules grow in stacks of rows. The spectrophotometric measurements of transmittance (T) and reflectance (R)spectra were carried out in the wavelength range 190-3000 nm. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Phthalocyanines; Chlorinated-phenoxy; Spin coated thin film; Solubility

# 1. Introduction

Phthalocyanines are potential materials in many applications and technologies. This class of compounds is of a great interest because of their critical role in emerging technologies that include photoconductors, solar cells, and chemical sensors [1-3]. Photoconductivity is one of the most important properties of phthalocyanines, and intensive research has been carried out to improve their electrical conductivity by doping mechanism or polymerization methods [1].

Electrical, optical, and structural properties of phthalocyanine thin films are dependent on various parameters such as evaporation rate, substrate temperature, and post-deposition annealing. Various methods have been described for deposition of oriented films of phthalocyanines such as vacuum deposition, organic molecular beam

epitaxy [4], Langmuir-Blodgett film formation [5], selfassembled monolayer films [6], and spin-coating technology [7,8]. The relationship between the physical properties of Pc films and the molecular orientation was extensively investigated by using various techniques [5,9].

Unsubstituted phthalocyanines are sparingly soluble in most organic solvents, hence, limiting their applications. The solubility of Pcs can be increased by attaching peripheral or non-peripheral solubility-enhancing substituents such as alkyl, alkoxy, phenoxy and macrocylic groups and/or the central metal [10]. These substituents enhance the solubility of phthalocyanines and modify the aggregation state in solution and other physical properties [11,12].

We report the synthesis of novel hexadecasubstituted phthalocyaninato zinc(II) by the substitution of Pc with hexyloxy groups in non-peripheral and chlorinated-phenoxy groups in peripheral positions. Thin films of the prepared ZnPcs were deposited by using spin coating technique onto microscope slide substrates, and their structural and optical parameters are described.

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### 2. Experimental

All solvents were HPLC grade and used without further purification. Melting points were determined using Kofler hot stage melting point apparatus. IR spectra were recorded on Shimadzu Fourier Transform Infrared Spectrometer FTIR-400 using KBr disks. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 MHz in the deuterated solvents specified, and are reported in parts per million (ppm,  $\delta$ ).

The films were deposited onto standard microscope slide substrates of thickness 1 mm at room temperature. The slide substrates were cleaned ultrasonically in acetone and then rinsed with deionized water. The films were deposited using spin coating technique (Specialty Coating Systems G3P-8 Spin Coater) under nitrogen flow at 2000 rpm for 2 min. The surface microstructure was measured by atomic force microscopy (AFM; Veeco CP-II) in non-contact mode with Si tips at a scan rate of 1 Hz. The film thickness of 45-50 nm was estimated from AFM measurements. Transmittance  $T(\lambda)$ , and reflectance,  $R(\lambda)$  spectra of the films were measured at normal incidence and at an incident angle of 5°. The measurements were acquired at room temperature in the spectral range 190-3000 nm by using a computer-aided double-beam spectrophotometer Shimadzu 3150 UV-VIS-NIR with a resolution of 0.1 nm. Phthalocyanine diffraction pattern was examined using Shimadzu XRD-6000 X-ray diffractometer using Cu Ka radiation  $(\lambda = 1.5418 \text{ Å})$ . The X-ray tube voltage and current were 40 kV and 30 mA, respectively.

# 2.1. Preparation of 4,5-dichloro-3,6-dihexyloxyphthalonitrile(2)

The compound was synthesized as reported before [13].

# 2.2. Preparation of 4,5-bis(3,5-dichlorophenoxy)-3,6bis(hexyloxy)phthalonitrile (3)

The compound was synthesized following the procedure reported before [13]. The resulting product was purified by column chromatography (silica gel, eluent: *n*-hexane:THF, 5:1) to yield 4,5-bis(3,5-dichlorophenoxy)-3,6-bis(hexyloxy)phthalonitrile (**3**) as a white solid (280 mg, Yield 85 %). IR (KBr):  $v_{max}$  cm<sup>-1</sup> 2933, 2851, 1596, 2220 (C $\equiv$ N), 1604 (C=C), 1468, 1315, 1263, 1125 (C–O–C), 963, 832. MS (GC–MS): *m/z* (CI) 650.  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 7.09 (2H, t, Ar–H), 6.71 (4H, d, Ar–H), 4.16 (4H, t, **OCH**<sub>2</sub>), 1.67 (4H, quint, –CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.2–1.48 (12H, m, –CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 0.82 (6H, t, 2 × CH<sub>3</sub>).

2.3. Preparation of 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16,17,23,24-octa-(3,5dichlorophenoxy)phthalocyaninato zinc(II) (4)

A mixture of 3,6-didecylphthalonitrile (40 mg 0.095 mmol), 4,5-bis(3,5-dichlorophenoxy)-3,6-bis(hexyl-

oxy)phthalonitrile (127 mg, 0.196 mmol), zinc acetate dihydrate 99.999% (excess) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry n-pentanol (10 mL) was heated to reflux for 12 h under an argon atmosphere. The reaction mixture was cooled down to room temperature and the solvent was rotaevaporated under reduced pressure. The resulting dark green compound was separated by silica gel column chromatography using the appropriate eluent. Column chromatography on silica gel with *n*-hexane/DCM 4:1 gave five bands. The required 1.4.8.11.15.18.22.25-octahexyloxy-2.3.9.10.16.17.23.24octa-(3.5-dichlorophenoxy)phthalocyaninato zinc(II) (4) was collected as the final fraction by changing the eluent to (n-hexane/DCM 3:2) and it was further purified by column chromatography (silica gel, eluent: petroleum ether (bp 40-60 °C)/THF 10:1) to afford a waxy green product (70 mg, Yield 9%). IR(KBr): v, cm<sup>-1</sup>, 3052 (Ar-CH), 2940 and 2850 (CH<sub>2</sub>).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ , ppm 6.90 (8H, t, Ar-H), 6.65 (16H, d, Ar-H), 4.17 (16H, t,  $8 \times OCH_2$ ), 1.02–1.60 (64H, m), 0.81 (24H, t,  $8 \times -CH_3$ ).  $\delta_{\rm C}$  (400 MHz, CDCl<sub>3</sub>) ppm 14.0 (CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 76.6 (OCH<sub>2</sub>), 114.4  $(2 \times CH)$ , 120.4 (C), 123.6 (CH), 135.6 (C), 146.1 (C), 146.9 (C), 157.8 (C), 164.3 (C). MS (GC-FAB): m/z (%) 2668 [M+H]<sup>+</sup>, MS (GC–FAB): *m*/*z* (%) 2668 [M+H]<sup>+</sup>.

#### 3. Results and discussion

#### 3.1. Synthesis

Preparation of the phthalonitrile derivative with the desired substituents is a critical step in phthalocyanine synthesis. In the key intermediate, aryloxy groups substituted with chlorine atoms were incorporated to increase the solubility of the resulting phthalocyanine. The oxygen atoms in the non-peripheral and peripheral positions cause a bathochromic shift of the long wavelength absorption maximum which helps to widen the visible window of the target ZnPc. Therefore, 4,5-bis(3,5-dichlorophenoxy)-3,6-bis(hexyloxy)phthalonitrile was prepared by the treatment of 4,5-dichloro-3,6-dihexyloxyphthalonitrile with 3,5-dichlorophenol, 1, and  $K_2CO_3$  in DMSO, Scheme 1.

It is difficult to synthesize the target ZnPc complex by direct cylotetramerization of 4,5-bis(dichlorophenoxy)-3,6-dihexyloxyphthalonitrile in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [14]. The steric effect of the bulky substituents on the phthalonitrile probably is the reason for the slow reaction progress. The target ZnPc complex was synthesized according to the statistical condensation of two different phthalonitriles procedure [13,15]. The procedure involves the reaction of 4,5-bis(3,5-dichlordphenoxy)-3,6-dihexyloxyphthalonitrile (**3**) and 3,6-didecylphthalonitrile (2:1 ratio) in *n*-pentanol in the presence of Zn(OAc)<sub>2</sub> · 2H<sub>2</sub>O and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 140 °C under argon atmosphere for 12 h (Scheme 2). The resulting crude product was subjected to TLC using *n*-hexane/DCM (3:2)



Scheme 1. Synthesis of 4,5-bis(dichlorophenoxy)-3,6-dihexyloxyphthalonitrile (3).



Scheme 2. Synthesis of 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16,17,23,24-octa-(3,5-dichlorophenoxy)phthalocyaninato zinc(II) (4).

as eluent and showed five bands. The first fraction contained the undesired symmetrical octadecylphthalocyanine (AAAA) compound. The following three bands were possibly AAAB, AABB and ABBB which can be isolated in a very small quantity. The final separable green fraction was the symmetrical phthalocyanine derivative (BBBB), **4**, which was further purified by a new column using petroleum ether (bp 40–60 °C)/THF 10:1 as eluent to yield 60 mg (8.4%) as green waxy product. The aromatic region showed two broad signals integrated for 24 protons and assigned to the phenoxy ring protons. A triplet at 4.17 ppm was assigned to the 16 methylenoxy protons. The FAB–MS showed an isotopic cluster at 2668 m/e corresponding to the expected structure. Attaching the chlorinated pheneoxy groups to the peripheral position and hexyloxy groups to the non-peripheral position of phthalocyanines enhanced the solubility in organic solvents [16]. The increased solubility might be due to that the steric hindrance of peripheral 3,5-dichlorophenoxy substituents makes it harder to form dimers of 4. The prepared ZnPcs show high solubility in various organic solvents such as acetone, benzene, toluene, dichloromethane, ethyl acetate and tetrahydrofuran.

#### 3.2. Electronic absorption spectrometry

The UV–Vis spectrum of **4** in THF solution is typical of phthalocyanine compound, having a soret and Q-bands



Fig. 1. UV-Vis absorption spectrum of 4 in THF solution at room temperature.

(Fig. 1). The introduction of dichlorphenoxy groups onto the phthalocynine periphary increases the Q-band absorption wavelength of these molecules. The absorption spectrum of 4 is characterized by a strong absorption in the red region and a weaker absorption in the blue region. It is clear that the absorption bands of the chlorinated pheneoxy phthalocyanine 4 are shifted to a longer wavelength compared with the unsubstituted Pc. The spectral shift is attributed to the distortion of the ZnPc macrocycle and the electron withdrawing chlorine substituents on the phenyl rings. It is possible that the high electron withdrawing character of chlorine atoms tends to depopulate the  $\pi$ -systems, which would lead from a highly symmetrical planar state to low symmetry state molecule. However, there is no apparent change in the spectral features by comparing the chlorinated-phenoxy with the fluorine substituted phthalocyanines [13].

#### 3.3. Structural studies

The structure and morphology of phthalocyanine thin film was examined by using AFM. Many investigations on the morphology of metal-phthalocyanine have been reported especially CuPc complexes [17–19]. The molecular orientation strongly depends on the growth conditions and substrates. The regular structure of phthalocyanine thin films is described as a stack of needle-like molecules with alternating tilt angles so that the molecules are arranged in zig-zag chains. The growth direction of the molecule columns (*b*-axis) is normally found either with the *b*-axis parallel to the surface or standing up from the substrate face with an angle of about 32° from the surface plane [17–19].

Fig. 2a and b shows  $5 \times 5 \,\mu\text{m}$  2D and 3D AFM images of the thin film surface. The molecular arrangement of the ZnPc crystallites is visible. The phthalocyanine molecules are growing in aggregation rows rather in the parallel or in the zig-zag arrangement. The roughness of the films was estimated to be about 4.2 nm.

The XRD results of the as-deposited ZnPc film are shown in Fig. 3. The film showed a low degree of crystal-



Fig. 2.  $5 \ \mu m \times 5 \ \mu m$  AFM surface pattern of thin film of 4: (a) 2-D as-deposited and (b) 3-D as-deposited.



Fig. 3. X-ray diffraction pattern of as-deposited thin film of 4.

linity as indicated by the small intensity of the diffraction peak at  $2\theta = 5.08^{\circ}$ . The pattern shows the  $\alpha$  form because it does not show the characteristic double intense peak that is observed with the  $\beta$  form. The individual crystallite grain size was determined using Scherrer's relation [20] and was found in the order of 16.56 nm.

#### 3.4. Optical studies

Fig. 4 shows the UV-near infrared spectral behavior of transmittance  $T(\lambda)$  and reflectance  $R(\lambda)$  of the as-deposited ZnPc thin film. In Fig. 5, we report the absorption spectra



Fig. 4. Spectral behavior of transmittance  $T(\lambda)$  and reflectance  $R(\lambda)$  of thin film of 4.



Fig. 5. Spectral distribution of absorbance A (v) of thin film of 4.

of ZnPc thin film as a function of photon energy, hv. There are two main absorption bands: Q<sub>I</sub> at about 728 and Q<sub>II</sub> at about 655 nm and identified as the Q-band and attributed to the monomer and dimer, respectively [21].

The optical parameters were calculated from the transmission, absorption, and reflectivity data. The average transmission of a thin film on a substrate is given by [20]:

$$T = \frac{(1-R)^2 (1+k^2/n^2)}{\exp(\alpha d) - R^2 \exp(-\alpha d)}$$
(1)

where

$$k = \frac{\alpha \lambda}{4\pi} \tag{2}$$

The parameters  $\alpha$ , k, d, n, and  $\lambda$  are the absorption coefficient, absorption index, thin-film thickness, refractive index, and wavelength of the incident light in air, respectively. In any practical experiments, where  $k^2 \ll n^2$ , the average transmission is simplified as

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)}$$
(3)

The reflectivity of an absorbing medium of indices n and k in air for normal incidence is given by:



Fig. 6. The variation of absorption coefficient  $\alpha$  as a function of wavelength of thin film of **4**.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{4}$$

where n is the refractive index.

Using Eqs. (2) and (3), the variation of absorption coefficient,  $\alpha$ , with the wavelength was calculated as shown in Fig. 6.

The spectral distribution of refractive index  $n(\lambda)$  for **4** in the range 200–2800 nm is shown in Fig. 7. The spectrum shows an anomalous scattering in the range 300–760 nm with various peaks and a normal dispersion in the wavelength range 760–2700 nm. A very high rate of decrease is seen the refractive index in the range of wavelength 760– 1400 nm followed by a very low rate of decrease until about 2550 nm whereas the refractive index becomes wavelengthindependent. Finally a sudden drop around ~2700 nm occurs.

The variation of absorption coefficient  $\alpha$  with photon energy hv and the optical energy gap  $E_g$  is obtained from the following formula [20]:

$$\alpha = \alpha_0 (hv - E_g)^s \tag{5}$$

where  $\alpha_0$  is a constant



Fig. 7. Spectral distribution of refractive index  $n(\lambda)$  of thin film of **4** in the range 200–2800 nm.



Fig. 8. Variation of  $\alpha^{1/2}$  and  $\alpha^2$  with photon energy hv of as-deposited thin film of 4.

The exponent *S* determines the type of transition and can take the values 1/2, 2, or 3/2 for direct, indirect, and forbidden transitions, respectively [20]. A satisfactory fit was obtained for  $\alpha^{1/2}$  and  $\alpha^2$  as a function of *hv*, Fig. 8. This indicates that the absorption mechanism is due to both the indirect and direct transitions. The optical band gap of the indirect and direct transitions ( $E_{gi}, E_{gd}$ ) can be obtained from the intercept of  $\alpha^{1/2}$  versus *hv* plots with the energy axis and  $\alpha^2$  versus *hv*, respectively (Fig. 8). The results obtained for indirect and direct optical band gaps for the as-deposited **4** thin film were determined as 3.81 and 4.48 eV, respectively.

#### 4. Conclusions

The present work describes the preparation, characterization and spin coated film of novel hexadecachlorinatedphthalocyaninato zinc(II), which have been peripherally substituted with eight chlorinated-phenoxy groups and non-peripherally substituted with eight hexyloxy groups. The synthesized complex possesses excellent solubility in various organic solvents such as  $CH_2Cl_2$ , THF, acetone and ethyl acetate.

The structure and optical properties of the spin coated ZnPc thin films of thickness about 45–50 nm have been studied. X-ray studies revealed the typical structure of phthalocyanines with the diffraction peak at  $2\theta = 5.08^{\circ}$ .

Studies using AFM showed that the phthalocyanine molecules are growing in aggregation rows.

The optical properties of the ZnPc thin film were studied in the range 200–2800 nm. The absorption spectra recorded show two main Q-bands: Q<sub>I</sub> at about 728 and Q<sub>II</sub> at about 655 nm. The spectral distribution of refractive index  $n(\lambda)$ , was obtained. The optical band gap of the indirect and direct transitions were found to be equal to 3.81 and 4.48 eV, respectively.

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