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COVER LETTER FOR SUBMISSION OF MANUSCRIPT

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I am enclosing herewith a manuscript entitled "Synthesis, characterization and spectral properties of novel zinc phthalocyanines derived from C_2 symmetric diol" for publication in Journal of Molecular Structure for possible evaluation.

Kobayashi and co-workers in 1993 succeeded in combining chiral BINOL with a phthalocyanine core and since then, limited number of reports have explored in the synthesis of phthalocyanine bearing optically active groups. The present paper reports the synthesis and characterization of two new optically active phthalonitriles and their zinc phthalocyanine derivatives.

The manuscript has not been previously published, is not currently submitted for review to any other journal, and will not be submitted elsewhere before a decision is made by this journal.

With kind regards,

Synthesis, characterization and spectral properties of novel zinc

phthalocyanines derived from C_2 symmetric diol

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Abstract

In this study, we described the syntheses of new zinc(II) phthalocyanine compounds derived from (1R,2R)-1,2-diphenyl-1,2-ethanediol units. The phthalonitrile precursors **3** and **4** were synthesized by the reaction of **4**,5-dichlorophthalonitrile with (1R,2R)-1,2-diphenyl-1,2-ethanediol. The synthesis of zinc(II) phthalocyanine **5** and zinc(II) phthalocyanine polymer **6** by cyclotetramerization of corresponding phthalonitrile derivative were accomplished in the presence of Zn(CH₃CO₂)₂ in a Schlenk tube containing quinoline under nitrogen atmosphere. The zinc(II) phthalocyanine **5** showed enhanced solubility in various organic solvents. The aggregation behavior of phthalocyanines was investigated at different concentrations in different solvents. Both phthalocyanines were found to exist in non-aggregated form at concentrations between 10 x 10⁻⁶ and 1 x 10⁻⁶ mol dm⁻³. As the concentration increased to 5 x10⁻⁵ mol dm⁻³, a deviation from ideality was observed for both phthalocyanines. The novel compounds were characterized by a combination of elemental analysis and ¹H NMR, ¹³C NMR, IR, UV-Vis and MS spectral data.

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Keywords: C_2 symmetric diol; Chiral; Phthalonitrile; Bisphthalonitrile; Zinc phthalocyanine; Polymeric phthalocyanine

1. Introduction

Metallophthalocyanines have been intensively investigated due to their high thermal and chemical stability along with their unique properties such as strong UV-Vis light absorption, high molar absorption coefficients, electron transfer abilities [1]. These features promote an extensive use of these molecules firstly as dyes and pigments [2], then as semiconductor devices, electrochromic display devices, liquid crystals, Langmuir–Blodgett films, non-linear optical (NLO) devices [1,3] and more recently as photosensitizers in photodynamic therapy for cancer [4]. A goal of research on the chemistry of phthalocyanines is to achieve control over the structure of synthetic molecules and enhance their solubility in various solvents. In order to improve their application capabilities in scientific and technological areas, many modifications on the peripheral or non peripheral position of the phthalocyanines have been reported [5].

Optically active compounds are ubiquitous and play a fundamental role in life, especially in the area of pharmaceutical and agricultural industries [6]. A large number of commercial drugs such as L-DOPA [7] and albuterol [8] contain enantiomerically pure compounds. The design and synthesis of new optically active compounds is one of the most important goals in modern chemistry [9]. In accordance with these goals, a lot of research has been devoted towards the synthesis of chiral ligands such as diols [10], diamines and disulfonamides [11], bisoxazolines [12]. Optically active diols are widely used in enantioselective reactions due to their high enantioselectivities [13].

Chiral macrocycles, metal complexes, linear oligomers and polymers have been synthesized for use in molecular recognition, asymmetric catalysis and as new functional materials [14]. Kobayashi and co-workers in 1993 [15] succeeded in combining chiral BINOL with a phthalocyanine core and since then, limited number of reports have explored in the synthesis of phthalocyanine bearing optically active groups [16]. Most of studies among these reports have concentrated on combining chiral binaphthol groups with a phthalocyanine core [16,17]. Studies on combining different chiral groups with a phthalocyanine core are still limited and spectral properties of these molecules are unknown. The functional phthalocyanines derived from C_2 symmetric diols can be interesting in enantioselective catalytic systems, metal binding studies and photodynamic therapy.

In this paper, we synthesized and characterized mononomeric and polymeric zinc(II) phthalocyanines **5** and **6** derived from (1R,2R)-1,2-diphenyl-1,2-ethanediol. In addition to that, the spectral studies of these phthalocyanines in different solvent were investigated.

2. Experimental

2.1. Materials and Equipment

4,5-dichlorophthalonitrile **1** was synthesized according to reported procedure in literature [18]. (1R,2R)-1,2-diphenyl-1,2-ethanediol **2** was efficiently prepared in high yield via a Sharpless asymmetric dihydroxylation [19] as enantiopure diol using the known procedure [20]. All reagents and solvents were reagent grade and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [21]. Melting points were determined with an electrothermal apparatus and are reported uncorrected. FTIR spectra were measured on a Perkin Elmer Spectrum 65

spectrometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using CDCl₃ and DMSO-d₆ (99.9%). Mass spectra were a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV-Vis region with a PG-T80+ spectrophotometer using 1 cm-path length cuvettes at room temperature. Elemental analyses were obtained with a LECO Elemental Analyser (CHNS 0932) spectrophotometer. The homogeneity of the products was tested at each step using TLC.

2.2. Synthesis

The optically active phthalonitrile precursors were prepared by a nucleophilic aromatic substitution of one of two chloro atoms 4,5-dichlorophthalonitrile **1** with one/two of two hydroxyl functions of (1R,2R)-1,2-diphenyl-1,2-ethanediol **2**.

2.2.1. Synthesis of 4-chloro-5-((1R,2R)-2-hydroxy-1,2-diphenylethoxy)phthalonitrile (3) and 5,5'-((1R,2R)-1,2-diphenylethane-1,2-diyl)bis(oxy)bis(4-chlorophthalonitrile) (4)

(1R,2R)-1,2-diphenyl-1,2-ethanediol **2** (1.3 g; 6.07 mmol) was dissolved in dry DMF (50 ml) containing potassium carbonate (2.51 g; 18.22 mmol) as the base and stirred at 50 ^oC under nitrogen atmosphere for 1 h. To this reaction mixture, a solution of 4,5-dichlorophthalonitrile **1** (1.43 g g, 7.28 mmol) in dry dimethylformamide (50 ml) was added to the above solution using a dropping funnel with stirring under dry inert gas over 1.5 h at 50 ^oC. After the addition was complete, the reaction mixture was stirred for another 22 h at 80 ^oC. The reaction was monitored by thin layer chromatography [hexane-ethyl acetate (7:3)]. When the reaction was complete, the mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The yellowish oil was dissolved in CH₂Cl₂. The organic layer

was washed twice with 125 ml portions of a 5% Na₂CO₃ solution and then twice with water. The combined organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure to give a crude product that was purified by silica gel chromatography. The elution was carried out with dichloromethane-hexane (9:1). The first and second band were collected and evaporated to dryness under reduced pressure to give optically active bisphthalonitrile **4** and the 4,5-differently substituted phthalonitrile, 4-chloro-5-((1R,2R)-2-hydroxy-1,2-diphenylethoxy)phthalonitrile **3** as white solids, respectively.

Experimental data for compound **3**: 1.3 g (57%). Mp 153-155 °C. Anal. calcd for $C_{22}H_{15}CIN_2O_2$: C, 70.50; H, 4.03; N, 7.47%. Found: C: 70.01; H: 4.16; N: 7.25%. IR (KBr disc) v_{max}/cm^{-1} : 3484 (OH), 3033 (CH_{Ar}), 2907 (CH_{Aliph}), 2234 (C \equiv N), 1584, 1549 1491, 1454, 1390, 1309, 1276, 1257, 1199, 1134, 1026, 973,767, 700, 601,530. ¹H NMR (CDCl₃) & 7.79 (s, H, ArH), 7.30-7.03 (m, 11H, ArH), 5.27 (d, $J_{AB} = 7.34$ Hz, H, CH), 5.10 (d, $J_{AB} = 7.34$ Hz, H, CH), 2.93 (s, br, 1H, OH). ¹³C NMR (CDCl₃) & 156.82, 137.56, 134.83, 134.22, 129.33, 128.93, 128.59, 128.28, 127.21, 126.91, 118.91, 118.80, 115.40, 114.63, 114.36, 108.76, 87.69, 78.04. [$\phi_{12}^{20} = +72.9$ (c, 1.0, CHCl₃). MS (ES-MS) m/z: 392.10 [M+H₂O]⁺ ($C_{22}H_{17}CIN_2O_3$; calc: 392.09).

Experimental data for compound **4**: 0.314 g (22.7%). Mp 118-120 °C. Anal. calcd for $C_{30}H_{16}Cl_2N_4O_2$: C, 67.30; H, 3.01; N, 10.46%. Found: C: 66.44; H: 3.33; N: 10.13%. IR KBr disc) v_{max}/cm^{-1} : 3036 (CH_{Ar}), 2925 (CH_{Aliph}), 2234 (C=N), 1585, 1550, 1491, 1454, 1388, 1308, 1274, 1259, 1199, 1134, 1026, 974,894, 854, 767, 700, 613, 529. ¹H NMR (CDCl₃) δ 7.79 (s, 2H, ArH), 7.35-7.13 (m, 12H, ArH), 5.68 (s, 2H, CH). ¹³C NMR (CDCl₃) δ 156.59, 135.02, 132.83, 129.89, 129.57, 129.08, 127.16, 118.81, 115.43, 114.61, 114.28, 109.08, 85.05. [d_{12}^{20} = + 67 (*c*, 1.0, CHCl₃). MS (ES-MS) m/z: 552.00 [M+H₂O]⁺ (C₃₀H₁₈Cl₂N₄O₃; calc: 552.07).

2.2.2. Synthesis of zinc(II) phthalocyanine (5)

A mixture of **3** (0.150 g, 0.401 mmol), anhydrous Zn(CH₃CO₂)₂ (0.022 g, 0.120 mmol) and quinoline (2 ml) was heated and stirred at 190 °C for 7h in a Schlenk tube under nitrogen. After cooling to room temperature, the product was precipitated by adding diethyl ether. The green-blue product was filtered off and then washed successively with cold and hot water and then 2-propanol. Finally, pure zinc(II) phthalocyanine was obtained by silica gel column chromatography using dichloromethane. The product was then dried under vacuum over P₂O₅. The yield was 0.033 g (22%). Mp > 300 °C. Anal. calcd. for C₈₈H₆₀Cl₄N₈O₈Zn: C, 67.55; H, 3.87; N, 7.16%. Found: C, 67.31; H, 3.60; N, 7.73%. IR (KBr disc) v_{max}/cm^{-1} : 3440 (OH), 3062 (CH_{Ar}), 2955 (CH_{Aliph}), 1734, 1604 (C=N), 1488, 1448, 1393, 1251, 1105, 1067, 1015, 743, 699. ¹H NMR (CDCl₃) 87.74 (s, 4H, ArH), 7.66-6.98 (m, 44H, ArH), 5.33 (m, 4H, CH), 5.12 (m, 4H, CH), 2.79 (s, br, 4H, OH). UV-Vis (DMF): λ_{max} , nm (log ϵ): 682 (4.74), 612 (4.01), 360 (4.42). MS (MALDI-TOF) m/z: 1561.24 [M+H]⁺, 1367.64 [M+H-C₁₄H₁₃O]⁺, 1170.87 [M+H-2C₁₄H₁₃O]⁺, 974.72 [M+H-3C₁₄H₁₃O]⁺, 778.66 [M+H-4C₁₄H₁₃O]⁺ (C₈₈H₆₁Cl₄N₈O₈Zn; calc: 1561.26).

2.2.3. Synthesis of zinc(II) phthalocyanine polymer (6)

A mixture of compound 4 (0.203 g, 0.379 mmol), anhydrous $Zn(CH_3CO_2)_2$ (0.034 g, 0.189 mmol) and quinoline (2 ml) was heated and stirred at 190 °C for 7 h in a Schlenk tube under nitrogen. After cooling to room temperature, the product was precipitated by adding ethanol (40 ml) and filtered off. The crude product was refluxed with ethanol (50 ml) in a Soxhlet extractor for overnight. The green product was then filtered and washed with

dimethylformamide, ethanol, ethyl acetate, acetone, and diethyl ether. The product was dried under vacuum over P₂O₅. The yield was 0.145 g (71%). Mp > 300 $^{\circ}$ C. Anal. calcd. for $(C_{120}H_{68}Cl_8N_{12}O_{16}Zn)_n(2276.18)_n$ for imide end groups: C, 63.13; H, 3.00; N, 7.36%. Found: C, 63.73; H, 3.67; N, 7.96%. IR (KBr disc) v_{max}/cm⁻¹: 3334 (imide N-H), 3062, 3030 (CH_{Ar}), 2970-2924 (CH_{Aliph}), 1774 (sym C=O), 1726 (asym C=O), 1655, 1602, 1434, 1343, 1248 (C-O-C), 1099, 1067, 1015, 887, 863, 744, 699. UV-Vis (H₂SO₄): λ_{nax}, nm (log ε): 824 (5.24), 732 (4.57), 312 (5.04). MS (MALDI-TOF) m/z: 2277.41 $[M+H]^+$ ((C₁₂₀H₆₉Cl₈N₁₂O₁₆Zn)_n; SANCE SALVE calc: (2277.17)_n).

3. Result and Discussion

3.1. Synthesis and Characterization

The synthetic route to these molecules is summarized in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ¹H NMR, ¹³C NMR, IR, UV-Vis and MS spectral data. 4,5-dichlorophthalonitrile 1 was synthesized according to reported procedure in literature [18]. (1R,2R)-1,2-diphenyl-1,2-ethanediol 2 was efficiently prepared in high yield via a Sharpless asymmetric dihydroxylation [19] as enantiopure diol using the known procedure [20].

The synthesis of 4-chloro-5-((1R,2R)-2-hydroxy-1,2-diphenylethoxy)phthalonitrile 3 5,5'-((1R,2R)-1,2-diphenylethane-1,2-diyl)bis(0xy)bis(4-chlorophthalonitrile) **4** was and performed starting from 4,5-dichlorophthalonitrile and (1R,2R)-1,2-diphenyl-1,2-ethanediol in N,N-dimethylformamide using K₂CO₃ as the base at 80 ^oC under nitrogen atmosphere for 22 h after purification by column chromatography. Nucleophilic aromatic displacement of one of two chloro atoms 4,5-dichlorophthalonitrile 1 with one of two hydroxyl functions of

(1R,2R)-1,2-diphenyl-1,2-ethanediol **2** gave the 4,5-differently substituted phthalonitrile, 4chloro-5-((1R,2R)-2-hydroxy-1,2-diphenylethoxy)phthalonitrile 3. The chiral phthalonitrile 3 was isolated by column chromatography in reasonable good yield (57%). To determine the exact structure of **3**, the ¹H NMR spectrum was acquired in CDCl₃ (Fig.1). The presence of significant resonance of OH group as broad singlet at $\delta = 2.93$ ppm is agreement with the proposed structure. The aliphatic CH protons were observed as two doublets at $\delta = 5.27$ and 5.10 ppm with a coupling constant of J = 7.34 Hz. A singlet at $\delta = 7.79$ ppm in the ¹H NMR spectrum corresponded to one of two protons of the tetrasubstituted aromatic group. The other sets of protons were appeared as multiplet between 7.30-7.03 ppm as expected. The ¹³C NMR spectrum of the same compound clearly indicated the expected carbon resonances. The nitrile carbons were observed at $\delta = 114.63$ and 114.36 ppm. The carbon resonances concerning hydroxyl-connected CH and the oxygen connected CH at $\delta = 87.69$ and 78.04 are in good agreement with the proposed structure. The IR spectrum of 3 was easily verified with the presence of characteristic vibrations related to OH and C^IN groups at 3483 and 2234 cm⁻¹, respectively (Fig.2). In addition to the elemental analysis results, the molecular ion peak at $m/z = 394.10 [M+H_2O]^+$ in the ES/MS mass spectra of **3** also confirms the proposed structure.

The synthesis of bisphthalonitrile **4** is based on the reaction of diol **2** with compound **1**. The bisphthalonitrile **4** was obtained as minor product from the above mentioned reaction. It was eluted as the first band from the purification of the crude product containing compound **3** and **4**. The structure and purity of bisphthalonitrile **4** was identified by a combination of elemental analysis and ¹H, ¹³C, IR and MS spectral data. The IR spectrum of **4** was very similar to that of **3** (Fig.2). The significant difference between the IR spectra of compounds **3** and **4** is the absence of characteristic vibration of OH group in the IR spectra of **4**, confirming the nucleophilic aromatic displacement of one of two chloro atoms 4,5-dichlorophthalonitrile **1** with the two hydroxyl group of **2**. The intense absorption band at 2234 cm⁻¹ corresponds to

the C IN group in the IR spectrum of 4. In the ¹H and ¹³C NMR spectra of 4, the number of the peaks of protons and carbon resonances was obviously less than those of 3 due to the C_2 symmetry of the compound 4. As a result of C_2 symmetry of this compound, oxygen and phenyl connected CH protons was observed at δ = 5.68 ppm as singlet. In addition to that, the disappearance of the OH signals at 2.93 ppm in ¹H NMR spectrum of 4 can be taken as a clear evidence of the formation of compound 4. The signals due to the aromatic protons was observed at δ = 7.13-7.35 ppm as multiplet. A singlet at δ = 7.79 ppm in the ¹H NMR spectrum of 4 was attributed to one of two protons of the tetrasubstituted aromatic group (Fig.1). The ¹³C NMR spectrum of this compound displayed the characteristic signals of the product as expected. Elemental analysis result was consistent with the theoretical values of the proposed structure of 4. In addition to that, the mass spectrum of 4 contained an intense peak at m/z = 552 [M+H₂O]⁺, which support the proposed structure.

The zinc(II) phthalocyanine **5** was synthesized directly by cyclotetramerization of the dicyano compound **3** in the presence of the anhydrous metal salt $Zn(CH_3CO_2)_2$ in a Schlenk system in quinoline. The blue green phthalocyanine was isolated by column chromatography on silicagel. In the IR spectrum of **5**, the disappearance of the sharp C=N vibration at 2234 cm⁻¹ and appearance of new resonance at 1604 cm⁻¹ corresponding to C=N vibration in phthalocyanine core of **5** confirmed cyclotetramerization of the phthalonitrile derivative **3**. The vibration for the OH group was observed at 3440 cm⁻¹. In the ¹H NMR spectrum of **5**, the characteristic signals relating to aliphatic and aromatic groups in the phthalocyanine skeleton gave significant resonances of the proposed structure. In addition to these results for structure, the mass spectrum of this compound was measured using MALDI-TOF technique. The molecular ion peaks at m/z: 1561.24 [M+H]⁺; the major fragment ions corresponding to loss of $C_{14}H_{13}O$, 1367.64 [M+H- $C_{14}H_{13}O$]⁺, 1170.87 [M+H- $2C_{14}H_{13}O$]⁺, 974.72 [M+H-

 $3C_{14}H_{13}O$ ⁺ and 778.66 [M+H- $4C_{14}H_{13}O$]⁺ were easily identified (Fig.3). These results confirm that the complex has been synthesized successfully.

The zinc(II) phthalocyanine polymer **6** was synthesized by heating mixture of **4** and anhydrous metal salt $Zn(CH_3CO_2)_2$ in a Schlenk system in quinoline. The zinc(II) phthalocyanine polymer **6** was not soluble in common organic solvents such as DMF and DMSO. Thus, the purification of metal phthalocyanine polymer was performed by washing with various solvents as hot and cold. Zinc(II) phthalocyanine polymer **6** was characterized by a combination of elemental analysis, IR, UV-Vis and mass spectral data. ¹H and ¹³C NMR could not be obtained due to the insolubility of metal phthalocyanine polymer **6** in polar solvents such as CHCl₃, DMF and DMSO. It was reported that the end groups of the metal-free phthalocyanine polymer are cyano groups while the end groups of the metallophthalocyanine polymers are imido groups [22]. The existence of imido groups in the case of the metallophthalocyanine polymers was attributed to the presence of moisture during work-up [23]. The IR spectrum of **6** was in good agreement with the proposed formulation. The characteristic vibration of imido groups for **6** was observed at 1726 and 1774 cm⁻¹ in the IR spectrum of **6**.

It is very difficult to determine the molecular weight of polymeric phthalocyanines because of their poor solubility in common organic solvents. One possible procedure to determine the degree of polymerization is IR spectroscopy, by comparison of the IR absorption bands of the end groups with those of the bridging groups [24]. The ratios of the absorption intensities of -C-O- (etheric) groups of the polymer (4240 cm^{-1}) to the asymmetric C=O–groups of the imides (4720 cm^{-1}) were calculated ($\log_{10} I_{1240} / I_{1720}$). The degree of polymerization of **6** was found as 1.44.

MALDI-TOF can be used for analysis of polymers with a great variety in structure, end groups, and chemical properties. The function of the matrix is to absorb the laser energy and

make the polymer molecules separate from each other into a single-molecule state [25]. According to the MALDI-TOF mass spectrum analysis of **6**, observation of the parent molecular ion peaks m/z: 2277.41 [M+H]⁺ in the MALDI-TOF spectrum (Fig.3) of **6** verified the proposed structures.

3.2. Absorption and aggregation properties

The best indication of the formation of phthalocyanine systems is their UV-Vis spectrum in solution. The metallophthalocyanines show typical electronic spectra with two strong absorption regions. One of them is in UV region at about 300-500 nm (B band) and the other one is in the visible region at 600-800 nm (Q band) [26]. The UV-Vis absorption spectra of zinc(II) phthalocyanines 5 in diethyl ether and conc. H_2SO_4 are shown in Fig.4 The electronic spectra of zinc(II) phthalocyanine 5 display intense Q bands in the visible region at $\lambda_{max} = 676$ nm in diethyl ether with a weaker absorptions at $\lambda_{max} = 612$ nm. B band absorption was observed at $\lambda_{max} = 352$ nm for zinc(II) phthalocyanine 5 in diethyl ether. The UV-Vis spectrum of zinc(II) phthalocyanine polymer 6 could be obtained in conc. H₂SO₄ due to its lower solubility (Fig.4). The expected intense single Q band absorptions appeared at $\lambda_{\text{max}} =$ 824 nm in H₂SO₄ with a weaker absorptions at $\lambda_{max} = 732$ nm. The solvent effects on the UV-Vis spectra of metal phthalocyanine polymers were reported before [27,28]. The red shift of the Q band in the UV-Vis spectrum of metal phthalocyanine polymer 6 showed clearly solvent effect. B band absorptions of 6 was observed at $\lambda_{max} = 312$ nm. Both zinc(II) phthalocyanine complexes 5 and 6 gave intense single Q band absorptions in their UV-Vis spectra. An intense Q band absorption is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [29].

The aggregation behaviors of zinc(II) phthalocyanines **5** and **6** were also investigated at different concentrations in DMF and conc. H₂SO₄, respectively (Fig.5). As shown in the figures, the Q band increases in intensity with increasing in the concentration of phthalocyanine complexes. Zinc(II) phthalocyanines **5** and **6** in DMF and conc. H₂SO₄, respectively, from concentrations between 1×10^{-6} and 10×10^{-6} mol dm⁻³ was found to obey the Beer-Lambert law. As the concentration increased to 5×10^{-5} mol dm⁻³, a deviation from ideality was observed due to the presence of aggregated species for all phthalocyanines. The increase of the aggregation properties with the increasing concentration can be seen in Fig.5.

Organic solvents are known to reduce aggregation whereas aqueous solvents result in highly aggregated complexes. However, many phthalocyanine complexes remain aggregated even in non-aqueous solutions. The effects of solvents on the state of aggregation of soluble phthalocyanines have been studied by several groups and reported in numerous papers [30,31].

Q band absorption data obtained for zinc(II) phthalocyanine **5** are summarized in Table 1. The UV-Vis absorption spectra of zinc(II) phthalocyanines **5** in various organic solvents are shown in Fig.6. In general, the red shift of the Q band increases with the ascending refractive index of the solvent. In our study, the red shift of the Q band due to the solvent for zinc(II) phthalocyanine **5** in the following order: dietheylether < tetrahydrofuran < dichloromethane < dimethlyformamide < dimethlysulfoxide. The electronic absorption spectra of zinc(II) phthalocyanine **5** in the various solvents was analyzed by using the method described originally by Bayliss [32]. The plot of $(n^2-1) / (2n^2+1)$, where n is the refractive index of the solvent, versus the red shift in the Q band is shown in Fig.7. The positions of the Q bands in these solvents show almost a linear dependence on this function. This result suggests that the red shifts in the Q band are mainly a result of the solvation rather than coordination [33,34].

4. Conclusion

In conclusion, we have reported the synthesis of zinc(II) phthalocyanines derived from C_2 symmetric diol and characterized by a combination of elemental analysis and ¹H NMR, ¹³C NMR, IR, UV-Vis and MS spectral data, all of which were in agreement with the proposed structures. A comprehensive investigation of solvent effects on the aggregation properties of zinc(II) phthalocyanine **5** was presented. It was found that the red shifts in the Q band are mainly a result of the solvation rather than coordination. The effect of changing concentration on the aggregation properties for zinc(II) phthalocyanines were found to exist in monomeric form at concentrations between 1 x 10^{-6} and 10×10^{-6} mol dm⁻³. As the concentration increased to 5×10^{-5} mol dm⁻³, a deviation from ideality was observed due to the presence of aggregated species for all phthalocyanines.

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Figure captions:

Scheme 1. (*i*) K_2CO_3 , DMF, 80 ^{0}C .; (*ii*) and (*iii*) anhyd. Zn(CH₃CO₂)₂, dry quinoline, N₂, 190 $^{\circ}C$.

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Fig. 1. ¹H NMR spectra of compounds 3 and 4

Fig. 2. FT-IR spectra of compounds 5 and 6

Fig. 3. MALDI-TOF spectra of zinc(II)phthalocanines 5 and 6

Fig. 4. UV-Vis spectrum of zinc(II) phthalocyanine 5 in diethyl ether and H₂SO₄, and zinc(II) phthalocyanine polymer 6 in H₂SO₄.

Fig. 5. Aggregation properties of zinc(II) phthalocyanine 5 in DMF and 6 in conc. H_2SO_4 at different concentrations 50 x 10⁻⁶, 25 x 10⁻⁶, 12.5 x 10⁻⁶, 10 x 10⁻⁶, 8 x 10⁻⁶, 6 x 10⁻⁶, 4 x 10⁻⁶, 2x 10⁻⁶, 1 x 10⁻⁶ mol dm⁻³. Inset: Beer-Lambert plot.

Fig. 6. UV-Vis spectra of zinc(II) phthalocyanine 5 in various organic solvents.

Fig. 7. Plot of the Q band frequency of ZnPc 5 against $(n^2-1) / (2n^2+1)$, where n is the refractive index of the solvent

Table 1. Location of the Q band of zinc(II) phthalocyanine 5 in various organic solvents

Table 1

Solvent	Refractive	Q band, λ_{max} ,	B band,
	index, n_D	(nm)	λ_{max} , (nm)
Diethylether	1.352	676, 612	352
Acetone	1.358	678, 610	358
THF	1.407	678, 612	356
DCM	1.424	680, 612	354
DMF	1.430	682, 612	360
DMSO	1.478	684, 616	358

Graphical abstract



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The present paper reports the synthesis and characterization of two new optically active phthalonitriles **3** and **4**, and their zinc phthalocyanine derivatives **5** and **6**, respectively. In addition to that, the spectral studies of these phthalocyanines in different solvent were investigated.

HIGHLIGHTS

Synthesis, characterization and spectral properties of novel zinc phthalocyanines derived from *C*₂ symmetric diol

▶ Phthalonitrile and bisphthalonitrile derived from C₂ symmetric diol. ▶ Monomeric and polymeric zinc(II) phthalocyanines were synthesized. ▶ Enhanced solubility for zinc(II) phthalocyanine **5** in various organic solvents.



1 1 8.00 ppm (t1) 7.00 . 5.00 3.00 2.50 2.00 1.50 1.00 0.50 0.00 7.50 6.50 6.00 5.50 4.50 4.00 3.50















Fig. 7.

