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Synthesis and characterization of a new *trans*-2,2′-azoquinoxaline bridged bisphthalocyanine

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Abstract—A new *trans*-2,2′-azoquinoxaline bridged bisphthalocyanine was synthesized from the corresponding quinoxaline-2(1*H*)-one oxime, which can be obtained by the reaction of s-*trans*-chloroethanedial with 2-(3,4-diaminophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc(II). 2-(3,4-Diaminophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc(II) was synthesized by reduction of 2-(4-amino-3-nitrophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc(II). Novel compounds were characterized by elemental analysis, UV/vis, IR and ^{1}H NMR spectroscopy. The conductivity and the humidity sensing properties of spin coated films of these compounds were investigated by measuring the complex impedance spectra at different humidities. Films of the final product show up to 10^3 orders of magnitude higher conductivity than the starting and intermediate compounds. The results indicate that the presence of water vapour always leads to a drop in the real and imaginary part of the complex impedance. At room temperature, the capacitance of the films exhibits reversible increase with relative humidity, which makes these films attractive for humidity sensing applications.

1. Introduction

The search for novel materials for molecular electronics and optoelectronics has prompted scientists to focus their attention on chemically versatile organic molecules that can be easily synthesized, modified and handled. Recently, substituted and unsubstituted phthalocyanine derivatives have aroused great interest due to their potential application in the fields of nonlinear optics,[1–4] photoelectrochemistry[5–8] and gas sensors.[9–13] From this point of view, the synthesis, electrical[14] and gas sensing properties of a large class of phthalocyanine derivatives have been investigated. Recently, a route for the one step synthesis of quinoxaline-2(1*H*)-one oximes, which can be converted into symmetrical *trans*-2,2′-azoquinoxalines by the template effect of cobalt(II) chloride or by treatment with potassium hydroxide has been reported.[15–17] In the first part of this study, we aimed to synthesize a new *trans*-2,2′-azoquinoxaline bridged bisphthalocyanine **5** starting from the corresponding quinoxalinone oxime by making use of the template effect of the cobalt(II) ions. Although, a number of reports have been published on the sensing properties of phthalocyanine films for oxidizing gases, such as NO_2,[18] limited research is available in the literature concerning the application of phthalocyanine films for the measurement of humidity. It is well known that humidity is an important environmental characteristic, which must be monitored and controlled either to maintain a comfortable living atmosphere, or to improve the quality of production, and in medical care.[19,20] For these reasons, in the second part of this research, we focused on the investigation of the conduction and humidity sensing properties of films of the phthalocyanines synthesized.

When a solution of the quinoxalinone oxime and cobalt(II) chloride in absolute ethanol was heated at 60 °C for 6 h compound **5** was isolated as a green precipitate. The quinoxalinone oxime was synthesized in one step by reaction of s-*trans*-chloroethanedial with 2-(3,4-diaminophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc II **4** and elimination of NH_2–OH. Compound **4** was synthesized by reduction of 2-(4-amino-3-nitrophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc(II) **3**, which was obtained from 4-(4-amino-3-nitrophenoxy)phthalonitrile **2** (Scheme 1). Elemental analysis,

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Keywords: Phthalocyanine; Azoquinoxaline; Zinc complex; Humidity sensing; Impedance spectra.

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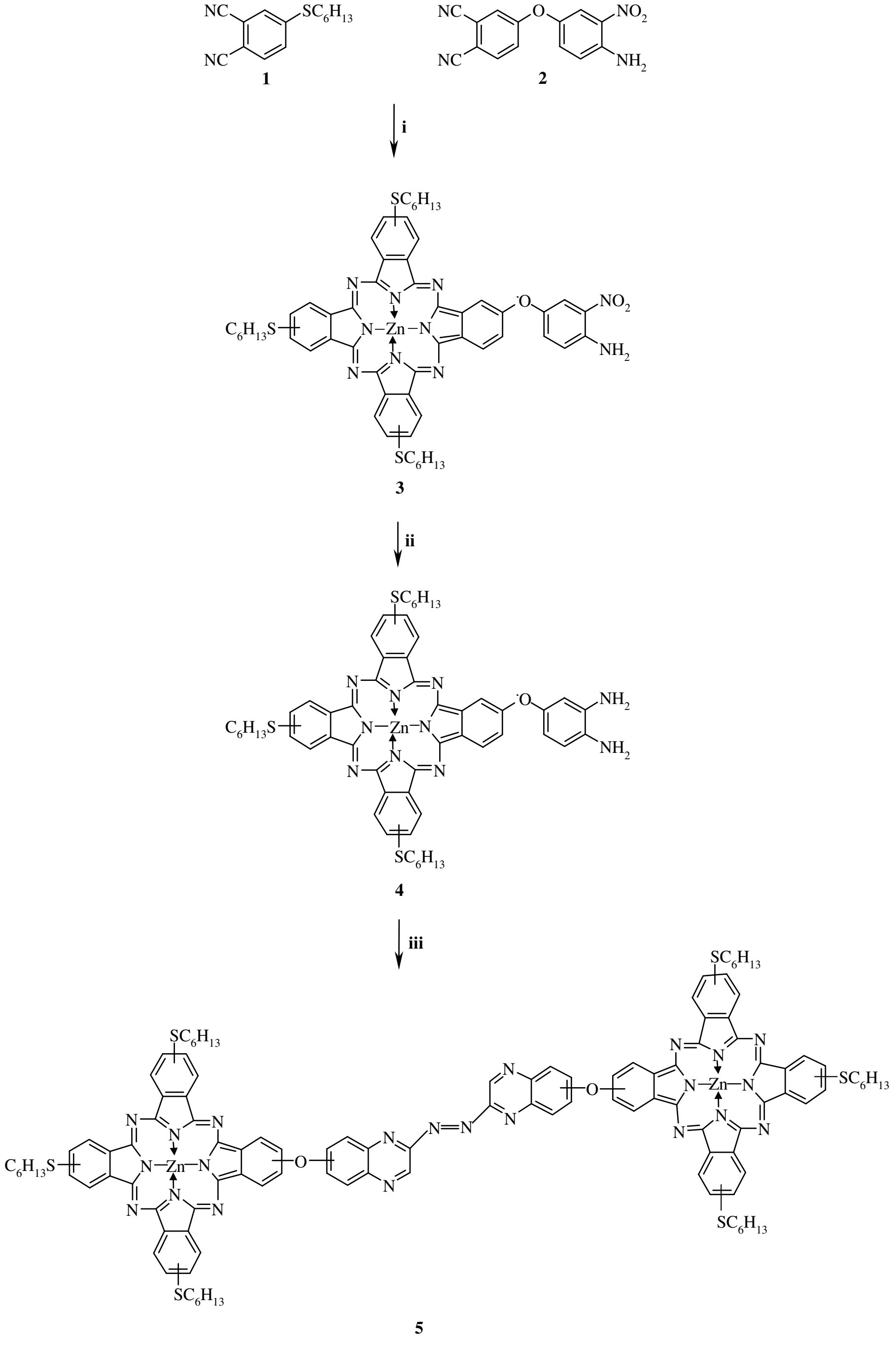

Scheme 1. Summary of the synthesis of compound **5**. Reagents: (i) $Zn(CH_3COO)_2{\cdot}2H_2O$, DMF; (ii) $Na_2S{\cdot}9H_2O$, DMF, THF; (iii) s-*trans*-chloroethanedial dioxime, EtOH, $CoCl_2{\cdot}6H_2O$, DMF.

IR, ^{1}H NMR and UV/vis spectra confirmed the proposed structures of all of the new compounds. A diagnostic feature of phthalocyanine formation from compound **2** was the disappearance of the sharp intense CN vibration band at 2238 cm^{-1}. The rest of the spectrum of compound **2** included the stretching bands at 3387 and 3514 cm^{-1} and the bending band at 1651 cm^{-1} of the amino group and the bending bands at 1319 and 1523 cm^{-1} due to the nitro group. The intense absorption bands at 1520 and 1340 cm^{-1} in the IR spectrum of **3** corresponding to the NO_2 bending vibrations disappeared after its conversion into compound **4**. In the ^{1}H NMR spectrum of compound **3**, the aromatic protons appeared at δ 6.80–7.80 ppm, the $–CCH_2C–$ protons in the long chain appeared at δ 1.26–1.71 ppm and the $–CH_3$ at the end of the chain at δ 1.20 ppm. The peak at δ 2.90 ppm indicated the presence of a $–SCH_2–$ group adjacent to an aromatic ring. The NH protons of compound **3** appeared as a broad singlet at δ 1.55 ppm, which disappeared after deuterium exchange on addition of D_2O. The ^{1}H NMR spectra of **4** showed similar chemical shifts when compared to the spectra of compound **3**. The spectrum of compound **4** showed four D_2O exchangeable protons at δ 1.32 ppm and at δ 0.90 ppm for the NH_2 groups. In addition, the aromatic protons were observed as a multiplet at δ 7.00–7.80 ppm and the alkyl protons at δ 0.96–3.20 ppm. The spectrum of compound **5** confirmed the proposed structure showing multiplets at δ 6.80–7.80 ppm for the aromatic protons and a singlet at δ 9.80 ppm for the $N{=}CH$ protons. The chemical shifts in the ^1H NMR spectrum of compound **5** were found to be in agreement with values reported for similar compounds.[21,22] In contrast to intermediate **4**, compound **5** is easily soluble in chloroform. The phthalocyanines show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (the B band) and the other in the visible portion at 600–700 nm (the Q band). The characteristic Q-band transition of metallophthalocyanines with D_{4h} symmetry is observed as a single band of high intensity in the visible region. The UV–vis absorption spectra of phthalocyanines **3**, **4** and **5** exhibit characteristic Q and B bands, one in the visible region at ca. 600–700 nm (the Q band) attributed to the $\pi \rightarrow \pi^*$ transition from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc^{-2} ring and the other in the UV region at 300–350 nm (the B band) arising from the deeper π-levels → LUMO transitions. In the UV–vis absorption spectrum of **3** dissolved in chloroform, an intense band around 682 nm was observed (with a shoulder at 615 nm) and a Soret-like $\pi \rightarrow \pi^*$ band at 355 nm. Intermediate **4** is slightly soluble in chloroform but easily soluble in DMF. Its spectrum in DMF is very similar with an intense Q band at 686 nm due to a single $\pi \rightarrow \pi^*$ transition with a shoulder at 621 nm and a B band at 368 nm, respectively. The spectrum of **5** in chloroform shows, the characteristic Q band absorption around 686 nm (with a shoulder at 621 nm) and a B band absorption around 404 nm (Table 1).

A remarkably high intrinsic dark conductivity was observed for compound **5** ($\sigma_{\text{d.c.}} = 1.48 \times 10^{-10}$ S/cm at room temperature) when compared to **3** and **4** ($\sigma_{\text{d.c.}} = 6.46 \times 10^{-13}$ S/cm, $\sigma_{\text{d.c.}} = 2.75 \times 10^{-13}$ S/cm at room temperature, respectively). A discontinuous point, such as the transition from intrinsic to extrinsic behaviour, in the $\ln \sigma_{\text{d.c.}}$ versus $1/T$ graphs was not observed. Thus, it is reasonable to assume the presence of only one conduction mechanism in the whole temperature range for films of compounds **3**–**5**. Good straight lines were obtained from the Arrhenius plot ($\ln \sigma_{\text{d.c.}}$ vs $1/T$ plot) indicating the applicability of the well-known expression for conductivity. The values of the activation energies, which were determined from the slope of the $\ln \sigma_{\text{d.c.}}$–$1/T$ graphs, are $E_A = 0.97$, 0.98 and 0.64 eV for compounds **3**–**5**, respectively. Impedance spectroscopy was employed in order to investigate the humidity sensing properties of compounds **3**–**5**. Figure 1 shows the typical real (Z') and imaginary (Z'') parts of the impedance data plotted in the complex impedance plane for compounds **3**–**5** with relative humidities (RH) 0% and 60%. On examining the impedance spectra, clear differences can be seen in the dependence of ω on both the real and imaginary parts of impedance between 0% and 60% RH for all samples. For 0 RH, the impedance spectra data of compounds **3** and **4** shows slightly curved lines. The impedance response is significantly changed on exposure to 60% RH for all samples. On the complex plane plot, only depressed semicircles with different radii were observed for compounds **3**–**5** for 60% RH, indicating a deviation from the Debye dispersion relation. It is well known that a semicircle in an impedance spectrum represents a resistor, R, in parallel with a capacitor, C. The values of resistor and capacitor, as well as the range of measuring frequency, determine whether the semicircle is complete or not. The radius of the Cole–Cole plot clearly decreases with exposure to 60% RH. In addition, the peak frequency, ω_p, of the imaginary part of the impedance is shifted to higher frequencies for all samples. The decrease in the radius of the Cole–Cole plot is explained by the increase of the dielectric constant

Table 1. UV–vis data for the phthalocyanines **3**–**5** in chloroform

Compound	λ, nm (log ε, $M^{-1}\,cm^{-1}$)
3	682 (4.016), 615 sh (3.848), 355 (4.204)
4[a]	686 (4.340), 621 sh (3.602), 368 (3.921)
5	686 (4.909), 621 sh (4.415), 404 (4.160), 313 (4.732)

sh = Shoulder.

[a] In DMF.

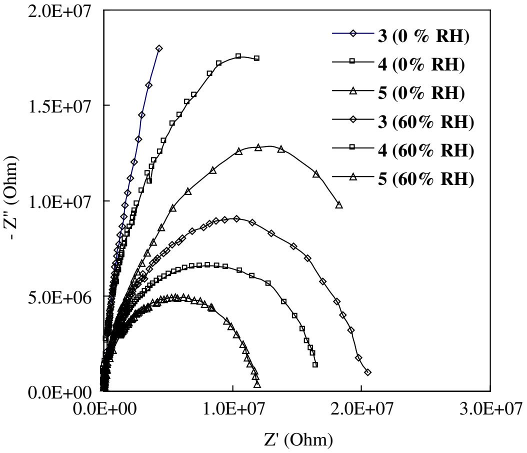

Figure 1. The impedance spectra of compounds **3**–**5** at room temperature.

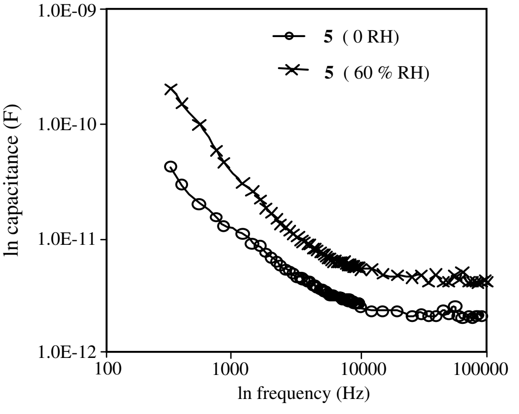

Figure 2. The variation of the capacitance with frequency at 0% and 60% RH for compound **5** at room temperature.

due to water vapour adsorption in the coatings. Due to the high dielectric constant of water, when a small amount of water is adsorbed by the film, the apparent dielectric coefficient of the film results in an increase in capacitance. This conclusion was supported by a $\ln\omega$ versus $\ln C$ plot. Figure 2 shows the variation of the capacitance with frequency at 0% and 60% RH for compound **5**. It is obvious that the capacitance values of the film at 60% RH is higher than at 0 RH for the whole frequency range.

2. Experimental

2.1. Synthesis of 4-(4-amino-3-nitrophenoxy)phthalonitrile 2

A mixture of 4-amino-3-nitrophenol (1 g, 6.49×10^{-3} mol) and 4-nitro-1,2-dicyanobenzene (1.12 g, 6.49×10^{-3} mol) in 50 mL Me_2SO was stirred at room temperature under argon. K_2CO_3 (1.38 g, 0.01 mol) was added to the mixture over a period of 2 h. After stirring the reaction mixture for a further 24 h, the undissolved salt was removed by filtration. The reaction mixture was poured into water (100 mL) and stirred. The solution was extracted with CH_2Cl_2 (3×50 mL). The residue was chromatographed on silica gel and eluted with CH_2Cl_2. Yield: 1.7 g (94%). This compound was soluble in $CHCl_3$ and CH_2Cl_2. Mp: 176 °C. IR (KBr pellet) $\nu^{-1}_{\max/\mathrm{cm}}$: 834, 961, 1089, 1165, 1268, 1319, 1421, 1523, 1600, 1651, 2238, 3080, 3387, 3514. Analysis calculated for $C_{14}H_8N_4O_3$, calculated C 60.00, H 2.86, N 20.00, found C 59.71, H 2.55, N 19.78. ^1H NMR ($CDCl_3$)δ 6.36 (br s, 2H), 6.93 (br d, $J = 9$ Hz, 1H), 7.16 (dd, $J = 9$ Hz and 2 Hz, 1H), 7.23 (d, $J = 2$ Hz, 1H), 7.26 (dd, $J = 9$ Hz and 2 Hz, 1H), 7.73 (d, $J = 9$ Hz, 1H), 7.90 (d, $J = 2$ Hz, 1H) ppm.

2.2. Synthesis of 2-(4-amino-3-nitrophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc(II) 3

A powdered mixture of compound **1** (800 mg, 3.28 mmol) and **2** (230 mg, 0.82 mmol) was dissolved in 5 mL dry DMF under an argon atmosphere. $Zn(CH_3COO)_2{\cdot}2H_2O$ (718 mg, 3.28 mmol) was added to this solution and the reaction was heated at 160–180 °C for 8 h to give an unsymmetrically substituted phthalocyanine. The reaction mixture was cooled to room temperature and precipitated by adding water. After filtration the product was washed with cold ethanol and diethyl ether. The residue was coarsely fractionated on a silica gel column eluting with $CHCl_3$and a gradient of $CHCl_3$–THF up to 100% THF. Yield: 150 mg (17%). This compound was soluble in $CHCl_3$ and CH_2Cl_2. Mp > 350 °C. IR (KBr pellet) $\nu^{-1}_{\max/\mathrm{cm}}$: 730, 820, 840, 1020, 1070, 1100, 1140, 1340, 1380, 1460, 1520, 1610, 1640, 2850, 2920, 2960, 3060, 3357, 3395. Analysis calculated for $C_{56}H_{56}N_{10}O_3S_3Zn$, calculated C 62.40, H 5.20, N 13.00, S 8.91, found C 62.68, H 5.50, N 12.95, S 8.65. ^1H NMR ($CDCl_3$) δ 1.22 (t, $J = 6$ Hz, 9H), 1.26–1.47 (m, 18H), 1.55 (br s, 2H), 1.71 (q, $J = 6$ Hz, 6H), 2.90 (t, $J = 6$ Hz, 6H), 6.80–7.80 (m, 15H) ppm.

2.3. Synthesis of 2-(3,4-diaminophenoxy)-9,16,23-tri(hexylthio)phthalocyanine zinc(II) 4

Compound **3** (300 mg, 2.78×10^{-4} mol) and $Na_2S{\cdot}9H_2O$ (670 mg, 2.78×10^{-3} mol) were dissolved in 32 mL DMF and 96 mL THF mixture under an argon atmosphere. The reaction mixture was stirred at 60 °C for 16 h. After cooling to room temperature, the reaction mixture was treated with water to precipitate a dark-green product and then filtered. It was then washed with water and ethanol. The crude green product was purified by column chromatography on silica gel (DMF). Yield: 170 mg (58%). This compound was soluble in DMF. Mp > 350 °C. IR (KBr pellet) $\nu^{-1}_{\max/\mathrm{cm}}$: 740, 810, 870, 900, 1020, 1100, 1130, 1260, 1450, 1490, 1610, 1630, 2850, 2923, 2974, 3050, 3400, 3450. Analysis calculated for $C_{56}H_{58}N_{10}O_1S_3Zn$, calculated C 64.18, H 5.54, N 13.37, S 9.17, found C 64.48, H 5.35, N 13.25, S 8.95. ^1H NMR (DMF-d_6) δ 0.90 (br s, 2H), 0.96 (t, $J = 6$ Hz, 9H), 1.32 (br s, 2H), 1.42–1.70 (m, 18H), 1.71 (q, $J = 6$ Hz, 6H), 2.90 (t, $J = 6$ Hz, 6H), 7.00–7.80 (m, 15H) ppm.

2.4. Synthesis of *trans*-2,2′-azoquinoxaline bridged bisphthalocyanine 5

Compound **4** (85 mg, 0.0812 mmol) was dissolved in 2 mL DMF and added to 18 mL of absolute ethanol. This solution, together with a solution of anti-dichloroglyoxime (10 mg, 0.0812 mmol in 2 mL ethanol) were simultaneously added dropwise over 1/2 h to absolute ethanol at room temperature under an argon atmosphere and stirring was continued overnight. The reaction mixture was evaporated. The residue (0.07 mmol, 75 mg) was stirred in dry DMF at 90 °C under an argon atmosphere. $CoCl_2{\cdot}6H_2O$ (0.07 mmol, 0.016 g) in dry DMF was added to the stirred solution. The mixture was refluxed for 3 h under argon. The resulting dark green precipitate was filtered off and washed with absolute ethanol. The crude product was purified by column chromatography with silica gel eluting with $CHCl_3$. Yield: 45 mg (51%). This compound was soluble in $CHCl_3$ and CH_2Cl_2. Mp > 350 °C. IR (KBr pellet) $\nu^{-1}_{\max/\mathrm{cm}}$: 740, 810, 870, 900, 1120, 1160, 1610, 1640, 2870, 2920, 2970, 3030. Analysis calculated for $C_{116}H_{110}N_{22}O_2S_6Zn_2$, calculated C 64.33, H 5.08, N 14.23, S 8.87, found C 64.78, H 5.09, N 13.88, S 9.17. ^1H NMR (DMF-d_6) δ 1.20 (t, $J = 6$ Hz, 18H), 1.26–1.47 (m, 36H), 1.71 (q, $J = 6$ Hz, 12H), 2.90 (t, $J = 6$ Hz, 12H), 6.8–7.8 (m, 30H), 9.80 (s, 2H) ppm.

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