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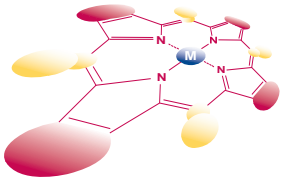

Synthesis, characterization, electrical and dielectric permittivity measurements of 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanines

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ABSTRACT: 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyanines were synthesized from 4-(4-amino-3-nitrophenoxy)phthalonitrile which was obtained from 4-nitro-1,2-dicyanobenzene and 4-amino-3-nitrophenol. 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanine and 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II) were synthesized in a one-step condensation reaction of ferrocenylaldehyde with 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyanine and 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II), respectively. The novel compounds were characterized by elemental analysis, Inductively Coupled Plasma (ICP-MS), UV-vis, IR and ^{1}H NMR spectroscopy. The effects of temperature and frequency on the conduction properties (a.c. and d.c.) and the dielectric constant were studied on pellet samples of 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyanine, 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanine, 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II) and 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II), with evaporated, ohmic gold electrodes in the frequency range 40-10^5 Hz. and within the temperature range 290-400 K. Unlike many metallophthalocyanines, a variable-range hopping model is found to most appropriately fit the experimental conductivity data of 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanine and 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II), while for 2,9,16,23-tetra(4-amino-3-nitrophenoxy)-phthalocyanine and 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II), thermally activated conduction with single activation energy is valid. Frequency and temperature dependence of the a.c conductivity were analyzed in terms of existing theory for 2,9,16,23-tetra-(4-amino-3-nitrophenoxy)phthalocyanine, 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanine, 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II) and 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II). It was found that the a.c. conductivity of the compounds depends on the frequency, obeying the empirical formula, $\sigma_{ac} = A(T)\omega^s$. The model parameters calculated are reasonable and consistent with the prediction of the correlated barrier hopping model for 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanine and 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II) and the quantum mechanical tunneling model for 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyanine and 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II). The dielectric constant of the compounds increased with temperature and decreased with frequency in the investigated range. Copyright © 2006 Society of Porphyrins & Phthalocyanines.

KEYWORDS: phthalocyanine, ferrocenyl, variable range hopping, dielectric permittivity.

INTRODUCTION

Phthalocyanines, which are synthetic, remarkably stable and versatile macrocyclic compounds, were

◊SPP full member in good standing

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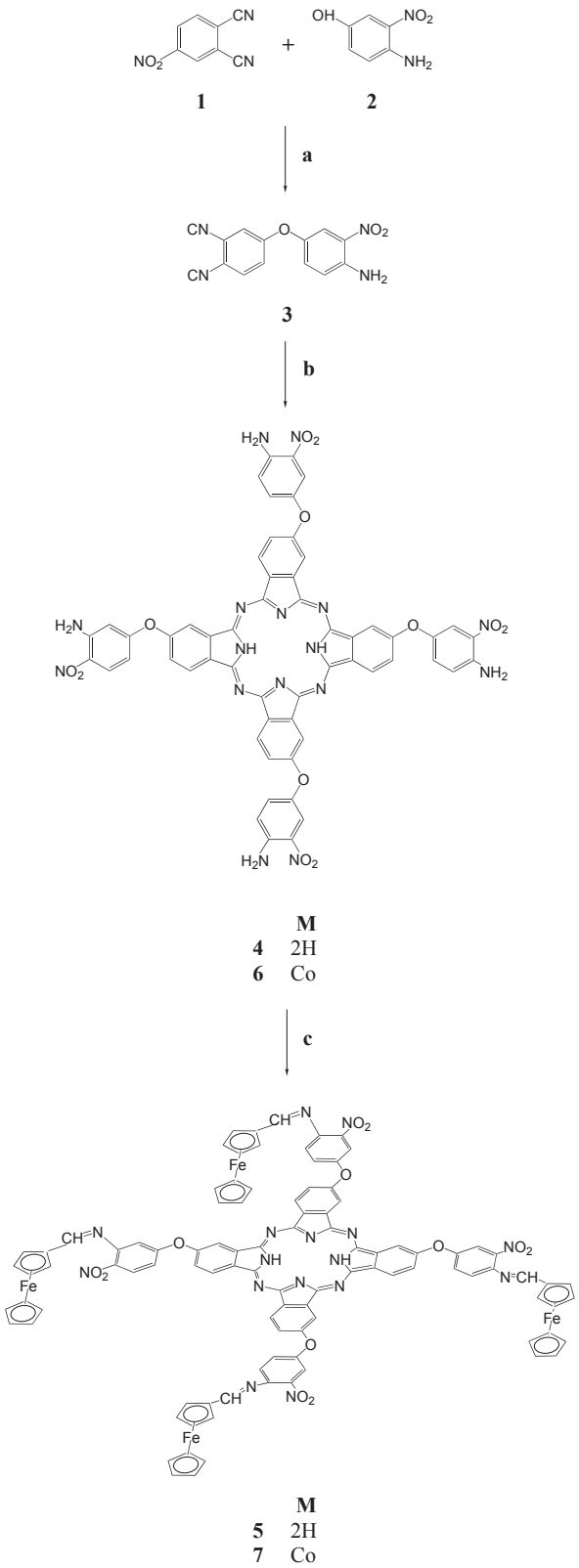
discovered over 90 years ago [1]. Metal phthalocyanines are generally prepared in high yield by cyclotetramerization of phthalic acid derivatives. A metal ion brings the reactants together by coordination and the reaction takes place in a series of stereochemically controlled steps. The synthesis of phthalocyanines that have been peripherally functionalized with appendages that can be included in the phalocyanine core, and its chemical versatility, allows the introduction of many different substituents at peripheral positions [2-4]. These peripheral units are particularly noteworthy as they allow for cation selectivity and complex stability to be enhanced through changing the number and type of the macrocycle donor [5, 6]. However, metal-free phthalocyanines are few, due mainly to the difficulty of preparing the precursors. Phthalocyanines and their symmetrically or unsymmetrically substituted derivatives have been studied extensively because of their broad applications. For example, such compounds are of interest for non-linear optical applications [7, 8], as gas sensors [9], as materials for optical data storage [10, 11], for catalysis and as sensitizers for photodynamic therapy [12]. In addition, their intense color and their thermal and chemical stability make them very useful as dyes and pigments in the textile and paint industries.

In this present paper, we report on a novel symmetrical metal-free (4-amino-3-nitrophenoxy)phthalocyanine **4** and (4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II) **6,** which were reacted through the formation of four Schiff's bases with ferrocenyl aldehyde [13]. A.c. and d.c. conductivities and impedance measurements were also carried out on pellets of compounds **4,** 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)-phthalocyanine **5, 6** and 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II) **7**. Compounds **5** and **7** showed "variable range hopping conductivity" as inorganic semiconductors [14]. The dielectric constant of the compounds was also calculated from measurements.

RESULTS AND DISCUSSION

The synthesis of **5** and **7** are shown in Scheme 1. The starting point as a precursor is 4-(4-amino-3-nitrophenoxy)phthalonitrile **3** which can be obtained by the reaction of 4-nitro-1,2-dicyanobenzene **1** and 4-amino-



Scheme 1. Summary of the synthesis of compound **5** and **7**. Reagents: (a) K_2CO_3, DMSO; (b) LiCl or $Co(CH_3COO)_2{\cdot}4H_2O$; (c) ferrocenylaldehyde, p-toluene sulfonic acid, DMSO

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3-nitrophenol **2**. When compound **3** and LiCl were heated at 180 °C, compound **4** was isolated as a green precipitate. Compound **6** was synthesized by the reaction of compound **3** with $Co(CH_3COO)_2{\cdot}4H_2O$. The condensation of the amine groups of compounds **4** and **6** with ferrocenylaldehyde resulted in new phthalocyanines **5** and **7** with four ferrocenylimino substituents.

The elemental analytical results of compounds **3**, **4**, **5**, **6** and **7** show good agreement with the calculated values. The difference between the IR spectra of phthalonitrile **3** and those of phthalocyanines **4** and **6** were clear, from the presence of a CN vibration in the compound **3** spectrum at 2238 cm^{-1}. The spectra of compounds **4** and **6** included stretching NH_2 bands at 3373 and 3448 cm^{-1} for compound **4**, 3326 and 3361 cm^{-1} for compound **6,** and bending bands at 1342 and 1521 cm^{-1} for compound **4**, 1350 and 1510 cm^{-1} for compound **6**, for the nitro groups. The comparison of the IR spectral data of compounds **4** and **5**, clearly indicates the conversion of NH_2 groups to ferrocenylaldehyde groups by the disappearance of the NH_2 band at 3373 and 3448 cm^{-1} and the appearance of new bands at 1569 and 1602 cm^{-1} for the imines in **5**. Moreover, the band around 3417 cm^{-1} can be attributed to the N-H stretching frequency of the inner core of the metal-free phthalocyanine **5**. The IR spectra of compound **7** is very similar to the spectrum of compound **5**. The UV-vis absorption spectra of compound **4**, **5**, **6** and **7** in a dimethyl sulfoxide (DMSO) solution (*ca.* 10^{-5} M) at room temperature are summarized in Table 1. In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one of which is in the visible portion at 600-700 nm (Q-band) and the other in the UV region (B-band). The D_{2h} symmetry of the metal-free phthalocyanine is verified by the two absorptions in the visible region.

The electronic spectra of **4** in DMSO showed the characteristic Q-band absorption around 709 and 676 nm. Such split Q-band absorptions are due to the $\pi \rightarrow \pi^*$ transition from the HOMO to the LUMO of the phthalocyanine ring related to the conjugated 18π electron system. The B-band absorption around 422 nm also shows a Soret region which corresponded to the deeper $\pi \rightarrow \pi^*$ levels of LUMO transition. When four bulky ferrocenylimino units are bound to the periphery of the metal-free phthalocyanine **5**, the Q-band appears to have three maxima at 705, 676 and 643 nm and a B-band absorption at around 410 nm [12]. However, in the case of the Co(II) derivative of phthalocyanine **6**, the average Q-band is slightly shifted to the blue with respect to the parent metal-free compound **4**. The Q-band appears without splitting and is centered at around 665 nm and the B-band at 350 nm, respectively. The single Q-band in the metal derivative, and the split form in its metal-free derivatives, are characteristic. The Q-band of **7** appears to have three maxima at 660, 620, 610 nm and the B-band at 410 nm (Table 1).

The ^1H NMR spectrum of **4** showed 8 NH_2 protons at δ 1.80 ppm. All these NH protons disappeared after a deuterium exchange on the addition of deuterium oxide (D_2O). In addition, the aromatic protons of compound **4** appeared at δ 6.90-8.10 ppm. The spectrum of compound **5** confirmed the proposed structure showing multiplets at δ 6.90-7.90 ppm for the aromatic protons and a broad singlet at δ 9.80 ppm for the N=CH protons. The spectrum of compound **5** also showed ferrocene protons at δ 4.00-4.80 ppm.

The d.c. conductivity of the samples was measured as a function of temperature from 290 to 400 K. The observed electrical conductivity values for **4**, **5**, **6** and **7** at room temperature are 2.7×10^{-11} S/cm, 5.4×10^{-10} S/cm, 3.6×10^{-11} S/cm, 6.8×10^{-10} S/cm, respectively. Room temperature d.c. current density-voltage (J-V) measurements on evaporated α-form metal-free phthalocyanine thin films, were carried out by Amar *et al.* [15]. They observed that the film showed a linear ohmic dependence at low voltages, followed by a power-law dependence, of exponent **4**, at higher voltage levels. Space-charge limited conduction controlled by an exponential distribution of traps above the valance band edge for a higher voltage in CoPc were also observed by Abdel-Malik [16]. Figure 1 shows the dependence of the measured d.c. conductivity on the inverse of the temperature for all samples. The linear dependence of the conductivity on the inverse of the temperature indicates that the conduction occurs through an activated process

Table 1. UV-vis data for the phthalocyanines **4**, **5**, **6**, **7** in DMSO

Compound	λ, nm (log ε, ε in $M^{-1}.cm^{-1}$)
4	709 (4.011), 676 (4.130), 610 sh (3.953), 422 (4.335)
5	705 (4.252), 676 (4.344), 643(4.247), 618 sh (4.154) 410 (4.647)
6	665 (4.800), 610 sh (4.400), 350 (4.815)
7	660 (4.670), 620 (4. 750), 610(4.400), 410 (4.810)

sh = shoulder

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which has single activation energy for compounds **4** and **6** in the operating temperature range. Thus, it is reasonable to represent the temperature dependence of conductivity for compounds **4** and **6** by the well-known expression:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_A}{kT}\right) \quad (1)$$

where E_A is activation energy, T is temperature, k is Boltzmann's constant and σ_0 is a constant of proportionality. The value of activation energy derived from the slope of the log $\sigma_{d.c}$ *vs* 1/T graph is 0.71 eV for compound **4** and 0.83 eV for compound **6.** A completely different conduction mechanism was observed for compounds **5** and **7**. The deviation from the linearity of the curve for compounds **5** and **7** cannot be accounted for, within the framework of a band conduction model. This type of conduction is described by variable-range hopping (VRH) of barriers in 3-dimensions as proposed by Mott and Davis [17]. The VRH model has been extensively applied to various amorphous semiconductors over the last decades, and recently it has also been applied with varying degrees of success to conducting polymer [18]. Recently, Altındal *et al*. have shown the applicability of Mott's VRH model in spin-coated phthalocyanine films [14]. According to the VRH model, the temperature dependence of conductivity is given by:

$$\sigma_{d.c.} = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\gamma}\right] \quad (2)$$

where σ_0 is the high temperature limit of conductivity and T_0 is associated with the degree of localization of electronic wave function. The exponent γ determines the dimensionality of the medium. The temperature dependence of d.c. conductivity in **5** and **7** suggests that the dominant conduction mechanism is by the hopping of excited carriers into the localized states around the Fermi level.

Higher conductivity and different temperature dependence of the compounds **5** and **7** can be expected here due to the nature of the ferrocenylimino group and differences in stacking arrangement of phthalocyanine molecules. This difference in arrangement may result in altering of the interaction of π electron systems between different molecules, which may affect the electrical conductivity of the phthalocyanine.

The frequency dependence of a.c. conductivity, $\sigma_{ac}(\omega)$, for different values of temperature in the range 290-400 K was investigated for all samples. Figure 2 shows the total measured a.c. conductivity as a function of frequency at 353 K. A similar variation of σ_{ac} with frequency is also observed at other temperatures. It is clear from Fig. 2 that the frequency has a pronounced effect on the measured a.c. conductivity; a.c. conductivity increased linearly with increasing frequency in the temperature range 290-400 K for all compounds. A general feature of disordered systems, such as phthalocyanine, is that frequency-dependent conductivity obeys the empirical power law of the form $\sigma_{ac}(\omega) = A(T)\,\omega^s$, where A(T) is a temperature-dependent parameter. To investigate the conduction mechanism involved, the variation of the exponent s with temperature, estimated from the slope of ln $\sigma_{ac}(\omega)$ *vs* ln ω graphs, was examined. The value of the exponent s at 353 K is 0.77, 0.55, 0.78 and 0.40 for compounds **4**, **5**, **6** and **7**, respectively. While a monotonic decrease in the s values with increasing temperature was observed for compounds **5** and **7**, temperature-independent s values were observed for compounds **4** and **6**. In general, two different models which are called Quantum Mechanical Tunneling (QMT) and hopping, are considered for charge carrier transports in molecular materials. In these two models, the frequency exponent s is found to have two different trends with temperature and frequency. According to the QMT model, the conduction occurs by means of thermally assisted Quantum Mechanical Tunelling. The QMT model predicts a temperature-independent s with a constant value around 0.8 which is given by,

$$s = 1 \frac{4}{\ln(\omega\tau_0)} \quad (3)$$

where ω is the angular frequency and τ_0 the characteristic relaxation time of the carrier.

On the other hand, the CBH model, which was developed by Eliot, is based on the concept of charged defects and in this case, bipolarons hop between two charged defect states D^+ and D^- over the barrier

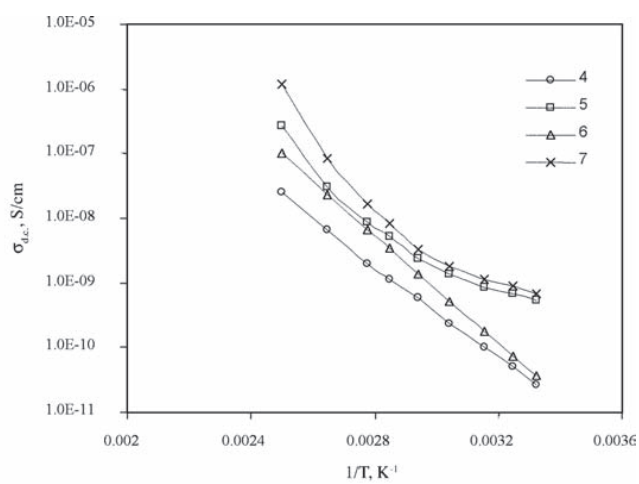

Fig. 1. Temperature dependence of the d.c. conductivity for **4**, **5**, **6** and **7**

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separating them, rather than tunneling through the barrier [19]. Unlike the QMT model, the CBH model gives a temperature-dependent frequency exponent which can be expressed as

$$s = 1 - \beta = 1 - 6k_BT/W_M \quad (4)$$

where W_M is the optical band gap, k_B Boltzman's constant and T is temperature. The variation of the frequency exponent, s, with temperature, gives information on the specific mechanism involved. Our calculations showed that s is definitely a function of temperature for compounds **5** and **7** but not for **4** and **6**. The comparison of the experimentally determined s values with the prediction of QMT and CBH models suggests that the dependence of exponent s on temperature is in agreement with the prediction of the CBH model for compounds **5** and **7** and of the QMT model for compounds **4** and **6**.

To complete the study of the electrical properties of the compounds, the impedance spectroscopy technique was used in the frequency range 40-10^5 Hz. The measured impedance spectra for the compounds at 353 K, on a complex plane, Cole-Cole plot, are presented in Fig. 3. At low temperatures, the results of impedance measurements indicated that the spectrum consists of a quasi-vertical line for all compounds.

A semicircular shaped curve in the impedance spectra indicated that the impedance becomes capacitive and can be modelled as a capacitor in parallel with a resistor in series with another resistor. As can be seen from Fig. 3, the effects of temperature on the impedance spectra of compounds **5** and **7** become clearly visible with a rise in temperature. On the complex plane plot, only a depressed semicircle with a different radius was observed for both compounds **5** and **7** at 353 K, indicating a deviation from the Debye dispersion relation. In this case, the relaxation time is considered as a distribition of values rather than a single relaxation time. Therefore, the equivalent circuit is modified to include a constant phase element (CPE). The observed differences between the impedance spectra of the **4**, **6** and **5**, **7** can be attributed to the existence of the ferrocenylimino group in **5** and **7**.

The complex dielectric constant has been used to describe the frequency-dependent properties of materials. The complex dielectric function, ε^*, can be expressed as:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \quad (5)$$

where $i = \sqrt{-1}$ and ε', ε'' are real and imaginary parts of the complex dielectric constant, respectively. The dielectric constant, ε', is given by the relation C/C_0, where C is the measured capacitance and C_0 is the geometrical capacitance which is given by the product of the vacuum permittivity and area A, divided by the distance apart t of the plates, namely:

$$C_0 = \varepsilon_0 \frac{A}{t} \quad (6)$$

The dielectric behavior of the samples was

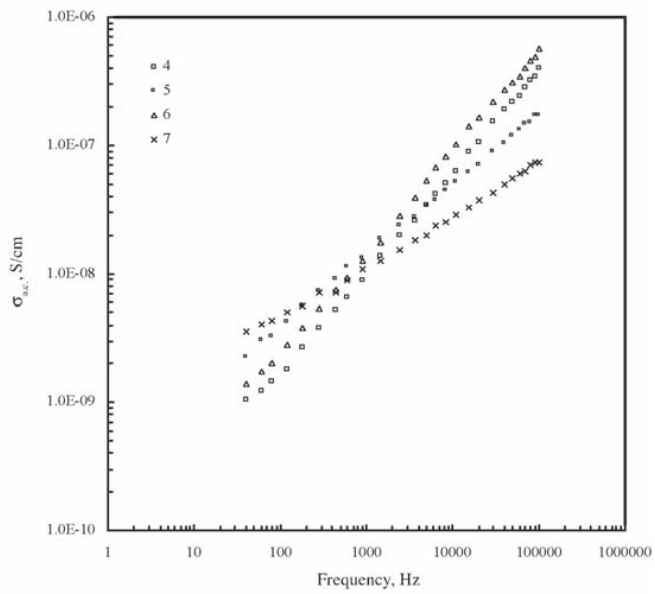

Fig. 2. Frequency-dependent conductivity of the samples at 353 K

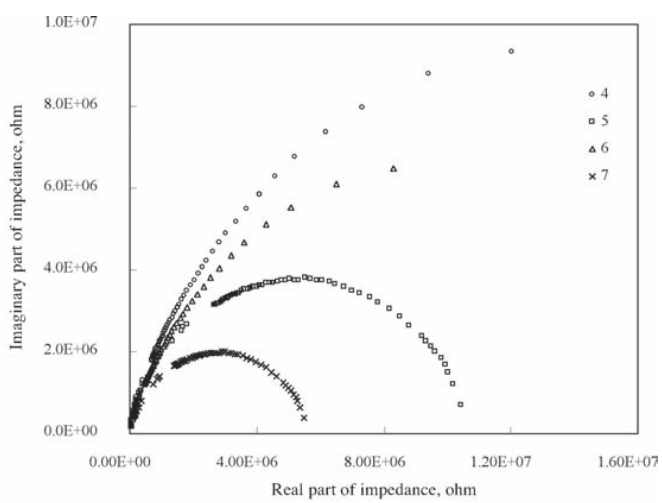

Fig. 3. The real and imaginary component of impedance as a function of frequency for the compounds at 353 K

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investigated in the temperature range 290-400 K. The values of dielectric constant, ε', were derived from the measured impedance data for the samples. Figure 4 shows the variation of ε' with frequency at 330 K. It can be seen that dielectric permittivity decreases monotonically with increasing frequency and attains a constant value at higher frequencies. At low frequencies and high temperatures, the rate of decrease of ε' is very high, while at higher frequencies the rate slows down. A similar variation of ε' with frequency is also observed at other temperatures. The behavior of ε' can be explained as follows: at low frequency, the dipoles align themselves along the field direction and fully contribute to the total polarization; as the frequency of the field is raised, the variation in the field becomes too rapid for the molecular dipoles to follow, as dipoles are unable to follow field variations at high frequencies, and are also due to electrode polarization effects [20, 21], so that their contribution to the polarization becomes less, with a measurable lag, because of internal fractional forces. It is also observed from the measurements that dielectric permittivity is found to increase with increasing temperature. This may be attributed to the electric field which is accompanied by applied frequencies. Such fields cause some ordering inside the samples as well as the formation of an electric moment in the entire volume of the dielectric and in each separate polarizing molecule. When the temperature rises the dipoles orientation is facilitated, and this increases the dielectric constant. Figure 4 also indicates the effect of the ferrocenylimino group on the dielectric constant of the compounds.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer using KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1601 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of Tubitak, Ankara. ^{1}H NMR spectra were recorded in deuteriodimethylsulfoxide with a Mercury-Vx 400 MHz instrument. Au/MPc/Au sandwich in the configuration were used for the electrical characterization. The phthalocyanine pellets were prepared (diameter 1 cm, thickness 0.5 mm) by pressing the powdered materials using a pressure ~10 tons.cm^{-2}. The pellets were sandwiched between two evaporated gold electrodes which provide ohmic contacts to the phthalocyanines. The temperature dependent d.c. and a.c. conductivity measurements were carried out in vacuum (≤ 10^{-3} mbar) in the temperature range 290-400 K, using a temperature controller (Model LTC-60). The measurement procedure for the temperature-dependent d.c., a.c. conductivity and impedance spectra was described in the literature [22].

Synthesis of compound 4-(4-amino-3-nitrophenoxy)phthalonitrile 3. A powdered 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) was dissolved in Me_2SO (50 mL) at room temperature under argon atmosphere. K_2CO_3 (1.38 g, 0.01 mol) was added to this solution over a period of 2 h. The reaction mixture was stirred at room temperature, for 24 h and then filtered. The reaction mixture was poured into water (100 mL) and stirred, then the solution was extracted with portions (3 × 50 mL) of CH_2Cl_2. The residue was coarsely fractionated on a silica gel column and eluted with CH_2Cl_2. This compound is soluble in $CHCl_3$ and CH_2Cl_2. Yield 1.70 g (94%), mp 176 °C. Anal. calcd. for $C_{14}H_8N_4O_3$: C, 60.00; H, 2.86; N, 20.00%. Found: C, 59.71; H, 2.55; N, 19.78. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H, ppm 6.36 (2H, br s),

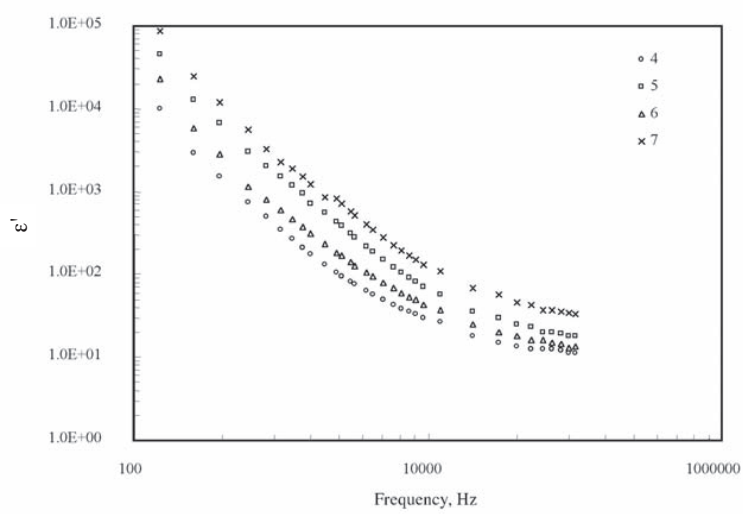

Fig. 4. Plot of dielectric permittivity (ε') *vs* log of frequency (f) for **4**, **5**, **6** and **7** at 330 K

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6.93 (1H, br d, J = 9 Hz), 7.16 (1H, dd, J = 9 Hz and 2Hz), 7.23 (1H, d, J = 2 Hz), 7.26 (1H, dd, J = 9 Hz and 2 Hz), 7.73 (1H, d, J = 9 Hz), 7.90 (1H, d, J = 2 Hz). IR (KBr pellet): ν, cm^{-1} 834, 961, 1089, 1165, 1268, 1319, 1421, 1523, 1600, 1651, 2238, 3080, 3387, 3514.

Synthesis of 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyanine 4. A mixture of compound **3** (250 mg, 0.89 mmol) and LiCl (76 mg, 1.78 mmol) was heated at 180 °C under nitrogen atmosphere for 10 minutes to give a symmetrically substituted phthalocyanine. The reaction mixture was cooled down to room temperature and dissolved with dimethylformamide (DMF), then treated with water to precipitate a green product. After filtration the product was washed with cold ethanol and diethylether. The crude green product was purified by column chromatography on silicagel (DMF). This compound is soluble in DMF and DMSO. Yield 205 mg (82%), mp >350 °C. Anal. calcd. for $C_{56}H_{34}N_{16}O_{12}$: C, 59.89; H, 3.03; N, 19.96%. Found: C, 59.64; H, 2.86; N, 19.80. ^{1}H NMR (400 MHz, DMSO): δ_H, ppm 1.80 (8H, br s), 6.90-8.10 (24H, m). IR (KBr pellet): ν, cm^{-1} 659, 823, 960, 1041, 1120, 1205, 1253, 1342, 1409, 1477, 1521, 1662, 3373, 3448.

Synthesis of 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyanine 5. Compound **4** (40 mg, 0.0356 mmol) was dissolved in dry DMSO. Ferrocenylaldehyde (61 mg, 0.285 mmol) and a catalytic amount of *p*-toluene sulfonic acid were added to this solution. The mixture was heated at 160 °C for 10 h. The reaction mixture was cooled to room temperature and the precipitate was filtered off, then the solvent was evaporated to dryness. The residue was washed with acetone several times to remove the unreacted materials. The product was washed with methanol then acetone and dried. This compound is soluble in DMF and DMSO. Yield 52 mg (77%), mp >350 °C. Anal. calcd. for $C_{100}H_{66}N_{16}O_{12}Fe_4$: C, 62.96; H, 3.46; N, 11.75%. Found C, 62.75; H, 3.23; N, 11.59. ICP-MS, calcd. Fe, 11.75%. Found: Fe, 11.57. ^{1}H NMR (400 MHz, DMSO): δ_H, ppm 4.00-4.80 (36H, m), 6.90-7.90 (24H, m), 9.80 (4H, br s). IR (KBr pellet): ν, cm^{-1} 659, 823, 960, 1041, 1120, 1205, 1353, 1417, 1477, 1510, 1569, 1602, 1639, 2870, 2958, 3417.

Synthesis of 2,9,16,23-tetra(4-amino-3-nitrophenoxy)phthalocyaninatocobalt(II) 6. A mixture of compound **3** (250 mg, 0.89 mmol) was dissolved in dry DMF under argon atmosphere. $Co(CH_3COO)_2{\cdot}4H_2O$ (1.78 mmol) was added to this solution and the reaction was carried out at 160-180 °C for 8 h to give a symmetrically 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 diethylether. The residue was coarsely fractionated on a silica gel column and eluted with DMF. This compound is soluble in DMF and DMSO. Yield 233 mg (89%), mp >350 °C. Anal. calcd. for $C_{56}H_{32}N_{16}O_{12}Co$: C, 57.00; H, 2.71; N, 18.99%. Found C, 56.65; H, 2.91; N, 19.20. IR (KBr pellet): ν, cm^{-1} 962, 1058, 1143, 1220, 1253, 1350, 1406, 1473, 1510, 1600, 3326, 3361.

Synthesis of 2,9,16,23-tetra(4-ferrocenylimino-3-nitrophenoxy)phthalocyaninatocobalt(II) 7. Compound **6** (60 mg, 0.0510 mmol) was dissolved in dry DMSO. Ferrocenylaldehyde (82 mg, 0.0430 mmol) and a catalytic amount of *p*-toluene sulfonic acid were added to this solution and the reaction mixture was heated at 160 °C for 10 h. The reaction mixture was cooled to room temperature and the precipitate was filtered off, then the solvent was evaporated to dryness. The residue was washed with acetone several times to remove the unreacted materials. The product was washed with methanol then acetone and dried. This compound is slightly soluble in DMSO. Yield 82 mg (82%), mp >350 °C. Anal. calcd. for $C_{100}H_{64}N_{16}O_{12}CoFe_4$: C, 61.13; H, 3.26; N, 11.41%. Found C, 61.05; H, 3.35; N, 11.55. ICP-MS: calcd. Co, 3.01; Fe 11.41%. Found Co, 2.92; Fe 10.90. IR (KBr pellet): ν, cm^{-1} 660, 813, 1010, 1037, 1124, 1190, 1402, 1560, 1596, 1647, 2870, 2929, 3263, 3400.

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