

Synthesis, Conductivity and Impedance Studies on across adjacent ring formed new metallo phthalocyanines

Assist.Prof.Dr. Sevil Şener,^[a] Assoc.Prof.Dr. Nursel Acar Selçuki,*^[b] Assoc.Prof.Dr. Fatih Dumludağ,^[c] Prof.Dr. Bekir Salih,^[d] Prof.Dr. Özer Bekaroğlu*^[e]

^aAliaga Vocational School, Ege University, Aliağa, İzmir, TR-35800, Turkey. E-mail: <u>sevil.sener@ege.edu.tr</u>; Tel: +90 232 6160671; Fax: +90 232 6161225

^bDepartment of Chemistry, Faculty of Science, Ege University, Bornova, İzmir, TR-35100, Turkey. E-mail: nursel.acar@ege.edu.tr; Tel: +90 232 3112387; Fax: +90 232 3888264.

^cDepartment of Physics, Faculty of Science and Arts, Marmara University, Göztepe, İstanbul, TR-34722, Turkey. E-mail: <u>fatihdumludag@marmara.edu.tr</u>, Tel: +90 216 3451186; Fax: +90 216 3478783

^dDepartment of Chemistry, Hacettepe University, Beytepe, Ankara, TR-06800, Turkey. Email: bekir@hacettepe.edu.tr; Tel: +90 312 288 2163; Fax: +90 312 297 7975.

^eFaculty of Pharmacy, Istinye- University, Istanbul, 34010, Turkey. E-mail: <u>obek@itu.edu.tr</u>; Tel: +90 216 3590130; Fax: +90 216 3860824.

Corresponding authors: e-mail: <u>nursel.acar@ege.edu.tr</u> Tel: +90-232-3112387 Fax: +90-232-3888264 <u>https://avesis.ege.edu.tr/nursel.acar/</u> ORCID : 0000-0001-9292-0637 e-mail: obek@itu.edu.tr Tel: +90-216-359013 Fax: +90-216-3860824 https://www.istinye.edu.tr/en/academic/

Abstract

The synthesis and characterization of Co(II), Zn(II) and Ni(II) phthalocyanines (Pcs) 4, 5 and 6, respectively containing two Bis[2-(4-hydroxyphenyl)-2-propyl]benzene across adjacent ring formed at the peripheral positions are described. The Pcs were synthesized by cyclotetramerization of the previously prepared precursor 4,4'-bis[1,3-propylbenzene-2-pphenoxy]phthalonitrile (3) with the presence of metal salt in boiling dry DMF under a dry nitrogen atmosphere. Elemental analysis, UV-Vis, FT-IR, MALDI-TOF mass and ¹H-NMR spectrometry techniques were used for characterization of 4. DC and ac conductivity and impedance spectra (IS) measurements were performed on the films 5, and 6 between the temperatures 293 - 523 K and frequencies 40-100 kHz. The dc conductivity values were calculated as 2.11×10^{-10} S/cm, 3.48×10^{-10} S/cm, and 1.90×10^{-10} S/cm for the films of **4**, **5**, and 6 at room temperature. Activation energy values of the films were also calculated. ac conductivity results suggest that dominant charge transport mechanisms can be explained by hopping model depending on temperature and frequency range. From impedance spectra, Cole-Cole plots, the relaxation time in Debye dispersion relation is considered as a distribution of relaxation time values, rather than as a single relaxation time. To elucidate the structural, spectroscopic and bonding properties of the obtained compounds, DFT/TD-DFT calculations were performed.

Introduction

Phthalocyanines (Pcs) are usually planar macro-cycle compounds. These tetrapyrolederived compounds with eight nitrogen atoms, 18 electrons and a central vacancy that can be entered by many metal ions are one of the areas of intense work in recent years. Unlike porphyrin, phthalocyanine (Pc) contains four benzo groups and four nitrogen atoms in the meso position. Because of their thermal and chemical stability, they are resistant to heat, light and chemical substances other than strong oxidizers, which is of great interest to researchers. By replacing the peripheral and nonprepheral or axial substituents and / or center atoms of the Pcs it is possible to produce unlimited new materials with different properties.^[1-3] Pcs complexes can be provided by the exchange of substituents attached to their peripheral positions, as well as the physical and chemical properties of the complexes.^[4,5]

New Pcs which are used in many places today are obtained by synthesis. They are used in many areas of high technology as photoconducting agent^[6,8], as photodinamic sensitizers for cancer therapy^[9-11], other medical applications^[12-14], as gas-sensor^[15,16], as electrochromic display devices. Other applications include uses in computer discs and information storage systems^[17,18], as laser dyes, in photovoltanic cell elements, in liquid-crystal display applications, as catalyst for many reactions like oxidation of olefins, for increasing the octane rate of the gasoline and non linear optic (NLO) and optic limiting (OL) materials.^[19-21]

There are recently published reports regarding the use of Pcs as catalysts for photodegradation of dyes, phenols, pesticides and other organic pollutants.^[22-24] These Pcs used as catalysts contain hydroxy benzene derivatives. Literature research have also involved patented studies on hydroxy benzene derivatives about Thermoplastic molding compositions with reduced water absorption^[25], Heat-sensitive recording material^[26], Benzoate

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homopolymers hindered phenolic groups as stabilizers^[27], method for polycarbonates prepared using 1,1-Bis(4-hydroxyphenyl)-3-alkylcyclohexanes.^[28]

We devoted our research to a new class "ball-type" Pcs and pioneered for fifteen years on those compounds which showed intrinsic more versatile chemical and physical properties.^[3,29] In this respect, a novel ball-type Pc was designed starting from commercial bis[2-(4-hydroxyphenyl)-2-propyl]benzene **1** and 4-nitrophthalonitrile **2**. The metallo Pcs obtained from this work were unexpectedly across adjacent ring formed Pcs instead of balltype Pcs. We encountered the same result in our former work starting with 1,1,2,2-tetrakis(phydroxy-phenyl)ethane which also resulted in across adjacent ring formed Pcs.^[30] This type of ring containing Pc is also rare in the literature; therefore, we find it worthy to synthesize the new metallophthalocyanines (MPcs), **4**, **5**, and **6**. All compounds were characterized spectroscopically and were then used to determine conductivity (dc and ac) and charge transport mechanisms of the compounds. In order to clarify these properties electrical measurements were performed on **4**, **5**, and **6** between the temperatures 293 - 523 K and frequency 40-100 kHz. Impedance spectra (IS) measurements were also obtained. Moreover, we carried out Density Functional Theory (DFT) and Time Dependent-Density Functional Theory (TD-DFT) computations to shed light on their structural and electronic properties.

Results and discussion

Synthesis and characterization of compounds

The key precursor **3** was obtained with a high yield of 84.44% after workup. Compound **3** was readily converted to the Pcs **4**, **5** and **6** via cyclotetramerization in anhydrous DMF with the corresponding metal salts $Co(OAc)_2 \cdot 2.H_2O$, $Zn(OAc)_2 \cdot 4.H_2O$ and Ni(OAc)_2 \cdot 4.H_2O, respectively as depicted in Scheme 1. The detailed synthesis procedures as well as the characterization data are presented in the Experimental Section. All MPcs dissolved with heating and mixing in DMSO.

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Scheme 1. Synthesis of 3, 4, 5 and 6 (i) K_2CO_3 , N_2 , ACN, 90 °C, 72 h, (ii) $Co(OAc)2.2H_2O$, $Zn(OAc)2.4H_2O$ and $Ni(OAc)2.4H_2O$, 155 °C , DMF, N_2 , 24 h.

In the IR spectra, the characteristic ν (C=N) stretching band at 2242 cm⁻¹ shows obvious evidence for the nucleophilic displacement of the nitro group, thus the formation of **3**. The IR spectrum displays the typical ν (C–H) absorption frequency at 3112, 3087 and 2971cm⁻¹, characteristic of *methyl groups*; typical Phthalociyanine ring ν (C=N) absorption frequency at 1715, 1594 (symmetric) and 1232, 1172 cm⁻¹ (unsymmetric) and typical Phthalociyanine ring ν (C–N) absorption frequency at 1407 cm⁻¹ (symmetric), 1075-78, 1043-45 cm⁻¹ (unsymmetric); typical ν (C=C) absorption frequency at 1503, 1474 cm⁻¹ characteristic of *aromatic ring groups*.

Structural characterization of **3** was supported with its ¹H-NMR spectrum (400 MHz) in Fig. S1. The spectrum in acetone showed two doublets at 8.01 (J = 8.8 Hz, 2H) and 7.50 (d, J = 8.8 Hz, 2H) and one singlet at 7.99 ppm (s, 1H)) corresponding to protons for phthalonitrile group. On the other hand, two doublets at 7.35 (J = 8.8 Hz, 4H) and 7.33 (J = 12.5 Hz, 4H) ppm were observed for phenoxly group. Propylbenzene hydrogens were

displayed as two doublets at 7.51 (J = 2.54 Hz, 1H), 7.09 ppm (J = 8.89 Hz, 2H) and as one singlet at 7.10 ppm (1H). One singlet was observed at 1.67 ppm for methyl groups. The amounts of the synthesized substances are very small and the MPcs compounds (**5** and **6**) are slightly soluble in organic polar solvent. The synthesized compounds are also dissolved by heating and stirring in coordinated solvents such as DMSO. Therefore, the NMR spectra of these compounds could not be recorded with high resolution. In ¹H-NMR spectrum (600 MHz) of **5** in Fig. S2 which was taken in DMSO, the aromatic protons appeared at 7.78-6.97 ppm as multiplets and methyl groups protons at 1.63 ppm as a singlet. NMR analysis of **4** was excluded due to its paramagnetic nature.

Positive ion and reflectron mode MALDI-TOF-MS spectrum of **3** was obtained and is given in Fig. S3. 2,5-dihydroxybenzoic acid MALDI matrix yielded intense sodinated and potasinated signals beside the low intensity of protonated molecular ion signal and no fragmentations under the MALDI-TOF-MS conditions for this compound. Positive ion and linear mode MALDI-TOF-MS spectra for Co, Zn and Ni complexes of this ligand were observed at high intensities without intense fragmentations when 2,5-dihydroxybenzoic acid MALDI matrix was used in Fig. S4-S6. However, any reasonable signal was obtained in reflectron mode for these three complexes maybe because of the life time of the complexes under the reflectron mode conditions. In the case of metal complexes, mainly potasinated ion adduct signals was found to be dominant compared to the protonated signals. This shows that gas-phase affinity of the complexes to potassium ion is more favorable compared to the molecular masses of the ligand and the complexes. From these results, it could be concluded that the ligand and metal complexes were synthesized in correct route as proposed in Scheme

2.



Scheme 2. Presentation of optimized structures for the investigated complexes in DMSO

DC Conductivity Properties

In order to clarify dc conductivity properties, current - voltage (I-V) characteristics of the films of the compounds were determined. Activation energy values (E_A) were also calculated. All the electrical measurements were performed in aluminum chamber in vacuum $(2x10^{-3} \text{ mbar})$ in dark (293 - 523 K). DC conductivity (σ_{dc}) of the films were calculated at different temperatures (293 - 523 K) by the slope of I-V graphs and the equation $\sigma_{dc} = (I/V)[s/(2n-1)lt]$ where, (I/V) is slope of the I–V graph, s is separation between the finger pair, n is number of the finger pair, l is overlap length and t is thickness of the electrodes. Fig. 1 shows the temperature dependence of dc conductivity of the films and fitting lines for 5 and 6 at different temperature regions. As seen from the figure, conductivity of the films increased with increasing temperature indicating semiconductor behavior. The dc conductivity values were calculated as 2.11×10^{-10} S/cm, 3.48×10^{-10} S/cm, and 1.90×10^{-10} S/cm for the films of 4, 5, and 6 at room temperature and can be represented as $\sigma_{(6)} < \sigma_{(4)} < \sigma_{(5)}$. The values were increased to 2.31×10^{-5} S/cm, 1.86×10^{-5} S/cm, and 1.60×10^{-5} S/cm for the films of **4**, **5**, and **6** at 523 K. DC conductivity values of 4 and 5 were found identical at the same temperatures and showed linear variation up to 478 K, after this temperature, increase rate was decreased with temperature. However, film of 6 showed different dc conductivity behavior with temperature.

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From room temperature to 333 K, the film showed linear behavior with temperature then the rate of the increase was decreased with temperature up to 378 K followed by increase up to 478 K. This type of variation may arise from absorption of oxygen by the films for the duration of the deposition of the film on the glass substrate. Similar observations were reported for other organic molecules. The behavior is interpreted by the authors as exhaustion of absorbed oxygen.^[31-34] DC conductivity values for CoPc (4) and ZnPc (5) at room temperature are calculated as 2.11×10^{-10} S/cm and 3.48×10^{-10} S/cm while it was formerly reported for similar across adjacent ring Pcs nearly as 3.4×10^{-12} S/cm and 1.3×10^{-12} S/cm for CoPc and ZnPc, respectively.³⁰



Figure 1. Variation of dc conductivity values of the films of 4, 5, and 6 between the temperatures 293 - 523 K.

The variation of ln dc conductivity (ln σ_{dc}) with inverse of temperature (1/*T*) indicates the applicability of well known relation (Eq. 1),

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

where σ_0 is pre-exponent factor that gives the specific conductivity for the conduction as $T \rightarrow \infty$, E_A is activation energy, *k* is Boltzmann's constant, and *T* is temperature. The activation energy values of $\mathbf{4} - \mathbf{6}$ were calculated by the slope of ln σ_{dc} -1000/*T* plots and given in Table1. Activation energies for CoPc (**4**) and ZnPc (**5**) at the temperature region *T*<452 K are calculated as 0.77 and 0.76 eV while the values were formerly reported as 0.75 and 0.68 eV for CoPc and ZnPc, respectively.³⁰

Table 1. Activation energies for the films **4**, **5**, and **6** (E_{A1} for T < 478 K, E_{A2} for $T \ge 478$ K, E_{A3} for $T \le 333$ K, E_{A4} for 478K $\ge T \ge 378$ K).

| Film | E_{A1} (eV) | E_{A2} (eV) | E_{A3} (eV) | $E_{A4}\left(\mathrm{eV}\right)$ |
|------|-----------------|---------------|-----------------|----------------------------------|
| 4 | 0.77 | 0.61 | np ^a | np ^a |
| 5 | 0.76 | 0.34 | np ^a | np ^a |
| 6 | na ^b | 0.12 | 1.67 | 0.77 |

^a Not presented.

^b Not applicable.

AC Conductivity Properties

In order to clarify ac conductivity properties and charge transport mechanism, ac conductivity measurements were carried out on **4–6** during the films heating up, depending on frequency (40 Hz – 100 kHz) in the temperature range of 293 - 523 K in vacuum (2x10⁻³ mbar) in dark. Fig. 2 presents ac conductivity values of **5** with frequency between the temperatures 293 K and 523 K, and it clearly indicates that ac conductivity of the film **5** increased with increasing temperature and frequency. It was also observed that the film of **5** showed different temperature dependence at different temperature regions. For $T \le 438$ K, conductivity values of the film strongly depend on frequency and the values directly

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proportional to frequency. For T > 438 K, temperature dependence of ac conductivity decreases. The curves shown in Fig. 2 were similar to that of **4** and **6**.



Figure 2. AC conductivity values of 5 with frequency at indicated temperatures.

The ac conductivity behaviors of 4 - 6 with frequency can be represented by Eq. 2.

$$\sigma_{ac} = A \omega^s$$
 (2)

where ω is the angular frequency and A and s are constants. Charge transport mechanism of the compounds was investigated by examining the exponent s values given in Eq. 2. S values were calculated by straight portions slopes of the curves given in Fig. 2 for $\mathbf{4} - \mathbf{6}$ at different temperatures and frequency regions ($f < 10^3$ Hz, 10^3 Hz $\leq f \leq 10^4$ Hz and 10^4 Hz $< f \leq 10^5$ Hz, low frequency, middle frequency and high frequency, and high frequency regions, respectively). S values in Eq. 2 in terms of temperature of $\mathbf{6}$ was presented in Fig. 3 (Because of the limits of the LCZ meter, s values at frequencies $f < 10^3$ Hz and at the temperatures T <348 K were not presented).

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The results obtained in this study showed that increasing temperature caused s values to decrease in measured frequency and temperature range (Fig. 3). The curves for s values for **4** and **5** were similar to that of film **6** as given in Fig. 3 with s < 1. According to the hopping model, as frequency increases ac conductivity also increases, where $s \le 1$. In the hopping model, it is considered that charge transport realized by mobile carriers and that hops between sites and the sites are separated by the potential barriers.^[35] The Correlated Barrier Hopping (C.B.H.) model^[35-37] suggest that exponent *s* is inversely proportional with temperature and given by Eq. 3.

$$s = 1 - \beta = 1 - \frac{6k_BT}{W_m} \qquad (3)$$

where k_B is Boltzmann's constant and W_m is the binding energy and T is temperature in terms of Kelvin. It is known that the small *s* values points out to multihopping process, and higher s values points out to single hopping process.



Figure 3. Variation of exponent *s* values (in Eq. 2) with temperature for the film 6.

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The results obtained in this study showed that the change in s with temperature and the change in ac conductivity with frequency are consistent with the prediction of the hopping model and ac charge transport mechanism for 4 - 6 can be interpreted as a function of temperature and frequency. The same type of temperature dependence for s was reported in literature for different phthalocyanine films.^[36,37]

For $T \le 438$ K, dominant conduction mechanism can be explained by single hopping. For T > 438 K, conduction mechanism can be explained depending on frequency region. Dominant conduction mechanism can be explained by multihopping for f < 1 kHz and by single hopping for $f \ge 1$ kHz for the studied films.

Impedance Measurements

Impedance spectra (IS) are a powerful technique in order to obtain essential parameters of the materials such as dielectric properties, real impedance, and dielectric loss. Complex Impedance data can be represented by $Z(\omega)^* = R(\omega) - jX(\omega)$, where $R(\omega)$ and $X(\omega)$ are real and imaginary components of complex impedance $Z(\omega)^*$. The curves $(-X(\omega) \text{ versus } R(\omega))$ in complex plan called the Cole-Cole (Nyquist) plot. Impedance spectra (Nyquist Plot) for film **4** were presented in Fig. 4A. At temperatures T < 458 K, as can be seen from the Figure, the curves can be characterized by the semicircular shaped curves and equivalent circuit can be represented by a parallel combination of a capacitor and a resistor and the parallel system is also in series with different resistor.^[38] **5** and **6** also showed similar behavior at these temperatures. For T \geq 458 K, as can be seen from the Fig. 4B, the curves can be characterized by full semicircles. Another observation is that the radius of the semicircles decreased with increasing temperature. Peak frequency (ω_p) of the semicircle at each measurement temperature satisfies $\omega_p t_D = 1$, where t_D is the time constant.^[39] When single-relaxation time process takes place in a compound, then ideal semicircular curves can be

observed in a Nyquist plot. The deviation from semicircular curves along $X(\omega)$ direction with different radii indicates also a deviations from the Debye dispersion relation. In our case, the relaxation time in Debye dispersion relation is considered as a distribution of relaxation time values, instead of a single relaxation time.^[40] Therefore, the equivalent circuit can be modified so that the circuit contains a constant phase element (CPE). In the equivalent circuit, series and parallel resistance gives information about *i*) ohmic losses in the experimental set-up, sheet resistance of the electrodes and *ii*) the bulk resistance of the material under investigation, respectively. Additional information can be obtained from the intersection point of the semicircular curves and real axis. The intersection point gives information about the bulk resistance of the compounds. Impedance spectra of the film **4** at the temperatures 458 K – 523 K were presented in Fig. 4B. It can be seen clearly from Fig. 4B that bulk resistance of the films **4** decreases with increasing temperature indicating semiconducting property and that supports the dc conductivity results. According the bulk resistance of **4** – **6**, $\sigma_{(5)} < \sigma_{(4)} < \sigma_{(6)}$ also supports dc conductivity results.



Figure 4. The Cole–Cole plot (A) for the film 4 at temperatures 293 K – 523 K (B) for the films 4 at temperatures 458 K – 523 K.

Imaginary parts of impedance versus frequency $(-X(\omega) - f)$ curves for the film **6** between 293 – 523 K were illustrated in Fig. 5A. For $T \le 438$ K, as can be seen from the Fig. 5A, rate of decrease in $X(\omega)$ decreased with increasing frequency towards 100 kHz indicates

that there is no current dissipation in this temperature region. Fig. 5B was presented in order to emphasize shift of the peak of imaginary impedance and broadening of the $(-X(\omega) - f)$ curves at T > 438 K. For T > 438 K, three different significant behaviors were observed. A maximum value (peak) of the imaginary part of the impedance was observed for each curve and the frequency of the peak shifted towards to higher frequencies as temperature increases. This shift may be attributed to occurrence of different electrical relaxation times in charge transport mechanism that supports the results obtained from Nyquist plot. Another observation was a broadening of the curves with increasing temperature. This behavior also suggests the occurrence of a number of different relaxation times in electrical process, depending on the temperature. The curves for the film **4**, **5** were similar to that of film **6** in the temperature range of 295 – 523 K.



Figure. 5. Variation of imaginary parts of impedance versus frequency for the film **6** (**A**) for 293–523 K (**B**) for 478–523 K.

DFT results

Gaussian09^[41], Gaussview5.0^[42] and Spartan08^[43] were used in the calculations. The ground state geometries were optimized using DFT^[44]. The hybrid DFT Becke's three-

parameter nonlocal exchange functional^[45,46], with Lee-Yang-Parr correlation functional (B3LYP)^[47] and CAM-B3LYP (Coulomb-Attenuating Method)^[48] in conjunction with LANL2DZ basis set^[49-52] for metals and with 6-31G(d,p) basis set for other atoms were used in DFT calculations. All optimized structures were determined as minima by frequency analysis. The calculations were repeated in DMSO. The TD-DFT calculations were carried out with the same method. First 100 singlet excited states were used in calculations. Ground state geometries were used to obtain molecular orbital energies as well as UV-Vis spectra of the studied systems. Total electron density surfaces of molecules based on electrostatic potential values were calculated in DMSO. Polarizable Continuum Model (PCM)^[53] was used in all DFT and TD-DFT calculations and the effects of solvent on the electronic transitions were calculated in DMSO.

All possible conformers of the molecules given in Scheme 1 were optimized and the most stable conformers were obtained. Scheme 2 shows the tube presentation of the most stable conformer of complexes. The ground-state molecular structures of **4**, **5** and **6** are given in Fig. 6. in DMSO at B3LYP/6-31G(d,p) and LANL2DZ level on metal. To evaluate the electronic transitions, structures of the related systems are required. The types and characteristics of electronic transitions are highly structure-dependent.

While phenyl groups of two sides are oriented towards out of plane, Pcs keep their planar structure except compound **5**. Due to its larger size compared to the other studied metals, Zn is oriented out of the Pc plane. These two directions from Pc have an approximate torsion angle of 50° (C1-O-C2-C3 angle) in gas phase and in DMSO.



Figure 6. Optimized structures of **4**, **5** and **6** in DMSO at B3LYP/6-31G(d,p) level; LANL2DZ for metals.

Complexation energies for the investigated systems were calculated in gas phase and in solution according to the synthesis reactions (Scheme 1, ii) and the stabilities of the formed complexes were determined. Table 2 shows dipole moments (μ , Debye), total electronic energies including zero point correction energies (E_{elec} +ZPE, Hartree), total electronic energies including free energy changes (E_{elec} + ΔG , Hartree), complexation energies (ΔE_C) and reaction free energies ($\Delta \Delta G$), and torsion angles (C1-O-C2-C3 angle) of studied compounds in the gas phase and in DMSO, $\varepsilon = 46.826$, calculated at B3LYP/6-31G(d,p)/LANL2DZ level.

Stable complexes are characterized by negative complexation energies in gas phase

and in DMSO. Most stable complexes are formed by **6** in both media. The negative ΔG values calculated in DMSO reveal that the complex formation is easier in solution than the gas phase. Dipole moment values of all studied systems increased in DMSO.

Table 2. Calculated dipole moments (μ , Debye), total electronic energies including zero point energies (E_{elec} +ZPE, Hartree), total electronic energies including free energy changes (E_{elec} + ΔG , Hartree), complexation energies (ΔE_C), reaction free energies ($\Delta \Delta G$) and C1-O-C2-C3 tortion angles of studied compounds in gas phase and in DMSO, $\varepsilon = 46.826$, at B3LYP/6-31G(d,p) level; LANL2DZ level applied for metals.

| | μ | E _{elec} +ZPE | $E_{elec} + \Delta G$ | $^{a}\Delta E_{C}$ | ^b ΔΔG | G1 0 G2 G2(|
|----------------------------|-------|------------------------|-----------------------|--------------------|------------------|-------------|
| | (D) | (Hartree) | (Hartree) | (kcal/mol) | (kcal/mol) | 01-0-02-03 |
| in gas phase | | | | | | |
| 3 | 7.70 | -1911.169532 | -1911.245391 | | | |
| Co(OAc) ₂ ·4H2O | 2.14 | -907.701535 | -907.751966 | | | |
| Zn(OAc) ₂ ·2H2O | 0.05 | -675.386379 | -675.434950 | | | |
| Ni(OAc) ₂ ·4H2O | 4.04 | -931.911687 | -931.960757 | | | |
| (OAc) ⁻ | 3.18 | -228.454099 | -228.481596 | | | |
| H ₂ O | 2.04 | -76.398374 | -76.416031 | | | |
| 4 | 3.71 | -3967.632345 | -3967.741364 | -58.63 | -79.02 | -50.99 |
| 5 | 3.53 | -3888.110010 | -3888.220255 | -56.17 | -56.34 | -51.70 |
| 6 | 3.78 | -3991.856781 | -3991.964739 | -67.60 | -88.18 | -51.29 |
| in DMSO | | | | | | |
| 3 | 18.17 | -1911.192207 | -1911.271056 | | | |
| Co(OAc) ₂ ·4H2O | 4.07 | -907.720138 | -907.771607 | | | |
| Zn(OAc) ₂ ·2H2O | 0.11 | -675.412168 | -675.462058 | | | |
| Ni(OAc) ₂ ·4H2O | 7.34 | -931.932668 | -931.981772 | | | |
| (OAc) ⁻ | 4.28 | -228.556791 | -228.582684 | | | |
| H ₂ O | 2.26 | -76.405319 | -76.422981 | | | |
| 4 | 5.12 | -3967.657138 | -3967.763951 | -180.37 | -192.97 | -49.96 |
| 5 | 5.68 | 3888.143703 | -3888.252852 | -170.27 | -163.16 | -51.03 |
| 6 | 5.16 | -3991.877649 | -3991.986088 | -185.38 | -200.49 | -51.54 |

Electronic structure calculations were performed at B3LYP/6-31G(d,p) level (LANL2DZ basis set for metals) in ground state by using TDDFT. The electronic transitions were calculated at B3LYP/6-31G(d,p) and CAM-B3LYP/6-31G(d,p) levels (LANL2DZ for metals) to choose the most appropriate level for comparing with the experimental results. Calculated and experimental UV-Vis absorption spectra of compound **5** in DMSO compared in Fig. S7. As seen fron the figure, B3LYP/6-31G(d,p) results fit better to experimental data and the discussion in the text is based on these results. Similar comparisons carried out for compounds **4** and **6** gave identical results.

Electron affinity and ionization potential are in correlation with lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), respectively. Fig. 7 displays the HOMO-LUMO transition energies for the complexes in DMSO. HOMO-LUMO levels and energy gaps, ΔE_{H-L} values are listed for comparison. Because of the d⁷ electronic configuration of doublet Co(II), single occupied molecular orbital (SOMO) was shown for compound **4**.

HOMO and LUMO energies of all investigated molecules have negative values in DMSO. Lower energy gaps enable intramolecular charge transfer much more easily by supporting intramolecular charge transfer interactions. Conjugated rings of MPcs of compound **5** host HOMO and LUMO in DMSO. While HOMOs of compound **4** (SOMO) and **6** located in Pc based orbital, LUMOs of those located Pc and central metal orbitals.

HOMO-LUMO energy gap of **5** is smaller (2.12 eV) than that of **4** and **6** in DMSO (2.15 and 2.13 eV) at B3LYP/6-31G(d,p)/LANL2DZ level in DMSO. SOMO-LUMO energy gap for **4** has the highest value as 2.15 eV at the same level in DMSO.

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Figure 7. Frontier molecular orbitals, orbital energies and HOMO-LUMO energy differences for investigated complexes calculated at at B3LYP/6-31G(d,p) level with LANL2DZ on metal in DMSO

Optimized ground state geometries were used to calculate the absorption wavelengths and excitation energies of all studied systems from S_0 to S_{100} states using TD-DFT at B3LYP/6-31G(d,p)/LANL2DZ level. Selected electronic transitions are listed in supplementary information using the related occupied and unoccupied molecular orbitals in DMSO (Table S1-S3).

Pc group in **5** has $S_0 \rightarrow S_1$ transition at 685 nm in DMSO and it has $\pi \rightarrow \pi^*$ character (LE, local excitation of Pc) between HOMO and LUMO (Q-band for Pc). Compound **6** shows LMCT (ligand-metal charge transfer) and LE at this wavelength transition (684 nm) between HOMO and LUMO (Fig. S7). While compound **4** has also LMCT (ligand to metal charge transfer) and LE at 674 nm between SOMO and LUMO, it has shorter wavelength than others

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(Table S1). Thus, **5** and **6**, able to make a charge transfer much easier, is more suitable than **4** for charge transfer systems.

Fig. 8 shows experimental UV-Vis absorption spectra of compounds **4**, **5** and **6** in DMSO. Maximum wavelengths in long wavelength region (Q-bands) are at 683 nm, 682 nm and 678 nm for compounds **4**, **5** and **6**, respectively. The experimental UV-Vis data also show a shoulder in this area at 605 nm, 636 nm and 625 nm, respectively. A comparison of experimental and calculated UV-Vis absorption spectra of compound **5** and **6** in DMSO is given in Fig. 9 and Fig. S8, respectively. As seen from the figure, $S_0 \rightarrow S_1$ transition has local excited Pc same as experimental. Electronic transitions at this region belong to the Pc based orbitals for other studied systems, too. At wavelengths shorter than 500 nm, intramolecular charge transfer from both phenly rings to Pc orbitals (ICT2) were observed. At much shorter wavelengths, metal-ligand charge transfers (MLCT) appears for compounds **5** (at 347 nm) and **6** (at 365 nm) (Table S2 ve Table S3). Additionally, ligand-metal charge transfer (LMCT) transitions were observed for compounds **4** and **6** in which metal based orbitals contribute to the transitions. A charge transfer character from middle phenyl ring to Pc (ICT3) was observed at 372 nm, 371 nm and 377 nm for compound **4**, **5** and **6**, respectively.



Figure 8. Measured UV-Vis absorption spectra of compound 4, 5 and 6 in DMSO.



Figure 9. Calculated and experimental $(1.98 \times 10^{-5} \text{ M})$ normalized UV-Vis absorption spectra of compound **5** in DMSO.

Fig. 10 shows the total electron densities for the investigated systems in DMSO. Electrostatic potential surface is used to map total electron densities. The colors represents the quantity of the electron density: red, electron rich, partially negative charge; yellow, slightly electron rich region; green, neutral; light blue, slightly electron deficient; blue, electron deficient, partially positive charge. The electron density was calculated using the Mulliken charge distribution. The upper and lower ranges of the total electron densitie values for the used colors are also given in Figure. In **5**, the positive electrostatic potential (blue area) is localized around Zn atom in the middle ring. Phenyl rings are nearly neutral. Oxygens between phenyl and Pc, and nitrogens on Pc have negative charges for compound **4** and **6**. Compound **5** shows nearly a neutral behavior except Zn atom. This observation may reveal why there is only ICT transition (π - π * and n- π * transitions) in compound **5** and metal based orbitals do not contribute to the electronic transitions.



Figure 10. Molecular electrostatic potential values for total electron density surfaces for investigated molecules in DMSO.

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Conclusions

In this study, we synthesized new Co(II), Zn(II) and Ni(II) phthalocyanine compounds with Bis [2- (4-hydroxyphenyl)-2-propyl] benzene. Their structural and electronic properties have been studied in details by experimental techniques, such as CHN elemental analysis, UV-Vis, FT-IR, ¹H-NMR, and MALDI-TOF mass spectroscopy, and also by DFT and TD-DFT methods in both gas phase and in DMSO solution. The calculated data and the experimental results are in good agreement. DC conductivity measurements revealed that as $\sigma_{(6)} < \sigma_{(4)} < \sigma_{(5)}$ at room temperature in vacuum in dark. It was observed that dc conductivity values increased with increasing temperature indicating semiconducting property. Activation energy values of the 4, 5, and 6 took placed between 0.76 - 0.77 eV in intrinsic region. AC conductivity results suggest that dominant charge transport mechanisms can be modeled by single hopping and multi-hopping model depending on temperature and frequency range. Nyquist plot showed that bulk resistance decreased with increasing temperature indicating semiconducting property as in the case of dc measurements. From impedance spectra, Cole-Cole plots, the relaxation time in Debye dispersion relation is considered as a distribution of relaxation time values, rather than as a single relaxation time. $(-X(\omega) - f)$ plots for 4 - 6 also supports this result. Compound 5 has the smallest calculated HOMO-LUMO gap. This result supports the conclusion that 5 has the best semiconducting property among all studied systems.

Experimental

Materials

Reagent grade quality reagents and solvents were used throughout all the measurements. Commercial 1,3-Bis[2-(4-hydroxyphenyl)-2-propyl]benzene (1) and 4-nitrophthalonitrile (2) were used as received. All reactions were carried out under a

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dinitrogen atmosphere. Microanalyses were performed using a CHNS-932 (LECO) Elemental Analyzer. The ¹H-NMR spectra were recorded on an Agilent-NMR-vnmrs 600 spectrometer or VARIAN-INNOVA-400 MHz. Chemical shift values for ¹H-NMR were referenced relative to Si(CH₃)₄. The UV-Vis spectra were recorded on a Perkin-Elmer lambda 35 spectrophotometer, with 1 cm quartz cuvettes at room temperature. The IR spectra were obtained as KBR pellets on a Perkin Elmer Spectrum FT-IR Spectrophotometer. Mass spectra were obtained on a Voyager-DETM PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) with a nitrogen UV-Laser operating at 337 nm, with an average of 100 shots in both positive and negative mode in both linear and reflex modes. MALDI matrix, 2,5-dihydroxybenzoic acid was prepared in H₂O-ACN (1:1, v/v) containing 0.1% trifluoroacetic acid at a concentration of 10 mg/mL. The MALDI sample was dissolved in Eppendorf® microtube (2 mg / mL with 0.1% trifluoroacetic acid in H2O-ACN mix (1: 1, v/v) with matrix solution (1:10, v/v) at 0.5 mL), 1.0 µL of this mixture was dried at room temperature on the sample plate and then analyzed.

Synthesis

Synthesis of 4,4'-bis[1,3-propylbenzene-2-p-phenoxy]phthalonitrile (3)

The anhydrous K₂CO₃ (2.0 g, 15.0 mmol) which was dried at 105 °C in the oven added to the solution of Compound **1** (0.694 g, 2.0 mmol) and 4-nitrophthalonitrile **2** (0.866 g, 5.0 mmol) in acetonitrile (25 ml). This solution was refluxed at 90 °C for 72 h under dry N₂ atmosphere. The solution was cooled to room temperature and washed with petroleum ether before filtration to remove K₂CO₃. The obtained solution was finally precipitated by addition of hexane to remove unreacted reagents and also impurities. The precipitate was washed with hexane and petroleum ether. It is readily soluble in polar solvents. Yield: 1.01 g (84.44%). Mp. 114 °C; Anal. Calculated for C₄₀H₃₀N₄O₂: C, 80.26; H, 5.02; N, 9.37%, found C, 79.95; H, 4.85; N, 8.95 %. ¹H NMR (400 MHz in the acetone) δ 8.01 (d, *J* = 8.8 Hz, 2H), δ 7.99 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 2.54 Hz, 1H), δ 7.50 (d, J = 8.8 Hz, 2H) 7.35 (d, J = 8.8 Hz, 4H), 7.33 (d, J = 12.5 Hz, 4H), 7.10 (s, 1H), 7.09 (d, J = 8.89 Hz, 2H), 1.67 (s, 12H). IR (KBr): $v_{\text{max}}/\text{cm}^{-1}$, 3112, 3087 (Alifatic-CH), 2242 (Ar-C=N), 1610, 1587, 1536, 1480 (Ar-Ring) (Ar-C=C), 1325, 1298, 1076 (Ar-C-N). MALDI-TOF MS: m/z 621.23 [M + Na]⁺.

Synthesis of 3,9,17,23-bis[1,3-propylbenzene-2-p-phenoxy]phthalocyaninato Co(II)] (4)

A mixture of **3** (0.30 g, 0.50 mmol) and Co(AcO)₂·4H₂O (0.12 g, 0.5 mmol) were dissolved in DMF under dry N₂ atmosphere, in a sealed glass tube. Then this was heated for 24 h at 155 °C. After cooling the mixture to room temperature, the green-dark product was obtained and purified by washing with plenty of hot DMF, THF, ethyl acetate, chloroform, ether, ethanol and water. Finally, it was dried in a vacuum oven at 105 °C. This compound is soluble in hot DMSO. Yield: 0.42 g (66.72%). Mp. 316 °C. Anal. Calculated for C₈₀H₆₀N₈O₄Co: C, 76.25; H, 4.77; N, 8.90%, found C, 75.95; H, 4.45; N, 8.59%. UV-Vis (DMSO): λ_{max} /nm (log ε): 467 (4.10), 603 (2.90), 683 (4.10). IR (KBr, ν_{max} /cm⁻¹): 2971 (Alifatic-CH) (Ar-CH), 1715, 1594, 1503, 1475 (Ar-C=N) (Ar-C=C), 1407 (Ar C-N), 1232, 1172 (Ar-C=N), 1075, 1045 (Ar C-N). MALDI-TOF MS: *m/z* 1297 [M + K]⁺.

Synthesis of 3,9,17,23-bis[1,3-propylbenzene-2-p-phenoxy]phthalocyaninato Zn(II) (5)

The synthesis of this compound was carried out with the same protocol used for **4**; the only exception was the of $Zn(AcO)_2 \cdot 2H_2O$ (0.09 g, 0.50 mmol) instead.

A mixture of **3** (0.30 g, 0.50 mmol) and $Zn(AcO)_2 \cdot 2H_2O$ (0.09 g, 0.50 mmol) was dissolved in DMF under dry N₂ atmosphere, in a sealed glass tube. Then this was heated for 24 h at 155 °C. After the mixture was cooled to room temperature, the green-dark product was obtained and purified by washing with plenty of hot DMF, THF, ethyl acetate, chloroform, ether, ethanol and water. Finally, it was dried in a vacuum oven at 105 °C. This

compound is soluble in hot DMSO. Yield: 0.38 g (60.13 %). Mp. 304 °C. Anal. Calculated for C₈₀H₆₀N₈O₄Zn: C, 74.77; H, 4.75; N, 8.86 %, found C, 74.89 ; H, 4.60; N, 9.10%. ¹H NMR (600 MHz in the DMSO): δ 7.78-6.97 (m), δ 1.63 (s). UV-Vis (DMSO): λ_{max}/nm (log ε): 347 (4.27), 634 (4.08), 682 (4.30). IR (KBr, v_{max}/cm^{-1}): 2971 (Alifatic-CH) (Ar-CH), 1599, 1469 (Ar-C=N) (Ar-C=C), 1393 (Ar C-N), 1228, 1171 (Ar-C=N), 1078, 1043 (Ar C-N). MALDI-TOF MS: m/z 1305 [M + K]⁺

Synthesis of 3,9,17,23-bis[1,3-propylbenzene-2-p-phenoxy]phthalocyaninato Ni(II)] (6)

This compound also was synthesized with the protocol developed for **4**; this time the exception was the use of Ni(AcO)₂·4H₂O (0.12 g, 0.5 mmol). The obtained green-dark mixture was washed successively with hot DMF, THF, ethyl acetate, chloroform, ethanol, water and ether. Finally, it was dried in a vacuum oven at 105 °C. This compound dissolves in hot DMSO. Yield: 0.41 g (65.18 %). Mp. 284 °C. Anal. Calculated for C₈₀H₆₀N₈O₄Ni: C, 76.31; H, 4.77; N, 8.90%, found C, 76.44; H, 5.04; N, 9.15%. UV-Vis (DMSO): λ_{max}/nm (log ε): 458 (3.32), 625 (3.49), 678 (2.57). IR (KBr, ν_{max}/cm^{-1}): 2971 (Alifatic-CH) (Ar-CH), 1715, 1594, 1503, 1475 (Ar-C=N) (Ar-C=C), 1407 (Ar C-N), 1232, 1172 (Ar-C=N), 1075, 1045 (Ar C-N). MALDI-TOF MS: m/z 1297 [M + K]⁺.

Preparation of Films for Electrical Measurements

Electrical measurements were performed using Interdigital Transducer (IDT) containing 21 gold electrodes with width of the electrodes is 100 μ m fabricated in our laboratory onto glass substrate. The compounds were dissolved in DMSO (Dimethyl Sulfoxide, C₂H₆OS) purchased from Merck, homogeneously at a concentration of 4x10⁻² M at room temperature. To prepare same films, 20 μ l of 4x10⁻² M solutions of the compounds were dispersively were dispersively.

evaporated at 323 K and thin films were obtained. The repeatability of the fabrication of the films was tested by examining dc and ac conductivity values at different temperatures. The values were changed by amount of 2-4% in six months.

Electrical Measurements

In order to clarify electrical properties, impedance spectra and dc and ac conductivity measurements were made on the films of **4**, **5**, and **6** between the temperatures 293 - 523 K and frequencies 40-100 kHz. Temperature of the substrate of the films was monitored by a chromel-alumel thermocouple. The measurements were done in vacuum (2x10⁻³ mbar) and in dark to avoid effects of atmospheric gases and photons on conductivity of the films, respectively. Sweep voltages from -1 to 1 V were applied to the terminals of the IDT and corresponding current values were recorded. DC and ac conductivity and IS measurements were done by using Keithley model 6417B programmable electrometer and Keithley model 3330 LCZ meter, respectively. Before performing the conductivity and IS measurements the current values of the films were allowed to reach stable state at each temperatures. All the electrical measurement system was computerized and equipped by IEEE-488.

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