

# Synthesis, Aggregation Behavior, and Electronic Properties of some Metallophthalocyanines with 2-Isopropyl-5-methylphenoxy Substituents

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**Abstract.** The aim of this study was to perform facile synthesis of novel phthalocyanines with high solubility. The synthesis and characterization of 2-isopropyl-5-methylphenoxy substituted copper, zinc, nickel, and cobalt phthalocyanines are reported. The compounds were characterized by using electronic absorption, nuclear magnetic resonance spectroscopy, infrared and elemental analysis. The aggregation investigations carried out in different concentrations indicate that 2-

isopropyl-5-methylphenoxy substituted phthalocyanine complexes do not have any aggregation behavior for the concentration range of  $1 \times 10^{-5}$  to  $1 \times 10^{-6}$  M in THF. Additionally, the ground-state geometries of the complexes were optimized using density functional theory methods at B3LYP/6-31G (d, p) level in order to obtain information about the 3D geometries and electronic structure.

## **1** Introduction

Phthalocyanines (Pcs) exhibit salient properties like intense brightness, high thermal, chemical stability, and high efficiency in electron transfer.<sup>[1,2]</sup> The applicability of these compounds has been investigated in different areas, in therapeutic medicine, in photodynamic therapy and antioxidant,<sup>[3]</sup> in materials science, including nonlinear optics,<sup>[4,5]</sup> liquid crystals,<sup>[6,7]</sup> semiconductors,<sup>[8]</sup> solar cells,<sup>[9]</sup> chemical sensor,<sup>[10]</sup> ink-jet printing,<sup>[11]</sup> Langmuir-Blodgett films,<sup>[12]</sup> optical read-write discs,<sup>[13]</sup> and catalysis.<sup>[14]</sup> Similar to other tetrapyrrolic macrocycles, phthalocyanines in water have a strong tendency for aggregate to form dimer and high order oligomers, induced by the tendency of the hydrophobic skeleton to avoid the contact with water.<sup>[15]</sup> Aggregation decreases photosensitizing efficacy.<sup>[16]</sup> Such a widespread diversity of possible applications is due to high stability of many phthalocyanine and a possibility of tailoring their properties by modification of central atoms and appropriate substitution with peripheral groups.[17,18]

In this study, the synthesis and characterization of phthalocyanines bearing 2-isopropyl-5-methylphenoxy substituents on the peripheral positions are described. This designed combination for the synthesis may improve the solubility of the systems in organic solvents such as DMF, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and DMSO, and add interesting chemical, biological, and electronic properties.

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## **2** Experimental Section

#### 2.1 General

ZnCl<sub>2</sub>, CuCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, CHCl<sub>3</sub>, THF, DMSO, and DBU were purchased from Merck. The solvents were purified according to standard procedure<sup>[19]</sup> and stored over molecular sieves (4 Å). All reactions were carried out in a dry nitrogen atmosphere. Melting points were measured with an electrothermal apparatus. Electronic spectra were recorded with a Hitachi U-2900 Spectrophotometer (Van YYU, Central Laboratory, Turkey). Routine FT-IR spectra were recorded with a Thermo Scientific FT-IR (ATR sampling accessory) spectrophotometer (Van YYU, Central Laboratory, Turkey). <sup>1</sup>H NMR spectra were recorded with a Bruker 300 MHz spectrometer (Malatya IBTAM, Central Laboratory, Turkey) with tetramethylsilane as internal standard.

#### 2.2 Synthesis of 4-(2-Isopropyl-5-methylphenoxy)phthalonitrile (3)

A mixture of thymol (5-methyl-2-isopropylphenol) (2) (0.7511 g, 5 mmol) and 4-nitrophthalonitrile (1) (0.865 g, 5 mmol) in dimethylformamide (25 mL, DMF) was stirred at room temperature in a nitrogen atmosphere. After stirring for 15 min, K<sub>2</sub>CO<sub>3</sub> (2.2 g, 16 mmol) was added into the mixture over a period of 2 h. The reaction mixture was further stirred for 24 h, and poured into cold water (200 mL) and stirred. The precipitate was filtered off, washed with water to neutralize it, and dried. The residue was recrystallized from ethanol. The product is soluble in ethyl acetate, acetonitrile, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, DMF, and DMSO. Yield 0.838 g (63%). Mp: 116 °C. C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O: calcd. C 78.24; H 5.84; N 10.14%; found C 78.17; H 5.86; N 10.19%. <sup>1</sup>**H NMR** (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 8.08, 7.74, 7.37, 7.25, 7.14, 6.90 (m, Ar-H), 4.36, 3.34, 2.95, 2.94, 2.51, 2.28, 1.21, 1.12, 1.06 (CH<sub>3</sub>) ppm. **FT-IR**  $\tilde{v}$  = 3086 (Ar–CH), 2970 (CH<sub>3</sub>), 2225 (CN), 1593, 1563, 1481, 1458, 1246, 1195, 1165, 1083, 1060, 960 cm<sup>-1</sup>.

#### 2.3 Synthesis of 2,10,16,24-Tetrakis(2-isopropyl-5-methylphenoxy phthalocyaninato) Copper(II) (4)

A mixture of 4-(2-isopropyl-5-methylphenoxy) phthalonitrile (3) (0.100 g, 0.36 mmol) and CuCl<sub>2</sub> (0.020 g) was powdered in a quartz

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crucible and heated in a sealed glass tube for 8 min in a nitrogen atmosphere at 200 °C. After cooling to room temperature, the product was washed with cold, hot ethanol and *n*-hexane, and filtered. The product was dissolved in THF to remove impurities. Afterwards, THF was evaporated to dryness to obtain final product. The product is soluble in DMF, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and DMSO. The yield was 0.038 g (36%). C<sub>72</sub>H<sub>64</sub>CuN<sub>8</sub>O<sub>4</sub>: calcd. C 73.98; H 5.52; N 9.59%; found: C 73.87; H 5.55; N 9.51%. **UV/Vis** (THF)  $\lambda$ max (log  $\varepsilon$ ) = 676(5.32), 608(4.77), 344(5.05). **FT-IR**  $\tilde{v}$  = 3080 (Ar–CH), 2958, 2870 (CH<sub>3</sub>), 1612, 1573, 1504, 1465, 1246, 1222, 1091, 1053, 956, 813, 744 cm<sup>-1</sup>.

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## 2.4 Synthesis of 2,10,16,24-Tetrakis(2-isopropyl-5-methylphenoxy phthalocyaninato) Zinc(II) (5)

The procedure was similar to the synthesis of compound **4** from **3**, except using ZnCl<sub>2</sub> and 7 min reaction time. The product is soluble in DMF, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and DMSO. The yield was 0.041 g (39%).C<sub>72</sub>H<sub>64</sub>N<sub>8</sub>O<sub>4</sub>Zn: calcd. C 73.87; H 5.51; N 9.57%; found: C 73.91; H 5.49; N 9.60%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 8.34; 7.55; 7.32; 6.87–6.66 (A–Hr); 3.36(CH); 2.39; 1.38–1.13 (CH<sub>3</sub>) ppm. UV/Vis (THF)  $\lambda$ max (log  $\varepsilon$ ) = 676 (5.32), 610 (4.76) 350 (5.08). FT-IR  $\tilde{v}$  = 3086 (Ar–CH), 2962, 2916, 2870 (CH<sub>3</sub>), 1608, 1573, 1504, 1261, 1215, 1087, 1041, 956, 806, 744 cm<sup>-1</sup>.

## 2.5 Synthesis of 2,10,16,24-Tetrakis(2-isopropyl-5-methylphenoxy phthalocyaninato) Nickel(II) (6)

The procedure was similar to the synthesis of compound **4** from **3**, except using NiCl<sub>2</sub>. The product is soluble in DMF, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and DMSO. The yield was 0.035 g (33%).C<sub>72</sub>H<sub>64</sub>N<sub>8</sub>NiO<sub>4</sub>: calcd. C 74.29; H 5.54; N 9.63%; found: C 74.18; H 5.67; N 9.55%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 8.07–6.91 (A–Hr), 3.34 (CH<sub>3</sub>); 2.94 (CH<sub>3</sub>); 1.21 (CH<sub>3</sub>); 1.12 (CH<sub>3</sub>) ppm. UV/Vis (THF)  $\lambda$ max (log  $\varepsilon$ ) = 672 (5.33), 606 (4.82), 330 (4.95). FT-IR  $\tilde{v}$  = 3070 (Ar–CH), 2962, 2924 (CH<sub>3</sub>), 1612, 1573, 1535, 1469, 1408, 1249, 1222, 1091, 1056, 960, 813, 748 cm<sup>-1</sup>.

#### 2.6 Synthesis of 2,10,16,24-Tetrakis(2-isopropyl-5-methylphenoxy phthalocyaninato) Cobalt(II) (7)

The procedure was similar to the synthesis of compound **4** from **3**, except using CoCl<sub>2</sub> and 7 min reaction time. The product is soluble in DMF, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and DMSO. The yield was 0.037 g (35%).  $C_{72}H_{64}CoN_8O_4$ : calcd. C 74.28; H 5.54; N 9.62%; found: C 74.13; H 5.61; N 9.72%. **UV/Vis** (THF)  $\lambda$ max (log  $\epsilon$ ) = 664(5.29), 602(4.79), 328(5.20). **FT-IR**  $\tilde{v}$  = 3095 (Ar–CH), 2958, 2927, 2866 (CH<sub>3</sub>), 1612, 1573, 1523, 1469, 1246, 1222, 1091, 1056, 960, 748 cm<sup>-1</sup>.

#### 2.7 Computational Method

Three-dimensional structures of the compounds were obtained by geometry optimization using density functional theory at B3LYP/6-31G(d,p) level with no symmetry restrictions. Gaussian 09 and Spartan14 package programs were used to perform all computational calculations.<sup>[20,21]</sup> The frequency analysis for each metal phthalocyanine did not yield any imaginary frequencies, indicating that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. The normal mode analysis was performed for 3N-6 vibrational degrees of freedom, N being the number of atoms forming the phthalocyanine molecule. The time-dependent density functional theory (TD-DFT) calculation was used to obtain the vertical excitation energies, oscillator strengths (f) and excited state compositions in terms of excitations between the occupied and virtual orbitals for metal complexes.<sup>[22,23]</sup> In this study, the TD-DFT method with the same basis set was performed to obtain absorption wavelengths and the oscillation strength (f) within visible to near-UV region.

## **3 Results and Discussion**

#### 3.1 Synthesis and Characterization

The synthesis route and structures of the 4-(2-isopropyl-5methylphenoxy) phthalonitrile (**3**) and metallophthalocyanines(**4–7**) are shown in Scheme 1. The 4-(2-isopropyl-5-methylphenoxy)phthalonitrile (**3**) was prepared by a base catalyzed nucleophilic aromatic nitro displacement reaction between 5methyl-2-isopropylphenol (**2**) and 4-nitrophthalonitrile (**1**) in the presence of dry  $K_2CO_3$  in dry DMF in a nitrogen atmosphere at room temperature for 1 d. The phthalocyanines (**4–7**) were synthesized by the reaction of the 4-(2-isopropyl-5-methylphenoxy) phthalonitrile (**3**) with CuCl<sub>2</sub>, ZnCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub> in a nitrogen atmosphere. The characterization of the compounds was carried out by the combination of several methods, including elemental analysis, IR, <sup>1</sup>H NMR, and UV/Vis spectra. The structures of the compounds were confirmed by the results of these analyses.



Scheme 1. Route for the synthesis of compounds 3–7.

The structure of compound **3** is confirmed by <sup>1</sup>H NMR for the 4-(2-isopropyl-5-methylphenoxy) phthalonitrile through aromatic ring protons in its respective regions. In the <sup>1</sup>H NMR spectrum of compound **3** in [D<sub>6</sub>]DMSO, aromatic protons appear at 8.08–6.90 (Ar–H), aliphatic protons at 4.36, 3.34, 2.52, and 1.12 (CH<sub>3</sub>). In the <sup>1</sup>H NMR spectrum of compound **5**  within [D<sub>6</sub>]DMSO, aromatic protons appear at 8.34–6.66 (A–Hr) and aliphatic protons at 3.36, 2.51, 2.39, 1.38, and 1.13 (CH<sub>3</sub>) ppm. <sup>1</sup>H NMR measurement of compounds **4** and **7** were excluded due to their paramagnetic properties. In the <sup>1</sup>H NMR spectrum of compound **6** in [D<sub>6</sub>]DMSO, aromatic protons appear at 8.07–6.91 (A–Hr), aliphatic protons at 3.34, 2.94, 2.51, 1.21 and 1.12 (CH<sub>3</sub>) ppm.

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Comparison of the IR spectroscopic data clearly indicated the formation of compound **3** by the appearance of new absorption bands at 3086 (Ar–CH), 2970 (CH<sub>3</sub>), 2225 (CN), 1595–1536 (C=C), 1246 (Ar–O–Ar). After conversion of the phthalonitrile derivative **3** into Pcs **4–7**, the sharp peak for the (CN) vibrations disappeared. The IR spectra of compounds **4–7** displayed aromatic CH peaks at 3070–3095 cm<sup>-1</sup>, aliphatic CH peaks at 2958–2962 cm<sup>-1</sup>, C=C (in phenyl rings) peaks at 1612–1573 cm<sup>-1</sup>, and Ar–O–Ar peaks at 1246– 1261 cm<sup>-1</sup>.

Figure 1 and Figure 2 show representative geometry optimized structure of compound **6** and the Mulliken charge<sup>[24]</sup> distribution in the center of the presented complexes, respectively. The optimization procedure was applied to two possible orientation of the substituents: (a) all methyl substituents up,



(b)

Figure 1. Top and side view of geometry optimized structure for Ni complex 6. (a) Four methyl substituents up. (b) Two methyl and two isopropyl substituents up.



Figure 2. Mulliken charge distribution for present metallocyanines.





Figure 3. Three-dimensional electrostatic potential map for Zn and Ni complexes.



Figure 4. Computed UV/Vis spectra of Zn (5) and Ni (6) complexes.



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orientations possess almost equal stability with the latter having  $0.3 \text{ kJ} \cdot \text{mol}^{-1}$  lower energy. The geometry optimized structures of the complexes **4–7** indicate square-planar arrangement at the parent phthalocyanine moiety at the center; however, the orientation of the peripheral substituents found perpendicular to the main circuit and positioned almost parallel to one another for all cases. Figure 2 shows a representative charge distribution model in the heart of the complexes. The charge distribution depends on the type of the metal. As seen in Figure 2, the formal charge +2 of the central metal atom decreased to the net charge ranging from +1.014 to +0.889, due to charge donation from coordinating nitrogens. All the coordinating donor nitrogen atoms have been calculated to develop negative charges. The coordinating nitrogen atoms are more negative than the connecting nitrogen atoms, which might be a consequence of lack of imino hydrogen atom. Upon coordination to the central metal atom the expected -1 formal charge on these atoms decreased absolutely to -0.688. The three-dimensional electrostatic potential maps for **5** and **6** complexes are given in Figure 3. The positive charge development was indicated by blue and green area, whereas red and yellow area shows the negative charge.





The electronic spectra are the best indication for the phthalocvanine compounds, which show characteristic O band and B bands in UV/Vis spectra. Also, a close investigation of the UV/ Vis spectra of the phthalocyanines 4–7 confirmed the proposed structures. The electronic absorption data of all these phthalocvanines were measured in THF at a concentration of  $1 \times 10^{-5}$  mol·L<sup>-1</sup>. The phthalocyanines showed characteristic absorptions in the Q band region at 676 nm for compound 4, 676 nm for compound 5, 672 nm for compound 6, and 664 nm for 7. These Q band absorptions were attributed to the  $\pi$ - $\pi$ \* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pcs ring and the other visible region at about 344 nm for compound 4, 350 nm for compound 5, 330 nm for compound 6 and 328 nm for compound 7 B band, which represents transition from the deeper  $\pi$  levels to the LUMO, respectively.

Secondly, the structures obtained from geometry optimizations were subjected to TD-DFT calculations at the same basis set (B3LYP/6-31G(d,p)) to predict the electronic spectra of the phthalocyanine compounds. Transition energies and molecular orbital energies and schemes were predicted for singlet state excitations. Molecular orbital energies indicate that transitions from HOMO to LUMO are responsible for the Q band of the experimental spectrum. Calculated UV/Vis spectra and threedimensional HOMO and LUMO molecular orbital schemes for compounds 5 and 6 are shown in Figure 3 and Figure 4, respectively. The absorption bands on the UV/Vis spectra may slightly differ from the experimental data due to the fact that, the computations were performed for isolated molecule, whereas experimental data obtained for the bulk system<sup>[25]</sup> (Figure 4). The carbon and nitrogen atoms of the central periphery contribute both HOMO and LUMO of the complexes with little contributions from the outer atoms (Figure 5).

Aggregation behaviors of compounds **4–7** investigated in THF at different concentrations range are presented in Figure 6, Figure 7, Figure 8, and Figure 9.



Figure 6. Aggregation behavior of phthalocyanine 4.



Figure 7. Aggregation behavior of phthalocyanine 5.



Figure 8. Aggregation behavior of phthalocyanine 6.



Figure 9. Aggregation behavior of phthalocyanine 7.

## 4 Conclusions

This study aimed to develop soluble and non-aggregate phthalocyanines bearing 2-isopropyl-5-methylphenoxy substit-

uents on the peripheral positions. The compounds were characterized by using electronic absorption, IR and NMR spectroscopy, elemental analysis. These compounds are easily soluble in organic solvents such as DMF, THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and DMSO. 2-Isopropyl-5-methylphenoxy groups can be efficient substituents to keep metallophthalocyanines away from aggregation. The computational calculations at B3LYP/6-31G(d,p) level was used to obtain three-dimensional geometries and important electronic data of the present structures. These phthalocynanine compounds can be used in application of sensor electrodes.

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