

Functional chalcone-substituted tetrakis-metallophthalocyanines: Synthesis and spectroscopic characterization

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Volkan Çakır

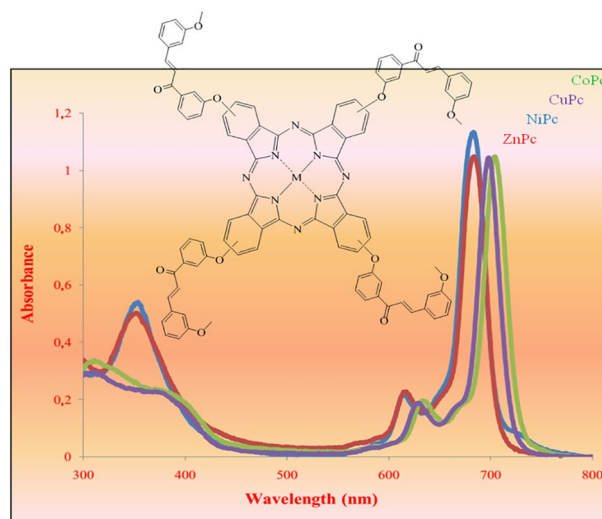
Abstract

In this study, a new phthalonitrile derivative, (*E*)-4-(3-(3-(3-methoxyphenyl)acryloyl)phenoxy)phthalonitrile, and four peripherally (*E*)-4-(3-(3-(3-methoxyphenyl)acryloyl)phenoxy) tetrasubstituted new Ni(II), Zn(II), Co(II), and Cu(II) phthalocyanine derivatives are synthesized and characterized. (*E*)-4-(3-(3-(3-Methoxyphenyl)acryloyl)phenoxy)phthalonitrile is synthesized by heating (*E*)-1-(3-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one and 4-nitrophthalonitrile in the presence of K_2CO_3 in dry DMF at 60°C for 96 h. The metallophthalocyanines are prepared by cyclotetramerization of (*E*)-4-(3-(3-(3-methoxyphenyl)acryloyl)phenoxy)phthalonitrile with $NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, and $CuCl_2$ in *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. Characterization of the new compounds is performed by means of IR, 1H NMR, ^{13}C NMR, and mass and UV-Vis spectroscopy techniques.

Keywords

characterization, cyclotetramerization, metallophthalocyanine, phthalonitrile, synthesis

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Introduction

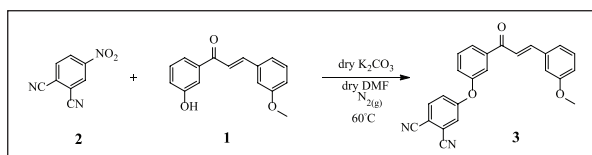
Metallophthalocyanines (MPcs) are useful and versatile types of organic dyes. Their substituted derivatives have been widely used as gas sensors,¹ fuel cells,² photovoltaic cell elements,³ organic light-emitting diodes,⁴ liquid crystals,⁵ nonlinear optics,⁶ electrodes,⁷ electronic devices,⁸ catalysis,⁹ and photosensitizers for photodynamic therapy (PDT) of cancer.^{10–12}

Department of Property Protection and Security, Emergency and Disaster Management Program, Espiye Vocational School, Giresun University, Giresun, Turkey

Corresponding author:

Volkan Çakır, Department of Property Protection and Security, Emergency and Disaster Management Program, Espiye Vocational School, Giresun University, Giresun 28600, Turkey.

Email: volkan.cakir@giresun.edu.tr



Scheme 1. The synthetic route of (*E*)-4-(3-(3-methoxyphenyl)acryloyl)phenoxyphthalonitrile (**3**).

Chalcones can easily be prepared via the Claisen–Schmidt condensation reaction. These compounds are α,β -unsaturated ketones having an enone system among two aromatic rings. They exhibit anticancer activity,¹³ antimicrobial,¹⁴ antibacterial,¹⁵ enzyme inhibition,¹⁶ thermal, fluorescence, and electrochromic properties.^{17–19}

The main problem with unsubstituted phthalocyanine (Pc) is its insolubility and aggregation. In addition, the aggregation and insolubility of Pcs restricts their use in many technological applications. Therefore, scientists have been focused on synthesizing non-aggregated and soluble Pcs. The solubility of phthalocyanines (Pcs) can be improved significantly by increasing the steric interactions in the Pc units having electron-withdrawing ($-F$, $-Cl$, $-Br$, $-NO_2$, etc.), electron-donating ($-NH_2$, $Ar-S-$, $RO-$, etc.), bulky, or long chain groups.²⁰ From this point of view, we initially designed and synthesized new peripherally tetrasubstituted metallophthalocyanine derivatives **3a**, **3b**, **3c**, and **3d** carrying four bulky chalcone moieties. **3a**, **3b**, **3c**, and **3d** complexes are generally soluble in common organic solvents such as chloroform, dichloromethane, dimethyl sulfoxide, dimethyl formamide, and tetrahydrofuran.

Solubility in common organic solvents facilitates the characterization of the new compounds.

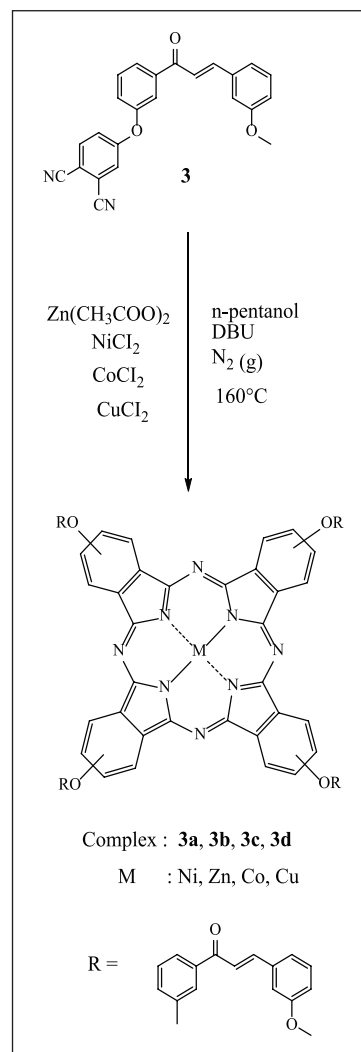
The objective of this research was to prepare and characterize new metallophthalocyanines (**3a**, **3b**, **3c**, and **3d**) containing chalcone moieties by cyclotetramerization of a novel compound **3**. The characterization of all new compounds was carried out by Fourier transform infrared spectroscopy (FTIR), 1H NMR, ^{13}C NMR, mass spectroscopy (MS), and UV-Vis techniques.

Results and discussion

Novel compounds **3**, **3a**, **3b**, **3c**, and **3d** were characterized using IR, NMR, UV-Vis, and mass spectroscopic techniques, and the proposed structures were confirmed from the spectroscopic data.

(*E*)-4-(3-(3-(3-Methoxyphenyl)acryloyl)phenoxy)phthalonitrile (**3**) was synthesized by heating (*E*)-1-(3-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (**1**) and 4-nitrophthalonitrile (**2**) in the presence of K_2CO_3 as a base in dry DMF at $60^\circ C$ for 96 h. The crude product was filtered, washed with water, and dried in vacuo over P_2O_5 . Finally, the product was crystallized from ethanol. The yield and melting point were 0.90 g (72%) and $87^\circ C$ – $88^\circ C$, respectively. The yield of the pure product is high and the melting point range is convenient for purity control. The synthetic route to **3** is summarized in Scheme 1.

According to IR spectral data, a vibration appeared at 2361 cm^{-1} , which belongs to the $C\equiv N$ groups and supported the proposed structures of compound **3** (Figure S1).



Scheme 2. The synthetic route of the metallophthalocyanines **3a**, **3b**, **3c** and **3d**.

In the ^{13}C NMR of **3**, the new peaks at 116.6 and 117.8 ppm belonging to nitrile carbons indicated evidence of the successful substitution (Figure S2). In the 1H NMR spectra of phthalonitrile compound **3**, the OH signal at 9.80 ppm for compound **1** disappeared (Figure S3). Mass spectral analysis of compound **3** confirmed that the target compound had been successfully prepared. The molecular ion $[M + H]^+$ peak was observed m/z at 381 in the mass spectrum of the compound **3** (Figure S4).

Conversion of **3** into the peripherally tetrasubstituted metallophthalocyanine derivatives **3a**, **3b**, **3c**, and **3d** was accomplished through conventional cyclotetramerization reactions in the presence of metal salts ($NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, and $CuCl_2$), with *n*-pentanol as the solvent. Phthalocyanines **3a**, **3b**, **3c**, and **3d** were purified by column chromatography. They were obtained in satisfactory yields (40% for **3a**, 32% for **3b**, 30% for **3c**, and 34% for **3d**). The phthalocyanines **3a**, **3b**, **3c**, and **3d** show good solubility in common organic solvents, for example, dichloromethane, chloroform, and Dimethylformamide (DMF). The obtained pure compounds were characterized by IR, 1H NMR, ^{13}C NMR, MS, and UV-Vis spectral data. The data are consistent with the assigned structures. The preparation of metallophthalocyanines **3a**, **3b**, **3c**, and **3d** is shown in Scheme 2.

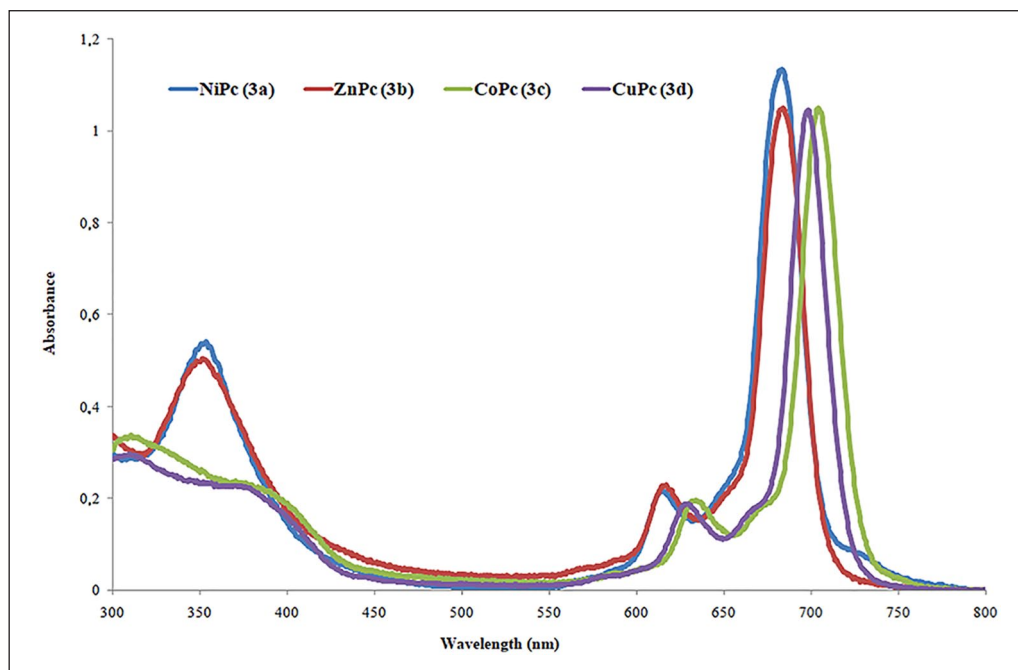


Figure 1. The UV-Vis spectra of nickel(II), zinc(II), cobalt(II), and copper(II) phthalocyanines **3a**, **3b**, **3c**, and **3d** in chloroform at room temperature (1×10^{-5} M).

The IR spectra of metallophthalocyanines **3a**, **3b** (e.g. Figure S5), **3c** and **3d** are very similar. After conversion of the dinitrile derivative **3** into the metallophthalocyanines **3a**, **3b**, **3c**, and **3d**, the sharp peak for the $\text{C}\equiv\text{N}$ vibration around 2361 cm^{-1} disappeared in the IR spectra.

The ^1H NMR spectrum of **3a** demonstrated aromatic protons between at 6.65 and 8.09 ppm as multiplet signals. The methoxy protons occurred at 3.37 ppm. The ^1H NMR spectrum of compound **3b** was almost the same as compound **3a**, except for some minor shifts. NMR measurements of the cobalt(II) and copper(II) phthalocyanines **3c** and **3d** were precluded due to their paramagnetic nature.²¹

UV-Vis spectroscopy is one of the best spectroscopic techniques for determination of the formation of phthalocyanines. Generally, two absorption bands are observed for phthalocyanine compounds in their electronic absorption spectra. One of them is observed at around 600–750 nm due to the $\pi\text{-}\pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring and is known as Q. The other is observed in the ultraviolet region of the spectrum at around 300–450 nm, arising from deeper π levels/LUMO, and is known as the B or Soret band.²² The ground state electronic absorption spectra of metallophthalocyanines **3a**, **3b**, **3c**, and **3d** in chloroform at room temperature show intense Q absorptions at $\lambda_{\text{max}} = 681, 682, 703$, and 697 nm , with weaker absorptions at $\lambda_{\text{max}} = 612, 614, 630$, and 626 nm , respectively. The single Q bands in metallophthalocyanine complexes **3a**, **3b**, **3c**, and **3d** are characteristic. The B band absorptions of compounds **3a**, **3b**, **3c**, and **3d** were observed at $\lambda_{\text{max}} = 350, 347, 384$, and 306 nm , respectively (Figure 1). This result is typical of metal complexes of substituted Pcs with D_{4h} symmetry.²³

The mass spectra of compounds **3a**, **3b**, **3c**, and **3d** were obtained using the matrix-assisted laser desorption

ionization-time of flight (MALDI-TOF) method; 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix.^{24,25} In the MALDI-TOF-MS of peripherally tetrasubstituted metallophthalocyanines **3a**, **3b**, **3c**, and **3d**, the molecular ion peaks were observed at $m/z = 1735$ as $[\text{M} + \text{H} + \text{DHB}]^+$ (Figure S6), 1727 as $[\text{M} + \text{DHB}-\text{CH}_3]^+$ (Figure S7), 1734 as $[\text{M} + \text{DHB}]^+$ (Figure S8), and 1739 as $[\text{M} + \text{DHB}]^+$ (Figure S9), respectively. The observation of these peaks clearly indicated the formation of the desired products.

Conclusion

The cyclotetramerization reaction of phthalonitrile derivative **3** resulted in the formation of novel tetrasubstituted Zn(II), Ni(II), Co(II), and Cu(II) phthalocyanines **3a**, **3b**, **3c**, and **3d** bearing four chalcone peripheral groups. The target symmetrical phthalocyanines were separated by column chromatography and characterized by a combination of FTIR, ^1H NMR, ^{13}C NMR, MS, and UV-Vis techniques.

Experimental

(*E*)-1-(3-Hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (**1**)²⁶ and 4-nitrophthalonitrile (**2**)²⁷ were prepared according to the literature. All reagents were of reagent grade quality and were obtained from commercial suppliers. All solvents were purchased from Merck and freshly distilled. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere using a Schlenk system. The IR spectra were determined using a Perkin Elmer 1600 Fourier Transform-Infrared (FTIR-ATR) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer in CDCl_3 , and chemical shifts (δ) are reported in ppm and coupling constants (*J*) are given in hertz (Hz). Mass spectra were

measured on a Bruker Microflex LT MALDI-TOF MS spectrometer. Melting points were measured on a Barnstead electrothermal 9200 series digital apparatus. Electronic spectra in the UV-Vis region were recorded on a Perkin Elmer-Lambda 25 spectrophotometer, using 1 cm path-length cuvettes at room temperature. Figures S1–S9 are supplied as Supplementary Information.

Synthesis of (*E*)-4-(3-(3-(3-methoxyphenyl)acryloyl)phenoxy)phthalonitrile (**3**)

4-Nitrophthalonitrile (**2**) (0.595 g, 3.44 mol) was dissolved in anhydrous DMF (10 mL) under nitrogen and (*E*)-1-(3-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (**1**) (0.875 g, 3.44 mol) was added. After stirring for 30 min, finely ground anhydrous K_2CO_3 (1.425 g, 10.33 mol) was added in portions over 2 h with stirring. The reaction mixture was stirred at 60°C for 96 h under nitrogen. The solution was poured into ice-water (100 mL) and stirred for 2 h. The solid product was filtered, washed with water, and dried in vacuo over P_2O_5 . The product was crystallized from ethanol. Yield: 0.90 g (72%). m.p. = 87°C–88°C. FTIR (KBr, cm^{-1}): 3727, 3708, 3625, 2361 ($C\equiv N$), 2348, 2308, 2158, 2046; 1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8 Hz, 1 H), 7.83 (d, J = 16 Hz, 1 H, B part of AB system), 7.77 (d, J = 8 Hz, 1 H), 7.64 (t, J = 8 Hz, 1 H), 7.50 (d, J = 16 Hz, 1 H, A part of AB system), 7.38–7.24 (m, 5H), 7.16 (s, 1H), 7.01 (s, 1H), 6.98 (s, 1 H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.8 ($C=O$), 161.2, 160.0, 154.1, 145.9, 140.8, 135.8, 135.6, 131.0, 130.0, 126.1, 124.8, 121.8, 121.6, 121.5, 121.2, 120.1, 117.8 ($-CN$), 116.6 ($-CN$), 113.7, 109.4, 55.4 ($-OCH_3$); ESI/MS (m/z): Calculated: 380.10; Found: 381.11 [$M + H$] $^+$.

General procedure for the synthesis of metallophthalocyanines **3a**, **3b**, **3c**, and **3d**

A mixture of compound **3** (150 mg, 0.41 mmol), equivalent amounts of related anhydrous metal salts (compound **3a**, $NiCl_2$ (27 mg, 0.21 mmol), compound **3b**, $Zn(CH_3COO)_2$ (38 mg, 0.21 mmol), compound **3c**, $CoCl_2$ (26 mg, 0.21 mmol) and compound **3d**, $CuCl_2$ (28 mg, 0.21 mmol)), dry *n*-pentanol (5 mL), and 1,8-diazabicyclo(4.5.0) (DBU) (5 drops) was heated to 160°C and stirred for 24 h. The crude products were precipitated by 20 mL of ethanol. After washing with hot ethanol, the products were purified by silica gel column chromatography.

Nickel(II) phthalocyanine (**3a**)

Chloroform/methanol (100:1) as eluent. Yield: 62 mg (40%). m.p. >300°C. FTIR (KBr, cm^{-1}): 3010 (ArH), 2951, 2158, 1577, 1527, 1472, 1255, 1092, 1043, 783. 1H NMR (400 MHz, $CDCl_3$): δ = 8.09–7.70 (m, 12H, ArH), 7.54–7.01 (m, 32H, ArH), 6.65–6.17 (m, 8H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 158.0, 154.1, 145.8, 141.1, 136.1, 129.4, 127.6, 126.4, 122.1, 120.8, 120.1, 119.0, 114.9, 114.6, 56.2; UV-Vis ($CHCl_3$): λ_{max} , nm: 681, 612, 350. MALDI-TOF-MS (m/z): Calculated: 1580.91; Found: 1735.98 [$M + H + DHB$] $^+$.

Zinc(II) phthalocyanine (**3b**)

Chloroform/methanol (100:1) as eluent. Yield: 50 mg (32%). m.p. >300°C. FTIR (KBr, cm^{-1}): 3295 (ArH), 2938, 2166, 1650, 1581, 1474, 1311, 1259, 1091, 952, 785. 1H NMR (400 MHz, $CDCl_3$): δ = 8.07–7.68 (m, 12H, ArH), 7.55–7.05 (m, 32H, ArH), 6.95–6.70 (m, 8H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.7, 159.6, 153.2, 144.0, 140.1, 135.9, 130.2, 128.1, 125.0, 121.2, 119.5, 119.8, 117.6, 114.4, 113.1, 55.3; UV-Vis ($CHCl_3$): λ_{max} , nm: 682, 614, 347. MALDI-TOF-MS (m/z): Calculated: 1587.89; Found: 1727.92 [$M + DHB-CH_3$] $^+$.

Cobalt(II) phthalocyanine (**3c**)

Chloroform/methanol (100:1.5) as eluent. Yield: 48 mg (30%). m.p. >300°C. FTIR (KBr, cm^{-1}): 3063 (ArH), 2360, 2166, 1662, 1577, 1471, 1312, 1255, 1094, 957, 781. UV-Vis ($CHCl_3$): λ_{max} , nm: 703, 630, 384, 306. MALDI-TOF-MS (m/z): Calculated: 1580.59; Found: 1734.65 [$M + DHB$] $^+$.

Copper(II) phthalocyanine (**3d**)

Chloroform/methanol (100:1) as eluent. Yield: 54 mg (34%). m.p. >300°C. FTIR (KBr, cm^{-1}): 3211 (ArH), 2360, 1662, 1576, 1509, 1470, 1313, 1252, 1091, 950, 780. UV-Vis ($CHCl_3$): λ_{max} , nm: 697, 626, 372, 305. MALDI-TOF-MS (m/z): Calculated: 1585.50; Found: 1739.53 [$M + DHB$] $^+$.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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ORCID iD

Volkan Çakır  <https://orcid.org/0000-0002-5817-0817>

Supplemental material

Supplemental material for this article is available online.

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