

SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC PROPERTIES OF PHTHALOCYANINES BEARING UMBELLIFERONE MOIETIES

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Abstract

The preparing and structure determination of new phthalonitrile complex bearing umbelliferone substituent and its phthalocyanine derivatives [M= metal-free, zinc (II), cobalt (II), copper (II)] were made. The structures of these original complexes were characterized by infrared, proton nuclear magnetic resonance, ultraviolet-visible and mass spectroscopic methods.

Keywords: Phthalocyanine; Coumarin; Spectroscopy.

UMBELLIFERON GRUPLARI İÇEREN FTALOSİYANİNLERİN SENTEZİ, KARAKTERİZASYONU ve SPEKTROSKOPİK ÖZELLİKLERİNİN İNCELENMESİ

Özet

Bu çalışmada umbelliferon süstitüe ftalonitril bileşiği ve non-periferal olarak süstitüe metalsiz, çinko (II), kobalt (II), bakır (II) metalli ftalosiyanın türevleri ilk kez sentezlenerek yapıları aydınlatılmıştır. Bu orjinal bileşiklerin yapıları infrared, proton nükleer magnetik rezonans, ultraviyole-görünür bölge ve kütle spektroskopisi gibi spektroskopik metodlardan elde edilen verilerle tayin edilmiştir.

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1. INTRODUCTION

Coumarins (benzopyran-2-one), generates an elite class of inherently happening complexes [1]. Umbelliferone (7-hydroxycoumarin or 7-hydroxychromen-2-one), esculetin and scopoletin are the most widespread coumarins in nature. [2] Different pharmacological activities of coumarins fundamentally depend on the kind of coumarin center which contains antibacterial [3], scavenging of reactive oxygen species (ROS) [4], anti-inflammatory [5], anticoagulant [6], and anticancer activity [7]. In addition the biologic using, the literature includes their applications from the equipment line of vision like additives in nutrition, fragrances, cosmetics, optical brighteners and would diffused fluorescent and laser dyes. [8-10].

Phthalocyanine (Pc) is a highly blue-green colorful aromatic macrocyclic complex [11]. Pcs are widely used as pigments, paints, nonlinear optical matters, liquid crystals, sensitizers, in photochemical effects or photovoltaic cells, and photodynamic reagents for carcinoma treatment [12-14]. Devoted specificity in numerous using of Pcs can be made by changing of the Pc circle or by replaces in the central metal or axial ligands [11, 12].

Lately, we have described on the preparing and structure determination of the various coumarin substituted Pcs [15-17]. In this work, the formation and characterization of original, solvable, Pcs (M = 2H, Zn, Co, Cu) having umbelliferone (7-hydroxycoumarin) moieties are reported.

2. EXPERIMENTAL

2.1. Materials and Equipment

Umbelliferone, zinc (II) acetate, potassium carbonate (K_2CO_3) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were acquired from Sigma-Aldrich. All solvents were dehydrated as explained by reference [19]. 3-Nitrophthalonitrile was obtained by noticed method [20]. The purity of the products was controlled at all state of reactions by TLC (SiO_2). FT-IR, UV-Vis and 1H NMR spectra were saved on a Shimadzu FTIR-8300, Shimadzu UV-2450 and Varian Unity Inova 500 MHz spectrometers, respectively. Mass spectra were made on a Bruker Autoflex III MALDI-TOF spectrometer using 2,5-dihydroxybenzoic acid (DHB, 0.02 g/mL in THF, tetrahydrofuran) as matrix.

2.2. Synthesis

2.2.1. 3-(2-Oxo-2H-chromen-7-yloxy) phthalonitrile (1)

A mixture of umbelliferone (1.00 g, 6.10×10^{-3} mol) and 3-nitrophthalonitrile (1.06 g, 6.10×10^{-3} mol) were mixed in dried dimethylformamide (DMF) (10 mL), and K_2CO_3 (1.70 g, 12.00×10^{-3} mol) was added. The reaction mixture was blended at $50^\circ C$ for 3 days. An iced HCl solution (10%) was added on the mixture. Occurring precipitate was filtered, washed with water to neutrality and dried. The raw products were cleaned by crystallization from ethyl alcohol.

Yield: 1.300 g (73%). M.p.: $229^\circ C$. FT-IR (KBr), $\nu_{max}/(cm^{-1})$: 3066-3028 (Ar-CH), 2225 ($C \equiv N$), 1720 ($C=O$), 1589-1450 ($C=C$), 1245 (Ar-O-C). 1H NMR (d-DMSO, 500 MHz): 7.25 (d, $J=2$ Hz, 1H, Ar-H), 7.80 (d, $J=8$ Hz, 1H, Ar-H), 7.55 (dd, $J=2$ Hz, 8 Hz, 1H, Ar-H), 7.91 (d, $J=2$ Hz, 1H, Ar-H), 7.15 (dd, $J=2$ Hz, 8 Hz, 1H, Ar-H), 8.07 (d, $J=8$ Hz, 1H, Ar-H), 8.13 (d, $J=8$ Hz, 1H, lactone 4-H), 6.45 (d, $j=8$ Hz, 1H, lactone 3-H). UV-VIS (DMF, 1.10^{-5} M) λ (log ϵ) (nm): 307 (3.98). MS (MALDI-TOF); m/z: 288 $[M]^+$, found: 288 $[M]^+$, 289 $[M+1]^+$.

2.2.2. 1,8,15,22-Tetrakis[4-(2-oxo-2H-chromen-7-yloxy)] phthalocyanine (2)

Ligand **1** 0.10 g (0.34×10^{-3} mol) and dry 2-(dimethylamino)ethanol (2 ml) were stirred at reflux temperature for 2 days in a closed glass tube. The green product was precipitated by adding methyl alcohol (2 ml). Obtained crude Pc filtered and cleaned with water, methyl alcohol, acetonitrile, ethyl acetate, acetone, acetic acid, tetrahydrofuran and diethyl ether.

Yield: 0.047g (47%). M.p. $>300^\circ C$. FT-IR (KBr), $\nu_{max}/(cm^{-1})$: 3292 (NH), 3068-2931 (Ar-CH), 1726 ($C=O$), 1602 ($C=C$), 1230 (Ar-O-C). UV-VIS (DMF, 1.10^{-5} M) λ (log ϵ) (nm): 677 (4.36), 630 (4.13), 320 (4.52). MS (MALDI-TOF, DHB as matrix); m/z 1154, found: m/z 1154 $[M]^+$.

2.3. Common preparing method for metallo phthalocyanines (3-5)

Metal salt $[Zn(AcO)_2 \cdot 2H_2O]$ (0.019 g, 0.085×10^{-3} mol), $Co(AcO)_2 \cdot 4H_2O$ (0.021 g, 0.085×10^{-3} mol) or $Cu(AcO)_2$ (0.016 g, 0.085×10^{-3} mol), ligand **1** 0.10 g (0.34×10^{-3} mol) and DBU (10 μL) were mixed in dried hexanol (2 mL). The mixture was blended at reflux temperature for 1 day in a closed glass tube. The green product was precipitated by adding methyl alcohol (2 ml). Obtained crude Pc filtered and cleaned with water, methyl alcohol, acetonitrile, ethyl acetate, acetone,

acetic acid, tetrahydrofuran and diethyl ether.

2.3.1. 1,8,15,22-Tetrakis[4-(2-oxo-2H-chromen-7-yloxy)] phthalocyaninato zinc (II) (3)

Yield: 0.075 g (71%). M.p.>300°C. FT-IR (KBr), $\nu_{\max}/(\text{cm}^{-1})$: 3082-2941 (Ar-CH), 1734 (C=O), 1587 (C=C), 1232 (Ar-O-C). UV-VIS (DMF, 1.10^{-5} M) λ (log ϵ) (nm): 685 (4.85), 316 (4.64). MS (MALDI-TOF, DHB as matrix); m/z 1217, found: m/z, 1217 [M]⁺.

2.3.2. 1,8,15,22-Tetrakis[4-(2-oxo-2H-chromen-7-yloxy)]phthalocyaninato cobalt (II) (4)

Yield: 0.072 g (69%). M.p.>300°C. FT-IR (KBr), $\nu_{\max}/(\text{cm}^{-1})$: 3076-2931 (Ar-CH), 1730 (C=O), 1602 (C=C), 1230 (Ar-O-C). UV-VIS (DMF, 1.10^{-5} M) λ (log ϵ) (nm): 674 (4.42), 319 (4.66). MS (MALDI-TOF, DHB as matrix); m/z 1211, found: m/z 1211 [M]⁺, 1212 [M+1]⁺.

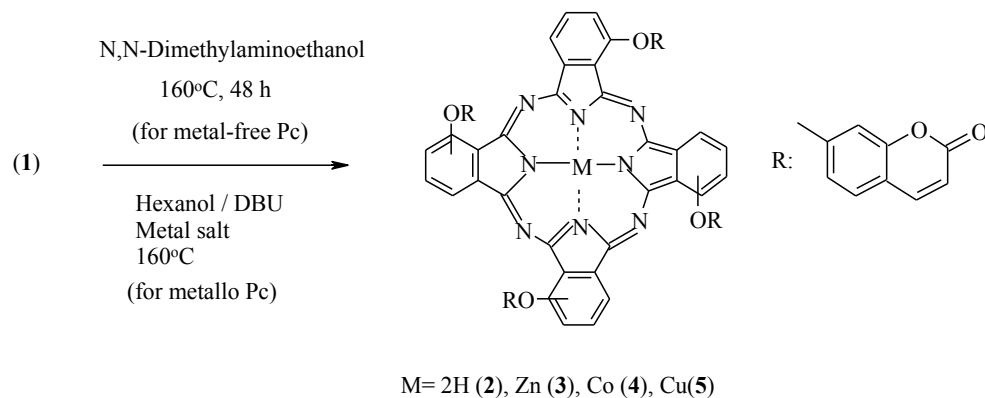
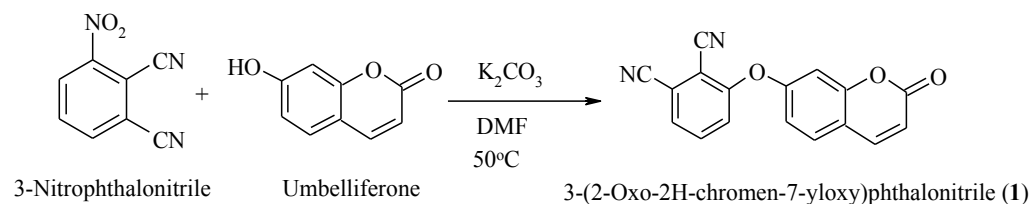
2.3.3. 1,8,15,22-Tetrakis[4-(2-oxo-2H-chromen-7-yloxy)]phthalocyaninato copper (II) (5)

Yield: 0.068 g (64%). M.p.>300°C. FT-IR (KBr), $\nu_{\max}/(\text{cm}^{-1})$: 3070-2958 (Ar-CH), 1730 (C=O), 1605 (C=C), 1232 (Ar-O-C). UV-VIS (DMF, 1.10^{-5} M) λ (log ϵ) (nm): 682 (4.11), 318 (4.35). MS (MALDI-TOF, DHB as matrix); m/z 1216, found: m/z 1216 [M]⁺.

3. RESULTS AND DISCUSSION

Starting from umbelliferone compound, the synthesis pathway of the novel phthalonitrile and Pcs is displayed in Scheme 1. Novel 3-(2-oxo-2H-chromen-7-yloxy) phthalonitrile (**1**) was prepared by a nucleophilic aromatic substitution reaction of 3-nitrophthalonitrile with umbelliferone under basic condition. Metal-free Pc (**2**) was obtained by refluxing of ligand **1** in 2-(dimethylamino)ethanol for 2 days. Zinc, cobalt and copper metallo Pcs (**3-5**) were synthesized by reaction of **1** with metal acetates in hexanol and DBU for 1 day. The non-peripherally tetrasubstituted Pcs were solvable in DMF and DMSO. The crude Pcs purified by washing with various hot solvents (water, methyl alcohol, ethyl alcohol, acetonitrile, ethyl acetate, acetone, acetic acid, tetrahydrofuran and diethyl ether). For characterization of the ligand and Pcs was used infrared, proton nuclear magnetic resonance, ultraviolet-visible and mass spectroscopic

methods.



Scheme 1. Preparing pathways of phthalonitrile (1) and Pc compounds (2-5).

The structure of compound 1 was proved by IR spectral data with the view of absorption bands at $3066\text{-}3028\text{ cm}^{-1}$ (Ar-CH), 2225 cm^{-1} ($\text{C}\equiv\text{N}$), 1720 cm^{-1} (C=O), $1589\text{-}1450\text{ cm}^{-1}$ (C=C) and 1245 cm^{-1} (Ar-O-C) (Figure 1).

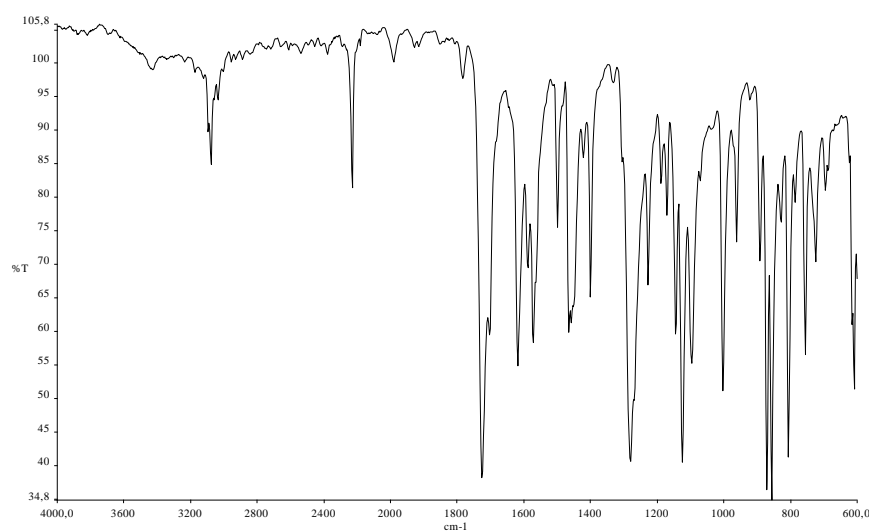


Figure 1. The Infrared spectra of compound 1

The $C\equiv N$ vibration band around 2225 cm^{-1} of **1** was not seen after the formation of Pcs (**2-5**). The IR spectra of the Pc **2** and the metal complexes (**3-5**) were very similar, with the exception of **2** showing NH stretching band. The NH band of the Pc **2** gave a low absorption at 3292 cm^{-1} . In the ^1H NMR analysis of **1** in deuterated DMSO, the protons of carbons 3 and 4 of coumarin lactone ring seen as doublets at δ 6.45 ppm and δ 8.13, respectively. The aromatic protons seen as doublets or double doublets at δ 8.07-7.15 ppm. The mass spectra of dinitrile derivative **1** and Pcs (**2-5**) approved the suggested structures. Molecular ion peaks were recognized at $m/z = 288\text{ [M]}^+$ for **1**. Suggested structure of Pcs (**2-5**) was proved by the mass spectra with the view of molecular ion peaks at $m/z = 1154\text{ [M]}^+$ for **2**, $m/z = 1217\text{ [M]}^+$ for **3** (Figure 2), $m/z = 1211\text{ [M]}^+$ for **4** and $m/z = 1216\text{ [M]}^+$ for **5**.

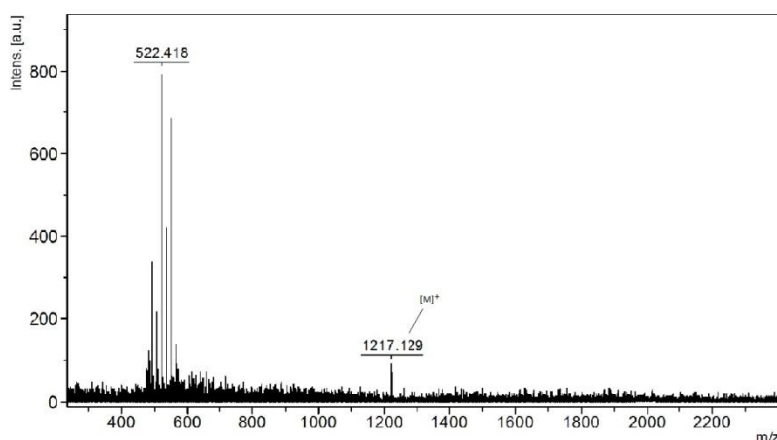


Figure 2. The mass spectra of zinc metallo Pc (**3**)

Pcs show two intense electronic absorption bands in UV-Vis spectroscopy. They have the “Q band” at around 600–750 nm when they show the “B” band (Soret band) at around 300 nm. The Q bands of the metal-free Pcs are noticed as two bands, because of D_{2h} symmetry and the lifting of degeneracy of the LUMO (e_g) level. Because of the D_{4h} symmetry, the metallo Pcs give a single band in the UV-Vis spectroscopy [12, 18]. The absorption spectra of Pcs (**2-5**) in DMF are given in Figure 3. The prepared Pcs displayed monomeric action for indicated by a single (narrow) Q band for **3-5** and divided two bands for **2** in DMF. These results are characteristic for Pc complexes. The characteristic absorption bands (Q) were noticed at 677, 630 nm for **2**, 685 nm for **3**, 674 nm for **4** and 682 nm for **5** in DMF. The Soret bands were seen between 316–320 nm.

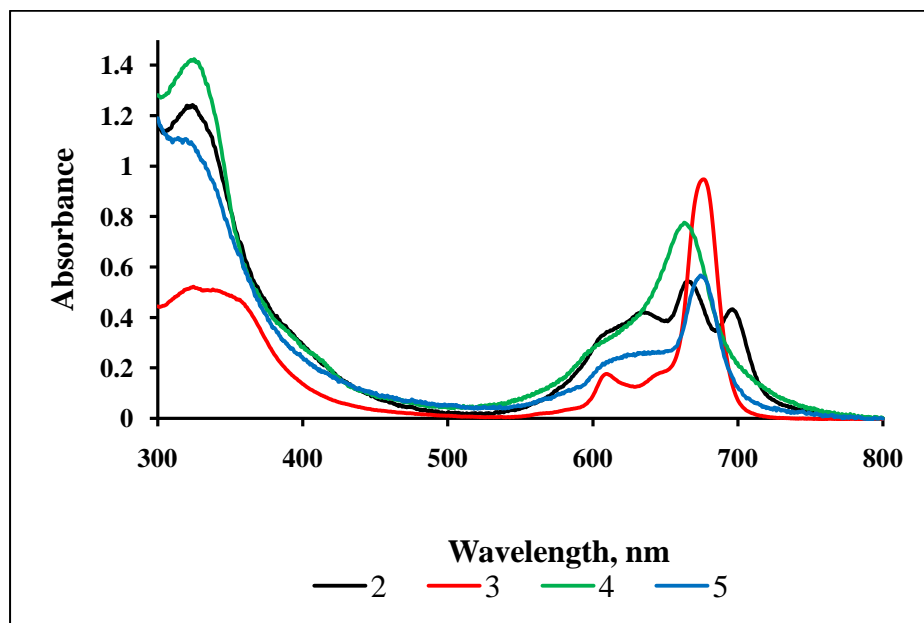


Figure 3. UV-Vis spectra of Pc complexes (2-5) in DMF. Concentration = 1.0×10^{-5} M.

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Symbols and abbreviations

Co: Cobalt

Cu: Copper

DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene

DMF: Dimethylformamide

DHB: 2,5-Dihydroxybenzoic acid

DMSO: Dimethyl sulfoxide

FT-IR: Fourier transform infrared spectroscopy

^1H NMR: Proton nuclear magnetic resonance

LUMO: Lowest unoccupied molecular orbital

MALDI-TOF: Matrix assisted laser desorption ionization time of flight

Pc: Phthalocyanine

ROS: Reactive oxygen species

THF: Tetrahydrofuran

UV-Vis: Ultraviolet Visible

Zn: Zinc

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