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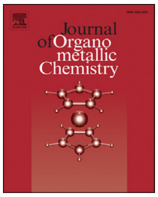

Novel 4-(2-(benzo[*d*]thiazol-2-yl)phenoxy) substituted phthalocyanine derivatives: Synthesis, electrochemical and *in situ* spectroelectrochemical characterization

Asiye Nas [a], Halit Kantekin [a,*], Atıf Koca [b]

[a] *Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey*
[b] *Department of Chemical Engineering, Engineering Faculty, Marmara University, Göztepe, 34722 İstanbul, Turkey*

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ABSTRACT

In this study, the new tetra peripherally 4-(2-(benzo[*d*]thiazol-2-yl)phenoxy)-substituted metal-free (**4**), zinc(II) (**5**), lead(II) (**6**), cobalt(II) (**7**) and copper(II) (**8**) phthalocyanine derivatives, which are organo-soluble, have been synthesized for the first time and their structures characterized by using electronic absorption, infrared spectroscopy, nuclear magnetic resonance spectroscopy, elemental analysis and mass spectra. Voltammetric characterization of the phthalocyanine derivatives (**4**–**7**) was performed with cyclic voltammetry and square wave voltammetry. Cobalt phthalocyanine (**7**) gave metal based electron transfer reactions in addition to the phthalocyanine ring based reduction and oxidation reactions. Although lead phthalocyanine (**6**) illustrated reversible reduction process during the voltammetric measurements, it was de-metallized and thus it turned back to the metal free phthalocyanine during the *in situ* spectroelectrochemical measurements under the applied potentials. Spectroelectrochemical measurements were performed to assign the redox processes and spectroscopic responses of the electrogenerated species.

1. Introduction

Metal complexes of N_4-ligands, such as porphyrins and phthalocyanines, are widely studied due to their numerous physical–chemical properties and the great variety of their applications in many fields [1]. Both series of phthalocyanines and porphyrins (tetrapyrrole macrocyles) are able to form several complexes with almost all the metals in Periodic Table [2] and it is known that at least seventy metal phthalocyanines have been prepared [3] thanks to their ability. Their favorable properties, such as extraordinary thermal and chemical stability, make them suitable as industrial pigments for a couple of decades [4].

Phthalocyanines, which are an important class of compounds use in inks, dyestuff for textiles and colorant for metals and plastics [5], have been used other applications such as liquid crystal displays [6,7], optical applications [8,9], electrochromism [10,11], chemical sensors [12,13], semiconductors for organic field-effect transistors (OFETs) [2,14] and photodynamic therapy [15–17].

Photodynamic therapy (PDT) is a new technique that uses a photosensitizing agent and a particular type of light [18]. Metallophthalocyanines which can be used as photosensitizing agent for photodynamic therapy have received increasing attention since 1985 [19]. This therapy results in a sequence of photochemical and photobiological processes that cause irreversible photo damage to tumor tissues [20].

For all applications mentioned, the solubility of phthalocyanine derivatives plays a consequential role. Metallophthalocyanines are unsoluble in aqueous solvent in the absence of hydrophilic peripheral substituents but dissolve in strongly coordinating solvents like pyridine [21]. The bulky peripheral substitution on phthalocyanine core is used for enhancing the solubility of phthalocyanine derivatives in most common organic solvents; whereas sulfo or quaternary ammonium groups enhance solubility in aqueous media [22].

Thiazoles, which are a class of organic compounds, contain three carbon atoms, one nitrogen atom, and one sulfur atom. Among the pentaatomic heterocyclic rings, thiazole is one of the most intensively investigated. Thiazoles and their derivatives exhibit a wide variety of biological activities [23]. The number of annual publications dealing with thiazoles is continuously growing, but there are very few articles about thiazole substituted phthalocyanines in literature [24–26]. Because of this reason, in this work, the thiazole substituted metal-free (H_2Pc) and metallophthalocyanines (MPcs) were synthesized.

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* Corresponding author. Tel.: +90 462 377 25 89; fax: +90 462 325 31 96.
E-mail address: halit@ktu.edu.tr (H. Kantekin).

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MPcs are used in many electrochemical technologies, especially electrosensing [27–30], electrochromic [31–33], and electrocatalytic [34–37] application due to the excellent redox properties. Changing the central metal and types, number and position of substituents alter molecule's the electrochemical responses as well as the usage fields of the MPc complexes [38–40].

Here, we report the synthesis and characterization of novel *4-(2-(benzo[d]thiazol-2-yl)phenoxy*-substituted **H_2Pc** (**4**), **ZnPc** (**5**), **PbPc** (**6**), **CoPc** (**7**) and **CuPc** (**8**) compounds. In this paper we aimed to investigate the electrochemical properties and possible application fields of the newly synthesized MPc complexes. Voltammetric characterizations of the phthalocyanines (**4**–**7**) were performed with cyclic voltammetry and square wave voltammetry for the first time. These organo-soluble phthalocyanines (**4**–**8**) have also been characterized by using electronic absorption, FT-IR, ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectra.

2. Experimental

2.1. Materials

All reagents and solvents were dried and purified as described in Perrin and Armarego [40]. 2-(benzo[*d*]thiazol-2-yl)phenol (**1**) was obtained from commercial supplier. 4-nitro phthalonitrile (**2**) [41] was prepared according to the reported procedure. All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers.

2.2. Equipments

Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer Frontier. Elemental analyses were obtained from Costech ECS 4010 Spectrometer Elemental Analyzer (C, H, N). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a Varian Mercury 200 MHz spectrometer (at Karadeniz Technical University, Turkey) and Varian Mercury 300 MHz spectrometer (at Sakarya University, Turkey) using TMS as an internal reference. Mass spectra were performed on a Brucker Microflex LT MALDI-TOF MS spectrometer (at Gebze Institute of Technology, Turkey). Optical spectra in the UV/Vis region were recorded with a Perkin Elmer Lambda 25 UV–Vis Spectrometer operating in the range 200–800 nm with quartz cells at the room temperature. Melting points were measured on an electrothermal melting point apparatus and were uncorrected.

All electrochemical measurements were carried out with Gamry Reference 600 potentiostat/galvanostat (at Marmara University, Turkey). An electrochemical cell with a three-electrode configuration was utilized with a Pt disc working electrode (surface area: 0.071 cm^2), a Pt wire counter electrode and saturated calomel reference electrode (SCE). Electrochemical grade TBAP in extra pure DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

An Ocean Optics QE65000 diode array spectrophotometer was used for UV–Vis absorption spectra and chromaticity diagram measurements (at Marmara University, Turkey). *In-situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell consisting a Pt tulle working electrode, a Pt wire counter electrode, and a SCE reference electrode. The spectroelectrochemical cell we used is a homemade cell. Three quartz necks were welded on a quartz fluorescence cuvette which has 2 mm light path. Three quartz necks were used as holder for the electrodes. 2 mm light path of the fluorescence cuvette supply a thin layer for the electroactive species in it. *In-situ* electrocolorimetric measurements, under potentiostatic control, were obtained using an Ocean Optics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell.

2.3. Synthesis

2.3.1. Preparation of 4-(2-(benzo[d]thiazol-2-yl)phenoxy) phthalonitrile (**3**)

A solution of 2-(benzo[*d*]thiazol-2-yl)phenol (**1**) (1 g, 4.4 mmol) and 4-nitro phthalonitrile (0.76 g, 4.4 mmol) (**2**) in dry DMF (15 mL) was stirred at 50 °C for 10 min under a nitrogen atmosphere. And then, finely ground anhydrous K_2CO_3 (2.43 g, 17.6 mmol) was added portionwise over a period of 2 h with stirring at this temperature. After stirring for 120 h at 50 °C, the reaction mixture was poured over crushed ice and the resulting white precipitate was filtered off, washed with distilled water, and then dried *in vacuo*. Yield: 1.5 g (97%), m.p.: 177–179 °C. Calc. for $C_{21}H_{11}N_3OS$: % C 71.37, % H 3.14, % N 11.89. Found: % C 71.39, % H 3.19, % N 11.85. FT-IR ν_{max}/cm^{-1} : 3070 (Ar–H), 2234 (C≡N), 1601, 1561 (C=N), 1485, 1251 (Ar–O–C), 1105, 955, 837, 759, 694 (C–S). ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.60 (ArH, 1H, d), 8.11 (Ar–H, 1H, d), 7.91 (ArH, 1H, d), 7.75 (ArH, 1H, d), 7.53–7.22 (ArH, 7H, m). ^{13}C NMR ($CDCl_3$) (δ: ppm): 161.01, 152.68, 151.14, 135.79, 132.70, 131.30, 127.33, 126.79, 125.91, 123.65, 122.06, 121.87, 121.68, 121.43, 118.12, 115.44, 115.06, 109.92. MALDI-TOF, *m*/*z*: Calc.: 353.40; Found: 353.12 [M]$^+$.

2.3.2. Preparation of metal-free phthalocyanine (**4**)

In dry *n*-pentanol (3 mL), compound **3** (0.3 g, 0.85 mmol) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene were stirred under reflux in a nitrogen atmosphere at 160 °C in a sealed glass tube for 24 h and degassed several times. Thereafter, the reaction mixture was left to cool to the room temperature. With adding ethanol (10 mL), the green crude product was precipitated and filtered off. After the refluxing with ethanol (40 mL) for 4 h, the obtained green product was filtered off again and was successively washed several times with hot ethanol, distilled water and diethyl ether in order to removing the unreacted organic materials. After drying *in vacuo*, it was purified by column chromatography using chloroform–methanol (93:7) solvent system as eluent. Yield: 110 mg (37%), m.p.: >300 °C (decomposition). Calc. for $C_{84}H_{46}N_{12}O_4S_4$: % C 71.27, % H 3.28, % N 11.87. Found: % C 71.33, % H 3.36, % N 11.89. FT-IR ν_{max}/cm^{-1}: 3287 (N–H), 3060 (Ar–H), 1610 (N–H, bend.), 1577 (C=N), 1447, 1228 (Ar–O–C), 1089, 925, 752, 692 (C–S). ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.50 (ArH, 4H, m), 8.05 (ArH, 4H, m), 7.37–6.98 (ArH, 36H, m). UV/Vis (THF): λ, nm (log ε): 700 (5.20), 665 (5.16), 638 (4.81), 605 (4.68), 383 (4.78). MALDI-TOF, *m*/*z*: Calc.: 1415.63; Found: 1415.57 [M]$^+$.

2.3.3. General procedures for metallophthalocyanine derivatives (**5**–**8**)

The mixture of compound **3** (0.3 g, 0.85 mmol), the related anhydrous metal salt [$Zn(CH_3COO)_2$ (38 mg, 0.21 mmol) for compound **5**, PbO (47 mg, 0.21 mmol) for compound **6**, $CoCl_2$ (27 mg, 0.21 mmol) for compound **7**, $CuCl_2$ (28 mg, 0.21 mmol) for compound **8**] and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene was heated at 160 °C with dry *n*-pentanol (3 mL) in a sealed tube, and stirred for 24 h. Later on, the reaction mixture was left to cool into the room temperature. With adding ethanol (10 mL), the green crude product was precipitated and filtered off. After the refluxing with ethanol (40 mL) for 4 h, the obtained green product was filtered off again and was successively washed several times with hot ethanol, distilled water and diethyl ether in order to removing the unreacted organic materials. After drying *in vacuo*, it was purified by column chromatography using chloroform–methanol ((93:7) for compound **5**, (91:9) for compound **6**, (92:8) for