



# Electrochemical and spectroelectrochemical properties of thiadiazole substituted metallo-phthalocyanines



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## ABSTRACT

4-Thiadiazole substituted phthalonitrile and peripherally tetra-substituted phthalocyanine Cu(II), Fe(II) and Ti(IV)O complexes have been synthesized for the first time. Electrochemical properties of these complexes were determined with voltammetric and in situ spectroelectrochemical measurements. CuPc has redox inactive Cu<sup>2+</sup> center, therefore it gave three Pc based reduction and two Pc based oxidation processes. TiOPc and FePc complexes gave metal based redox processes in addition to Pc based redox reactions due to the redox activity of Ti<sup>4+</sup>O and Fe<sup>2+</sup> metal centers. Although FePc also gave three reduction and two oxidation reactions, peak potentials of these processes are different than those of CuPc due to the different assignments of the redox reactions. TiOPc went to five reduction and one oxidation reactions. Assignments of the redox processes were carried out with in situ spectroelectrochemical measurements. Spectra and color of the electrogenerated redox species of the complexes were also determined with in situ spectroelectrochemical and in situ electrocolorimetric measurements. Distinct color differences between the electrogenerated redox species were observed, which indicated their possible electrochromic usages.

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## 1. Introduction

Phthalocyanines (Pcs), intensely blue-green aromatic macrocyclic compound, have been an important class of dyes since their accidental discovery. Firstly they are only used as dyes and pigments, but today their use includes chemical sensors, photodynamic therapy of cancer, liquid crystals and non-linear optical materials [1–4]. Due to their excellent electron transfer properties, they are also used in areas such as electrochromism, energy producing equipments and so to analyze the redox properties of these compounds is important.

There have been many studies on compounds containing thiadiazole rings, a five membered ring system that have sulphur and nitrogen atom, due to their interesting pharmacological properties [5]. Especially 1,3,4-thiadiazoles are an important class of bioactive compounds [6]. In recent years our group has successfully prepared phthalocyanines containing thiazole group and investigated their electrochemical properties [7,8]. However, to the best of our knowledge, there is no study on thiadiazole substituted phthalocyanines in literature. Therefore we have planned to prepare a phthalocyanine containing substituted 1,3,4-thiadiazole compounds as substituents on peripheral positions.

In this paper, substituted thiadiazole bearing phthalocyanine redox active Cu(II), Fe(II) and Ti(IV)O complexes have been synthesized and characterized. Electrochemical characterizations of the complexes were performed with different voltammetric and in situ spectroelectrochemical measurements. Electrochemical responses of the complexes will give information about the possible usage of the complexes in different electrochemical application fields.

## 2. Experimental

### 2.1. Materials

All reactions were carried out under dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 5-methyl-1,3,4-thiadiazole-2-thiol (1) and 4-nitrophthalonitrile were purchased from their commercial supplier. All solvents were dried and purified as described by Perrin and Armarego (1989) before use [9].

### 2.2. Equipments

<sup>1</sup>H NMR and <sup>13</sup>C NMR (for phthalonitrile compound) spectra were recorded on a Varian XL-200 NMR spectrophotometer in CDCl<sub>3</sub> and chemical shifts were reported (δ) relative to Me<sub>4</sub>Si as internal standard. FT-IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR

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spectrometer. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC–MS/MS spectrometer using chloroform–methanol as a solvent system. All experiments were performed in the positive ion mode. Melting points were measured on an electrothermal apparatus and are uncorrected. Absorption spectra in the UV–visible region were recorded with a Shimadzu 2101 UV–vis spectrophotometer.

### 2.3. Electrochemical and In Situ Spectroelectrochemical Measurements

The cyclic voltammetry (CV), square wave voltammetry (SWV), and controlled potential coulometry (CPC) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm<sup>2</sup>. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade TBAP in dimethylformamide (DMF) was employed as the supporting electrolyte at a concentration of 0.10 mol dm<sup>-3</sup>. Ferrocene was used as universal indicator and ΔE<sub>p</sub>'s of ferrocene were changed from 60 to 110 mV with increasing scan rates from 0.010 to 1.00 Vs<sup>-1</sup> in our system.

UV–vis absorption spectra and chromaticity diagrams were measured with an OceanOptics QE65000 diode array spectrophotometer. In situ spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was a Pt gauze electrode. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. In situ electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The standard illuminant A with a 2 degree observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (x, y, and z values) were taken at open-circuit, using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and final of each redox processes were reported.

### 2.4. Synthesis of the New Compounds

#### 2.4.1. 4-(5-Methyl-1,3,4-thiadiazol-2-ylthio)phthalonitrile (3)

5-Methyl-1,3,4-thiadiazole-2-thiol (**1**) (2 g, 15.13 mmol) and 4-nitrophthalonitrile (**2**) (2.62 g, 15.13 mmol) were dissolved in dry DMF (15 mL) under inert N<sub>2</sub> atmosphere. Anhydrous K<sub>2</sub>CO<sub>3</sub> (6.26 g, 45.39 mmol) was added portion wise within 2 h. The reaction mixture was stirred at 50 °C for 3 days. Then the mixture was poured into 200 mL ice-water and was filtered off. The solid product was crystallized from ethanol. Yield 2.38 g, (61%), mp = 139–141 °C. FT-IR (ν<sub>max</sub>/cm<sup>-1</sup>): 3101, 3063, 2234, 1584, 1549, 1474, 1369, 1289, 1199, 1120, 1052, 977, 892, 864, 844, 657. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ ppm): 7.87–7.75 (m, 3H, Ar-H), 2.83 (s, 3H, –CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) (δ ppm): 169.40, 158.83, 140.25, 133.98, 133.96, 133.94, 117.01, 114.89, 114.76, 114.43, 16.01. MS (ESI), (m/z): Calculated: 258.00, Found: 259.20 [M + H]<sup>+</sup>, 281.11 [M + Na]<sup>+</sup>.

#### 2.4.2. General Method for the Synthesis of Metallophthalocyanines (4–6)

The mixtures of compound (**3**) (0.2 g, 0.77 mmol), dry n-pentanol (4 mL), DBU (5 drops) and equivalent amounts of related anhydrous metal salts (for compound **4** CuCl<sub>2</sub>, for compound **5** Fe(CH<sub>3</sub>COO)<sub>2</sub>, for compound **6** Ti(OBu)<sub>4</sub>) were heated to 160 °C and stirred for 24 h. After cooling to room temperature the mixtures were precipitated by ethanol and filtered off. After washing with hot ethanol, acetone and ethyl acetate the product was chromatographed on silica gel column

with chloroform–methanol solvent system. The chemical and physical characteristics of these Pc metal complexes have been given below.

2.4.2.1. *CuPc* (**4**). Solvent system for column chromatography: chloroform:methanol (100:7). Yield: 0.089 g, (42 %). m.p. >300. FT-IR (ν<sub>max</sub>/cm<sup>-1</sup>): 3056, 1581, 1540, 1479, 1341, 1282, 1201, 1124, 1051, 988, 864. MS (ESI), (m/z): Calculated: 1094.94, Found: 1095.78 [M + H]<sup>+</sup>. UV–vis (Chloroform): λ<sub>max</sub>/nm (log ε): 682 (4.89), 617 (4.25), 364 (4.96).

2.4.2.2. *FePc* (**5**). Solvent system for column chromatography: chloroform:methanol (100:5). Yield: 0.118 g, (56 %). m.p. >300. FT-IR (ν<sub>max</sub>/cm<sup>-1</sup>): 3077, 1581, 1542, 1466, 1369, 1287, 1195, 1111, 1055, 975, 896, 862, 845. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ ppm): 7.92–7.62 (bm, 12H, Ar-H), 2.85 (bs, 12H, –CH<sub>3</sub>). MS (ESI), (m/z): Calculated: 1087.95, found: 1111.25 [M + Na]<sup>+</sup>. UV–vis (chloroform): λ<sub>max</sub>/nm (log ε): 683 (4.92), 618 (4.41), 354 (4.93).

2.4.2.3. *TiOPc* (**6**). Solvent system for column chromatography: chloroform:methanol (100:8). Yield: 0.059 g, (28 %). m.p. >300. FT-IR (ν<sub>max</sub>/cm<sup>-1</sup>): 3095, 1574, 1541, 1465, 1370, 1288, 1195, 1110, 1056, 975, 887, 862. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ ppm): 7.89–7.55 (bm, 12H, Ar-H), 2.84 (bs, 12H, –CH<sub>3</sub>). MS (ESI), (m/z): Calculated: 1095.96, Found: 1097.58 [M + H]<sup>+</sup>. UV–vis (chloroform): λ<sub>max</sub>/nm (log ε): 705 (5.06), 672 (4.62), 643 (4.49), 353 (4.81).

## 3. Results and Discussion

### 3.1. Synthesis and Characterization

The synthetic route of the preparation of substituted phthalonitrile (**3**) and their corresponding metallophthalocyanine complexes (**4–6**) is shown in Fig. 1. The structural characterizations of new compounds have been achieved by a combination of <sup>1</sup>H and <sup>13</sup>C NMR, FT-IR, UV–vis spectroscopy and mass spectral data.

Generally, scientists use substituted phthalonitrile derivatives as starting compound to prepare new Pcs and mostly 4-substituted phthalonitriles are used for the preparation of the phthalocyanines containing substituents on peripheral positions [10]. In this context, compound **1** and 4-nitrophthalonitrile were used for the synthesis of thiadiazole substituted phthalonitrile compound (**3**) and the preparation of metallophthalocyanine complexes (**4–6**) have been achieved by using compound **3**.

### 3.2. Spectral Evaluation of the Synthesized Compounds (3–6)

In the IR spectra of the substituted phthalonitrile (**3**), the presence of C≡N absorption at 2234 cm<sup>-1</sup> clearly proves the formations of this compound (**3**). In the <sup>1</sup>H NMR spectra of the compound **3**, the –SH signals of the compound **1** disappeared as expected and in their <sup>13</sup>C NMR spectra new signals belong to nitrile carbon atoms at around 117.01 and 114.89 ppm appeared. Additionally, in the mass spectra of compounds **3**, the presence of molecular ion peaks at m/z = 259.20 [M + H]<sup>+</sup> confirmed the proposed structure.

Cyclotetramerization of the substituted phthalonitrile derivative (**3**) to metallophthalocyanines (**4–6**) was confirmed by the disappearance of the C≡N vibration in their IR spectra. The <sup>1</sup>H NMR spectra of the compounds **5** and **6** were similar to that of their corresponding starting materials (**3**) and the <sup>1</sup>H NMR measurement of compound (**4**) could not be done because of the presence of paramagnetic copper (II) ion [11]. In the mass spectra of the substituted metallophthalocyanines (**4–6**), parent molecular ion peaks at m/z = 1095.78 [M + H]<sup>+</sup>, 1111.25 [M + Na]<sup>+</sup> and 1097.58 [M + H]<sup>+</sup>, respectively, verified the proposed structures (see Supplementary information).

Absorption spectroscopy is one of the most reliable methods for defining the formation of the Pcs. In general, Pcs have two strong

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