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## The electrochemical and spectroelectrochemical properties of metal free and metallophthalocyanines containing triazole/piperazine units



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### ABSTRACT

The synthesis and characterization of novel peripherally tetra [1,2,4]-triazole substituted metal-free phthalocyanine and its metal complexes (Zn(II), Ni(II), Pb(II), Cu(II) and Fe(II)) and the investigation of electrochemical and spectroelectrochemical properties of metal-free, Zn(II), Pb(II), Fe(II) phthalocyanines were performed for the first time in this study. Electrochemical characterizations of the complexes were performed with voltammetric and in situ spectroelectrochemical measurements. Voltammetric responses of the complexes supported the proposed structures, since complexes bearing redox inactive Pc ring metal centers just gave Pc based electron transfer reactions, while iron phthalocyanine went to metal based electron transfer reaction in addition to the Pc based ones. Electron withdrawing nature of [1,2,4]-triazole substituents shifted the redox processes toward the positive potentials. All complexes were electropolymerized during the oxidation reactions in dichloromethane (DCM) solvent. Types of the metal center of the complexes altered the electropolymerization reactions of the complexes. Spectra and colors of the electrogenerated redox species of the complexes were also determined with in situ spectroelectrochemical and in situ electrocolorimetric measurements.

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## 1. Introduction

Thanks to strong delocalized 18- $\pi$  electronic structure, good thermal stability and UV/visible optical properties, phthalocyanines are significant compounds in production of new high-tech materials such as chemical sensors [1–3], electrochromic displaying systems [4], non-linear optics [5], solar cells [6], photovoltaic optics, molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10], laser dyes [11], catalyst [12] and photo dynamic therapeutic agents (PDT) [13].

Because of the well known pharmacological and biological properties [14], [1,2,4]-triazoles are used as anti-inflammatory [15], antiviral/anti-HIV and anti-tuberculosis [16], and antibacterial agents [17] in medicine. In addition, triazoles are used as corrosion inhibitors in some electrochemical studies [18–20] and their electrosorption and polymerization properties have been discussed [21–23].

There are only few studies about the preparation of [1,2,4]-triazole containing phthalocyanines. Although electrochemical and spectroelectrochemical properties of phthalocyanine ring have widely known, the investigation of electrochemical and spectroelectrochemical

properties have been made for only a few of [1,2,4]-triazole bearing phthalocyanine [24].

In our previous works we successfully synthesized different phthalocyanine molecules [25,26] and investigated electrochemical and spectroelectrochemical properties of some [27,28]. In this study we aimed to prepare tetra substituted [1,2,4]-triazole containing phthalocyanine and its Zn(II), Ni(II), Pb(II), Cu(II), Fe(II) metal complexes. Furthermore we investigated the electrochemical and spectroelectrochemical properties of this novel metal-free, Zn(II), Pb(II), Fe(II) complexes. We aimed to synthesize these complexes for the possible usage in different electrochemical applications. For practical application, if a complex can be coated on working electrode with the electropolymerization, it can supply most of the requirements of a modified electrode. For the purpose in this study, MPcs bearing piperazine units on the substituents were synthesized and electrochemically characterized. Moreover their electropolymerization tendencies were investigated and electropolymerization processes were optimized.

## 2. Experimental

### 2.1. Materials and equipment

All reactions were carried out under dry and nitrogen atmosphere using schlenk system. DMF (dimethylformamide) was dried and

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purified as described by Perrin and Armarego [29], 5-[[4-(2-Methoxyphenyl)piperazin-1-yl]methyl]-4-phenyl-4H-1,2,4-triazole-3-thiol (**1**) [30] and 4-nitrophthalonitrile (**2**) [31] were prepared as described in the literature.

## 2.2. Equipments

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were recorded on a Varian XL-400 NMR spectrometer  $\text{CDCl}_3$  (deuterated chloroform), and chemical shifts were reported ( $\delta$ ) relative to  $\text{Me}_4\text{Si}$  (tetramethylsilane) as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique. The MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. Methanol, chloroform were used as solvents in mass analysis and all mass analyses were conducted in positive ion mode. UV-vis spectra were recorded by Perkin Elmer Lambda 25 spectrometer, using 1 cm path length cuvettes at room temperature. Melting points were measured by an electrothermal apparatus.

## 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  $\text{cm}^2$ . 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 tetrabutyl ammonium perchlorate (TBAP) in dichloromethane (DCM) and dimethyl sulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10  $\text{mol dm}^{-3}$ . Ferrocene was used as universal indicator and  $\Delta E_{\text{p}}$ s of ferrocene were changed from 60 to 110 mV with increasing scan rates from 0.010 to 1.00  $\text{Vs}^{-1}$  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 thin-layer 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 electrochromic 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 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

### 2.4.1. 4-(5-((4-(2-methoxyphenyl)piperazin-1-yl)methyl)-4-phenyl-4H-1,2,4-triazole-3-ylthio)phthalonitrile (**3**)

5-[[4-(2-methoxyphenyl)piperazin-1-yl]methyl]-4-phenyl-4H-1,2,4-triazole-3-thiol (**1**) (2 g. 4.64 mmol) and 4-nitrophthalonitrile (**2**) (0.90 g. 4.64 mmol) was dissolved in dry DMF (15 mL) under inert  $\text{N}_2$  atmosphere. Anhydrous  $\text{K}_2\text{CO}_3$  (1.8 g 13.10 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 1.22 g (46%), mp 276–278 °C,  $\text{C}_{28}\text{H}_{25}\text{N}_7\text{O}_5$ . IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3096,

3049, 2970, 2819, 2231 ( $\text{C}\equiv\text{N}$ ), 1585, 1549, 1498, 1439, 1366, 1312, 1266, 1240, 1131, 1075, 942  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 7.65–7.63 (m, 3H/ArH), 7.54–7.47 (m, 3H/ArH), 7.22–7.20 (m, 2H/ArH), 6.99–6.97 (m, 1H/ArH), 6.90–6.83 (m, 3H/ArH), 3.84 (s, 3H/ $\text{OCH}_3$ ), 3.62 (s, 2H/ $\text{CH}_2$ ), 2.94–2.90 (t, 4H/ $\text{NCH}_2$ ), 2.63–2.60 (t, 4H/ $\text{NCH}_2$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 155.02, 152.19, 146.22, 140.96, 140.18, 133.71, 133.14, 132.96, 131.74, 130.38, 129.58, 127.18, 123.09, 120.93, 118.10, 116.68, 114.82 ( $\text{C}\equiv\text{N}$ ), 114.43 ( $\text{C}\equiv\text{N}$ ), 114.20, 111.27, 55.36, 53.01, 51.94, 50.49. MS (ESI), (m/z): calculated: 507.18; found: 508.16 [ $\text{M} + \text{H}$ ] $^+$ .

### 2.4.2. General procedure for synthesis of phthalocyanines (**4–9**)

The mixture of compound (**3**) (0.2 g. 0.39 mmol), dry n-pentanol, 1,8-diazabicyclo [4.5.0] undec-7-ene (DBU) (5 drops) and equivalent amounts of related anhydrous metal salts (for compound **5**  $\text{Zn}(\text{CH}_3\text{COOH})_2$ , **6**  $\text{NiCl}_2$ , **7**  $\text{Pb}(\text{CH}_3\text{COOH})_2$ , **8**  $\text{CuCl}_2$ , **9**  $\text{Fe}(\text{CH}_3\text{COOH})_2$ ) was heated to 160 °C and stirred for 24 h. After cooling to room temperature the mixture was 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.

**2.4.2.1. Metal-free phthalocyanine (**4**).** The green solid product was purified by column chromatography with chloroform:methanol (100:1.5) as eluent. Yield: 60 mg (29%), mp > 300 °C,  $\text{C}_{112}\text{H}_{102}\text{N}_{28}\text{O}_4\text{S}_4$ . IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3288, 3127, 2933, 2815, 1595, 1498, 1448, 1308, 1238, 1136, 1006, 924 1450, 1233, 1169, 1117, 1092, 1014, 963, 842.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 7.85–7.45 (m, 24H/ArH), 7.28–7.20 (m, 24H/ArH), 3.84 (s, 12H/ $\text{OCH}_3$ ), 3.64 (s, 8H/ $\text{CH}_2$ ), 2.88–2.69 (t, 16H/ $\text{NCH}_2$ ), 2.65–2.56 (t, 16H/ $\text{NCH}_2$ ). UV-vis (DMSO)  $\lambda_{\text{max}}/\text{nm}$ : [(10 $^{-5}$   $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 706 (5.23), 671 (5.18), 641 (4.78), 600 (4.45), 345 (4.99). MS (ESI), (m/z): Calculated: 2031.76, Found: 2032.94 [ $\text{M} + \text{H}$ ] $^+$ .

**2.4.2.2. Synthesis of zinc (II) phthalocyanine (**5**).** Eluent for column chromatography: chloroform:methanol (100:2). Yield: 96 mg (47%), mp > 300 °C,  $\text{C}_{112}\text{H}_{100}\text{N}_{28}\text{O}_4\text{S}_4\text{Zn}$ . IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3056, 2918, 2815, 1594, 1497, 1381, 1305, 1238, 1136, 110, 907.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 8.01–7.65 (m, 16H/ArH), 7.46–7.56 (m, 16H, ArH), 6.90–6.78 (m, 16H/ArH), 3.79 (s, 12H/ $\text{OCH}_3$ ), 3.64 (s, 8H/ $\text{CH}_2$ ), 2.88–2.76 (t, 16H/ $\text{NCH}_2$ ), 2.69–2.62 (t, 16H/ $\text{NCH}_2$ ). UV-vis (DMSO)  $\lambda_{\text{max}}/\text{nm}$ : [(10 $^{-5}$   $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 687 (5.25), 618 (4.59), 360 (4.96). MS (ESI), (m/z): calculated: 2093.67, found: 2094.99 [ $\text{M} + \text{H}$ ] $^+$ .

**2.4.2.3. Synthesis of nickel (II) phthalocyanine (**6**).** Eluent for column chromatography: chloroform:methanol (100:3). Yield: 51 mg (25%), mp > 300 °C,  $\text{C}_{112}\text{H}_{100}\text{N}_{28}\text{NiO}_4\text{S}_4$ . IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3056, 2931, 2814, 1594, 1497, 1447, 1313, 1238, 1098, 1023, 1006, 930.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 8.05–7.96 (m, 16H/ArH), 7.37–7.22 (m, 16H, ArH), 6.85–6.75 (m, 16H/ArH), 3.75 (s, 12H/ $\text{OCH}_3$ ), 3.68 (s, 8H/ $\text{CH}_2$ ), 2.84–2.77 (t, 16H/ $\text{NCH}_2$ ), 2.69–2.60 (t, 16H/ $\text{NCH}_2$ ). UV-vis (DMSO)  $\lambda_{\text{max}}/\text{nm}$ : [(10 $^{-5}$   $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 670 (5.00), 608 (4.53), 343 (5.10). MS (ESI), (m/z): calculated: 2087.68, found: 2126.55 [ $\text{M} + \text{K}$ ] $^+$ .

**2.4.2.4. Synthesis of lead (II) phthalocyanine (**7**).** Eluent for column chromatography: chloroform:methanol (100:1). Yield: 64 mg (29%), mp > 300 °C,  $\text{C}_{112}\text{H}_{100}\text{N}_{28}\text{O}_4\text{PbS}_4$ . IR (KBr tablet)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3061, 2931, 2814, 1594, 1497, 1380, 1313, 1238, 1136, 1005, 923.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ), ( $\delta$ : ppm): 7.95–7.68 (m, 16H/ArH), 7.39–7.24 (m, 16H, ArH), 6.75–6.66 (m, 16H/ArH), 3.78 (s, 12H/ $\text{OCH}_3$ ), 3.71 (s, 8H/ $\text{CH}_2$ ), 2.82–2.76 (t, 16H/ $\text{NCH}_2$ ), 2.69–2.57 (t, 16H/ $\text{NCH}_2$ ). UV-vis (DMSO)  $\lambda_{\text{max}}/\text{nm}$ : [(10 $^{-5}$   $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 725 (5.21), 652 (4.65), 369 (4.79). MS (ESI), (m/z): calculated: 2237.72, found: 2238.66 [ $\text{M} + \text{H}$ ] $^+$ .

**2.4.2.5. Synthesis of copper (II) phthalocyanine (**8**).** Eluent for column chromatography with chloroform:methanol (100:2.5). Yield: 95 mg

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