



# Synthesis, structural characterizations, and electrochemical and spectroelectrochemical properties of novel peripherally octa-substituted metallophthalocyanines

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## ABSTRACT

In this study, we report the synthesis and characterization of N-(3-(4-methoxybenzyl)-5-(4-chorophenyl)-4H-1,2,4-triazol-yl)-4-methylbenzenesulfonamide (**3**) and peripheral functionalized ligand, 1,2-Bis(2-N-(3-(4-methoxybenzyl)-5-(4-chorophenyl)-4H-1,2,4-triazol-yl)-4-methylbenzene sulfonamide)-4,5-dicyanobenzene (**4**). The reaction of compound **4** with the corresponding metal salts (Zn(CH<sub>3</sub>COO)<sub>2</sub>, CoCl<sub>2</sub>, PbO) in the presence of DMAE with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7ene (DBU) gave novel Zn(II) (**5**), Pb(II) (**6**) and Co(II) (**7**) phthalocyanine derivatives. These new metallophthalocyanines (**5–7**) have been characterized by using UV–Vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS spectroscopic data. Electrochemical and spectroelectrochemical measurements show that while **CoPc** gives a metal-based reduction process in addition to the ring-based reduction process, all other complexes give common ring reduction reaction of MPCs having redox inactive metal center. Redox behaviors of **ZnPc**, **PbPc** and **CoPc** were determined in solution with voltammetric and in situ spectroelectrochemical measurements. While **ZnPc** and **PbPc** complexes gave three reduction and one oxidation reactions, three reduction and two oxidation processes were observed with **CoPc**. All redox reactions of the complexes were chemically and electrochemically reversible except the second oxidation of **CoPc**. Analyses of voltammetric and in situ spectroelectrochemical measurements indicated metal based electron transfer reaction character for the first reduction and the first oxidation processes of **CoPc**. All other redox reactions of the complexes were proposed as ligand based processes.

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## Introduction

Phthalocyanines, with colors ranging from blue to brown, condensation products of four iminozindol units, are planar macro ring with 18  $\pi$ -electron system [1]. Phthalocyanines with their unique properties find applications in many different fields such as electrochromic display devices [2], catalysts [3], chemical sensors [4], liquid crystals [5], Langmuir–Blodgett films [6], solar cells [7], non-linear optics application [8], gas sensors [9], photodynamic therapy (PDT) and nanotechnology [10,11].

A large number of heterocyclic compounds containing 1,2,4-triazole rings are associated with diverse pharmacological

properties such as antimicrobial, antifungal, anticancer, antiviral, anticonvulsant, antioxidant, anti-HIV, antimycobacterial, pesticidal and insecticidal activities [12–15]. In addition, various compounds containing 1,2,4-triazole ring are well known as drugs like vorozole, letrozole and anastrozole (anticancer drugs) [16], fluconazole, itraconazole, ravuconazole, voriconazole and posaconazole (antifungal drugs) [17,18], and ribavirin (antiviral drug) [19]. Apart from their pharmacological significance, 1,2,4-triazoles have found applications in coordination chemistry and bioinorganic chemistry because of their different binding behavior, either bidentate-bridging or monodentate, depending on the position and the nature of the substituent at the triazole ring [20–22]. Moreover, 1,2,4-triazole metal complexes have also potential uses as magnetic materials, optical sensors and photochemically driven molecular devices [23].

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There are a lot of methods used for synthesizing phthalocyanines. In the last decade microwave is a widely preferred method because of advantages such as reduction of reaction time and side reactions, increasing the yield unlike classical method [24].

Recently the electrochemistry of phthalocyanines has attracted much attention in relation to their industrial applications, such as electrochromic properties, electrocatalytic properties, and semiconductivity [25–28]. The most important properties of the phthalocyanines are their stability and non-toxicity. Phthalocyanine complexes are well known for electrochemical and spectroelectrochemical properties [29]. Phthalocyanine complexes show perfect electrochromic properties in solution. Electrochemical and spectroelectrochemical responses of the complexes have been used for the proposition of the application of the complexes in different electrochemical fields, such as electrocatalysis for  $H^+$  reduction [30], electrochemical oxygen reduction reaction [31], electrochemical metal ion sensor [32] and electrochromism [33].

In this study, we synthesized new Pc compounds containing triazole units and investigated them with different voltammetric techniques and in situ spectroelectrochemical measurements in various electrocatalytic systems.

## Experimental

### Materials and equipment

All reagents and solvents were of reagent grade and obtained from commercial suppliers. 3-(4-Methoxybenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-4-amine **1** was synthesized and purified according to well known literature [34]. 4,5-Bis(2-iodoethylthio)phthalonitrile **2** was synthesized and purified according to well known literature [35]. All solvents were dried and purified as described by Perrin and Armarego [36].  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded on a Varian XL-200 NMR spectrometer in  $CDCl_3$ , and chemical shifts were reported ( $\delta$ ) relative to  $Me_4Si$  as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer with ATR technique. MALDI-MS of complexes were obtained in dihydroxybenzoic acid as the MALDI Matrix using a nitrogen laser accumulating 50 laser shots, with a Bruker Microflex LT MALDI TOF mass spectrometer.

### Synthesis

#### Synthesis of N-(3-(4-methoxybenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-yl)-4-methylbenzenesulfonamide (**3**)

3-(4-Methoxybenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-4-amine (**1**) ( $2.1 \times 10^3$  mg, 6.68 mmol) was dissolved in 90 mL pyridine under  $N_2$  atmosphere at room temperature. Then, 4-methylbenzene-1-sulfonyl chloride ( $1.27 \times 10^3$  mg, 6.68 mmol) dissolved in 10 mL of pyridine was added dropwise during 2 h with the temperature maintained at  $-10^\circ C$ . The mixture was stirred for 20 h at  $-10^\circ C$ . At the end of this time, the reaction mixture was poured into ice-water and 37% HCl (23 mL) was added dropwise during 2 h. This mixture was stirred at room temperature for 18 h to yield a crude product. The mixture was filtered and dried in vacuum over  $P_2O_5$  for 4 h and recrystallized from ethanol to give white crystalline powder. Yield: 1.6 g (51%). mp:  $197-199^\circ C$ . IR (KBr pellet),  $\nu_{max}/cm^{-1}$ : 3237 (N–H), 3011 (Ar–H), 2935–2839 (Aliph. C–H), 1661, 1605 (N–H), 1583, 1509, 1480, 1462, 1247 (Ar–OCH<sub>3</sub>), 1172 (–OCH<sub>3</sub>).  $^1H$  NMR. (DMSO), ( $\delta$ : ppm): 8.0 (d, 2H, J = 8.4 Hz, Ar–H), 8.02 (d, 2H, J = 8.0 Hz, Ar–H), 7.57 (d, 2H, J = 8.4 Hz, Ar–H), 7.24 (d, 2H, J = 8.4 Hz, Ar–H), 6.86 (d, 2H, J = 8.0 Hz, Ar–H), 6.85 (d, 2H, J = 8.0 Hz, Ar–H), 6.07 (s, 2H, –CH<sub>2</sub>–), 4.07 (s, 3H, –OCH<sub>3</sub>), 3.71 (s, 3H, –CH<sub>3</sub>), 2.48 (s, H, –NH–).

$^{13}C$  NMR. (DMSO), ( $\delta$ : ppm): 158.44, 156.22, 152.02, 134.59, 130.37, 129.99, 128.97, 128.86 (C≡N), 114.29 (C≡N), 55.51, 45.21, 38.25, 29.18. MALDI-TOF-MS, ( $m/z$ ): Calculated: 468.96; Found: 315.96 [ $M - Ts + 2H$ ]<sup>+</sup> (Fig. 7).

#### Synthesis of 1,2-bis(2-N-(3-(4-methoxybenzyl)-5-(4-chlorophenyl)-4H-1,2,4-triazol-yl)-4-methylbenzene sulphonamide)-4,5-dicyanobenzene (**4**)

Compound **3** (800 mg, 1.7 mmol) was dissolved in 10 mL dry DMF under  $N_2$  atmosphere, then dry NaI ( $1.19 \times 10^3$  mg, 2.55 mmol) and dry  $K_2CO_3$  (500 mg, 3.62 mmol) was added to the solution. 4,5-Bis(2-iodoethylthio)phthalonitrile (500 mg, 1 mmol) was dissolved in 10 mL dry DMF and added dropwise during 2 h into the mixture. The reaction mixture was stirred under  $N_2$  at  $60^\circ C$  for 7 days. The reaction progress was monitored by thin layer chromatography (TLC) using chloroform-methanol (1:1) solvent system. At the end of this time, the reaction mixture was poured into ice-water and stirred at room temperature for 18 h to yield a crude product. Then it was filtered and dried in vacuum over  $P_2O_5$  for 4 h and recrystallized from ethanol to give pink crystalline powder. Yield: 390 mg (39%) mp:  $224-230^\circ C$ . IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3079, 3007 (Ar–H), 2956–2849 (Aliph. C–H), 2229 (C≡N), 1566, 1515, 1461, 1417, 1287, 1223 (ArOCH<sub>3</sub>), 1166 (–OCH<sub>3</sub>).  $^1H$  NMR. (DMSO), ( $\delta$ : ppm): 8.20 (m, 2H, Ar–H), 7.82 (m, 4H, Ar–H), 7.61 (m, 4H, Ar–H), 7.43 (m, 4H, Ar–H), 7.22 (m, 4H, Ar–H), 6.91 (m, 12H, Ar–H), 5.80 (t, 4H, J = 8.0 Hz, CH<sub>2</sub>–S), 4.55 (t, 4H, J = 8.0 Hz, CH<sub>2</sub>–N), 3.84 (s, 6H, CH<sub>3</sub>–O), 2.63 (s, 6H, –CH<sub>3</sub>).  $^{13}C$  NMR. (DMSO), ( $\delta$ : ppm): 138.79, 133.05, 126.11, 120.09, 116.09, 112.98, 109.90, 50.60, 55.91, 43.12, 38.56, 27.92. MALDI-TOF-MS, ( $m/z$ ): Calculated: 1180.25; Found: 1179 [ $M - H$ ]<sup>+</sup> (Fig. 8).

#### Synthesis of zinc(II) phthalocyanine (**5**)

A mixture of phthalonitrile (**4**) (100 mg, 0.084 mmol) and anhydrous  $Zn(CH_3COO)_2$  (7.75 mg, 0.042 mmol) in DMAE (1 mL) was irradiated in a microwave oven at  $175^\circ C$ , 350 W for 10 min. After cooling to room temperature, a precipitate was formed by the addition of ethanol, and green precipitate was filtered off. The green crude product was refluxed with ethanol for 5 h. The obtained green product was filtered off, washed with ethanol and diethyl ether and then dried in vacuo. Purification of the solid product was accomplished by column chromatography using silica gel and  $CHCl_3:CH_3OH$  (5:1) as solvent system. Yield: 25 mg (35%), mp:  $>300^\circ C$ . IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3014 (Ar–H), 2952–2833 (Aliph. C–H), 1579, 1510, 1464, 1463, 1290 (ArOCH<sub>3</sub>) 1175 (–OCH<sub>3</sub>).  $^1H$  NMR. (DMSO), ( $\delta$ : ppm): 7.88–7.87 (m, 16H, Ar–H), 7.83–7.81 (m, 16H, Ar–H), 7.81–7.77 (m, 32H, Ar–H), 7.66–7.46 (m, 4H, Ar–H), 7.30–7.21 (m, 4H, Ar–H), 6.27–6.23 (m, 32H, Ar–H), 7.20 (s, 24H, –OCH<sub>3</sub>), 4.11 (t, 16H, J = 7.8 Hz, CH<sub>2</sub>–S), 3.47 (t, 16H, J = 7.8 Hz, CH<sub>2</sub>–N), 2.91 (s, 24H, CH<sub>3</sub>), 2.55 (s, 16H, –CH<sub>2</sub>).  $^{13}C$  NMR. (DMSO), ( $\delta$ : ppm): 169.40, 158.82, 140.23, 129.11, 116.99, 114.88, 114.76, 114.43, 110.00, 86.78, 76.70, 69.01, 58.58, 57.59, 42.55, 42.23, 36.83, 29.45. UV–Vis (DMSO):  $\lambda_{max}$ , nm (log  $\epsilon$ ): 713 (4.98), 639 (4.42), 356 (5.11), 329 (4.99). MALDI-TOF-MS, ( $m/z$ ): Calculated: 4783.37; Found: 940.44 [ $M - 8C_{24}H_{20}N_4O_3CIS - 3H$ ]<sup>+</sup> (Fig. 9).

#### Synthesis of lead(II) phthalocyanine (**6**)

A mixture of phthalonitrile (**4**) (100 mg, 0.084 mmol), anhydrous PbO (9.5 mg, 0.042 mmol) and catalytic amount of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) in 2 mL dry DMAE was heated and stirred at  $145^\circ C$  in a sealed glass tube for 7 h under  $N_2$ . After cooling to room temperature the green crude product was precipitated with ethanol, filtered and washed with ethanol then dried in vacuo. Purification of the solid product was accomplished by column chromatography using silica gel and  $CHCl_3$  as solvent. Yield: 20 mg (20%), mp:

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