



# Redox chemistry, spectroelectrochemistry and catalytic activity of novel synthesized phthalocyanines bearing four schiff bases on the periphery



Hüseyin Karaca\*

Department of Chemistry, Sakarya University, 54187 Sakarya, Turkey

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## ABSTRACT

The synthesis and characterization of novel metallophthalocyanines (M = Zn, Co) carrying four schiff base on four peripheral positions were realized. These complexes have been characterized by a combination of FT-IR, <sup>1</sup>H NMR, HRMS and UV–Vis spectroscopy techniques. Electronic absorption spectra showed that both Pcs are nonaggregable molecules and also well solubles common organic solvents such as dichloromethane, chloroform, THF, DMSO and DMF. Cyclic voltammograms give two reduction reaction for **Pc-6** and one reduction reaction for **Pc-7**. The spectroelectrochemical investigation shows the ring based reduction potential for MPc's. **Pc-7** cobalt(II)phthalocyanine was investigated as catalyst in the catalytic oxidation of 2-mercaptoethanol. Turnover number, initial reaction rate and the oxygen consumption was found in the catalytic oxidation of 2-mercaptoethanol as 18.6, 0.34, 2.75 respectively.

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## 1. Introduction

Phthalocyanines (Pcs) are very interesting molecules because of their structural flexibility [1]. Over the years, metallophthalocyanines have been subjected to several investigations. Because peripherally functionalization of phthalocyanines uncovers the unique properties. So these properties have being applied on the areas such as dyes and catalysts [2], organic photovoltaic devices [3–6], photodynamic therapy [7–12], electrochemical applications [13–15], low-dimensional conductors [16–18], chemical sensors [19–23], optical data storage [24], Langmuir–Blodgett films [25,26] and liquid crystals [27–29]. As two-dimensional planar aromatic molecules phthalocyanines are having 18  $\pi$ -electron system and giving hope for new properties arises from their conjugated macrocycle units. The synthesized molecule must be soluble either in organic solvents or water in order to obtain and study new properties by derivatization [30]. This issue could be coped with two ways. One, by substituting the bulky groups in peripheral positions or non-peripheral positions. Two, changing the central metal atom that can bind solvents [2].

Schiff base chemistry is a versatile tool in organic synthesis and

has impressive various achievements. It has played an important role in the development of coordination chemistry. Most of the articles are about to form complexes with transition metals [31]. Schiff bases are important for various fields of chemistry and biochemistry because of having the biological activity. They are subjected to medicine, antifungal, antibacterial and anticancer researches [32,33]. Furthermore many studies of these compounds have been published on the complexation with metals for the construction of new molecular materials since they have attractive biological, catalytic and physicochemical properties [34–39]. In addition to all those mentioned above schiff bases have photochromic properties [40–43]. Combining the schiff bases with phthalocyanines will reveal interesting new features. Schiff base substitutes phthalocyanines could make complexes with many metals, have photoluminescence properties and have chance to use as a catalyst. In this study we have investigated redox chemistry, spectroelectrochemistry and the catalytic activity of metallophthalocyanines combined with a schiff base. The oxidation of 2-mercaptoethanol was investigated for Co(II)phthalocyanine as catalytic activity.

The newly designed MPcs having imine moiety on their peripheral positions were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MALDI-TOF, and UV/Vis spectra. In this study, I report the preparation and characterization of new imine substituted

\* Tel.: +90 264 295 60 49; fax: +90 264 295 59 50.

E-mail address: [karaca@sakarya.edu.tr](mailto:karaca@sakarya.edu.tr).

phthalocyanines and their redox chemistry, spectroelectrochemistry and catalytic activity in oxidation of 2-mercaptoethanol.

## 2. Experimental

### 2.1. General

All glassware was heated at 150 °C for 1 h and then was cooled under inert atmosphere of nitrogen then was used in the experiments of this work. The reaction solvents were distilled from the indicated drying agents: DMAE (CaH<sub>2</sub>), DMF (CaH<sub>2</sub>). All fine chemicals purchased from commercial suppliers and used without further purification. Melting points of the synthesized molecules were obtained on a Barnstead Electrothermal 9200 model melting point apparatus. Thick-walled glass column was used for flash column chromatography with flash grade silica (Merck Silica Gel 60). The precoated silica gel plate (Merck Silica Gel PF-254) was used to achieve the reaction monitoring through thin layer chromatography (TLC). UV-light and polymolibdenum phosphoric acid in ethanol was used to visualize the spots on the TLC plate. All extracts were dried over anhydrous magnesium sulfate and solvents was evaporated under vacuum by using a rotary evaporator.

### 2.2. Spectroscopy

The NMR spectra, <sup>1</sup>H NMR and <sup>13</sup>C NMR, were taken in CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> on a VARIAN Infinity Plus 300 MHz NMR spectrometer. Chemical shifts were expressed in ppm relative to CDCl<sub>3</sub> (δ7.26 and 77.0 for <sup>1</sup>H and <sup>13</sup>C NMR, respectively) and DMSO-*d*<sub>6</sub> as the internal standards. For recording of Infrared spectra a Perkin Elmer Spectrum Two FT-IR spectrometer was used. HRMS and MALDI-TOF spectra were taken on Bruker Daltonics flexAnalysis. UV–visible spectroscopy was measured on a Shimadzu UV 2600 model Spectrophotometer.

### 2.3. Catalytic oxidation of 2-mercaptoethanol

Catalytic oxidation of 2-mercaptoethanol was carried out by CyberScan DO 300 dissolved oxygen meter in the closed system. 0.148 μmol Co(II)phthalocyanine (Co(II)Pc) (Pc-7) was dissolved in 50 mL THF. Reaction vessel was bubbled with air in order to obtain oxygen saturation in the solution. Then 14.7 μL (2.07 mmol) 2-mercaptoethanol was added. The molar ratio 2-mercaptoethanol as substrate to Co(II)phthalocyanine as catalyst was 14,000:1 and this was a good ratio for catalytic studies. After adding the 2-mercaptoethanol 1 mL of 0.25 wt% aqueous sodium hydroxide solution was added to the reaction vessel and system was closed. The measurement of the residual oxygen in the reaction mixture was started at the same time. The oxygen level was measured then time dependent oxygen consumption was calculated. The catalytic activity of Co(II)phthalocyanine Pc-7 is characterized by turnover number TON (conversion mol oxygen per mol phthalocyanine), initial reaction rate (μmol oxygen consumption per second) and the oxygen consumption (μmol/min) [44–46].

### 2.4. Synthesis

#### 2.4.1. (E)-4-((phenylimino)methyl)phenol, **3**

1 g (8.19 mmol) of 4-hydroxybenzaldehyde (**1**) and 763 mg (8.18 mmol) of aniline (**2**) were mixed in the methanol (MeOH) in a round-bottomed flask. The reaction mixture was stirred under nitrogen atmosphere at 60 °C for 24 h. The reaction mixture was refluxed under vacuum and washed with a little methanol. Recrystallized in methanol and columned by hexane: ethyl acetate.

Bright yellow solid (1.196 g, 74.1% chemical yield). Melting point: between 191 and 197 °C. Soluble in common organic solvents such as dichloromethane, chloroform, ethyl acetate, hexane, ACN. FT-IR (ATR System, cm<sup>-1</sup>): 3046, 3030, 3003, 2864, 2792, 1829, 1611, 1601, 1573, 1514, 1484, 1477, 1442, 1402, 1386, 1316, 1308, 1283, 1264, 1240, 1189, 1163, 1110, 1078, 1022, 1000, 977, 967, 934, 879, 840, 816, 792, 722, 621. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ8.18 (s, 1H), 7.63–7.56 (m, 2H), 7.27–7.16 (m, 2H), 7.06–6.93 (m 3H), 6.81–6.71 (m, 2H), 6.59–6.48 (m, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 163.7, 161.0, 160.2, 156.8, 132.3, 130.9, 129.3, 129.2, 120.9, 118.7, 116.1, 116.0, 115.5. HRMS: *m/z* [M] calcd.197.08 For C<sub>13</sub>H<sub>11</sub>NO: found [M+H]<sup>+</sup>198.1.

#### 2.4.2. (E)-4-4-((phenylimino)methyl)phenoxy)phthalonitrile, **5**

377 mg **3** (1.91 mmol) and 331 mg 4-nitrophthalonitril (1.91 mmol) were dissolved in 10 mL of DMSO in a round-bottom flask and stirred under the nitrogen atmosphere for 30 min. Potassium carbonate (301 mg, 2.17 mmol) was added then continued stirring for 24 h. The reaction was monitored by TLC. The mixture was poured into 40 mL cold water. The white solid was obtained and filtered through a sintered funnel then dried over MgSO<sub>4</sub> in chloroform. The obtained product was columned by hexane: ethyl acetate. The white solid (0.367 g, 59.3% chemical yield). Melting point: 177.178 °C. FT-IR (ATR System, cm<sup>-1</sup>): 3084, 3051, 3030, 2890, 2839, 2229, 1756, 1690, 1626, 1605, 1584, 1498, 1446, 1416, 1405, 1366, 1310, 1277, 1247, 1204, 1188, 1166, 1158, 1148, 1101, 1084, 1071, 1036, 1012, 1000, 988, 979, 955, 948, 910, 878, 851, 828, 804, 760, 743, 726, 716, 697, 648, 634, 614. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.66 (s, 1H), 8.14 (dd, *J* = 9 Hz, *J* = 3 Hz, 1H), 8.04 (dd, *J* = 9 Hz, *J* = 3 Hz, 2H), 7.90 (t, *J* = 3 Hz, 1H), 7.51 (dt, *J* = 9 Hz, *J* = 3 Hz, 1H), 7.46–7.38 (m, 2H), 7.32 (dd, *J* = 9 Hz, *J* = 3 Hz, 2H), 7.28–7.23 (m, 3H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ160.9, 160.2, 157.2, 152.0, 137.1, 134.0, 131.7 (overlapped 2C signals), 129.9 (overlapped 3C signals), 126.7, 124.2, 123.6, 121.7 (overlapped 3C signals), 120.9, 117.5, 116.6, 109.7. HRMS: *m/z* [M] calcd. 323.11 For C<sub>21</sub>H<sub>13</sub>N<sub>3</sub>O: found [M+H]<sup>+</sup> 324.1.

#### 2.4.3. Synthesis of Zinc phthalocyanine, **Pc-6**

**5** (331 mg, 1.02 mmol) was dissolved in the 15 mL mixture of DMEA/DMF (1:2). Zinc acetate dihydrate (56.2 mg, 0.26 mmol) was added to this stirring mixture then refluxed at 160 °C under the nitrogen atmosphere for 24 h. Reaction was finished after TLC controlling. Then the reaction mixture was poured into the mixture of methanol water (1:1) to stop the reaction. Obtained dark green solid was dried under vacuum and columned by hexane: ethyl acetate. Dark green solid, mp > 300 °C, (162.7 mg, 46.8% chemical yield). FT-IR (ATR System, cm<sup>-1</sup>): 3059, 2769, 2323, 2166, 2050, 1980, 1713, 1657, 1591, 1502, 1468, 1392, 1360, 1334, 1309, 1260, 1226, 1158, 1090, 1043, 1013, 943, 829, 747, 693. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ8.48–8.42 (m, 4H), 8.00–7.88 (m, 12H), 7.46–7.35 (m, 22H), 7.25–7.19 (m, 14H). MALDI-TOF MS: *m/z* [M]<sup>+</sup> calcd. For-C<sub>84</sub>H<sub>52</sub>N<sub>12</sub>O<sub>4</sub>Zn: 1356.35; found [M+4H]<sup>+</sup>1360.4. Anal. Calc. for C, 74.25; H, 3.86; N, 12.37; O, 4.71; Zn, 4.81. Found: C, 74.28; H, 3.89; N, 12.32%.

#### 2.4.4. Synthesis of Cobalt phthalocyanine, **Pc-7**

**5** (300 mg, 0.92 mmol) was dissolved in the 15 mL mixture of DMEA/DMF (1:2). Cobalt(II) acetate tetrahydrate (57 mg, 0.23 mmol) was added to this stirring mixture then refluxed at 160 °C under the nitrogen atmosphere for 24 h. Reaction was finished after TLC controlling. Then the reaction mixture was poured into the mixture of methanol water (1:1) to stop the reaction. Obtained dark green solid was dried under vacuum and columned by hexane: ethyl acetate. Dark green solid, mp > 300 °C, (146 mg, 46.5% chemical yield). FT-IR (ATR System, cm<sup>-1</sup>):3058,

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