



# Synthesis, characterization of metal-free, metallophthalocyanines and catalytic activity of cobalt phthalocyanine in cyclohexene oxidation



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## ABSTRACT

In this work, the new phthalonitrile derivative **3** bearing 4-pentylphenol **1**, metal-free phthalocyanine **4**, metallophthalocyanines **5** and **6** have been synthesized. Metal free phthalocyanine **4** and metallophthalocyanines **5** and **6** bearing four 4-(4-pentylphenoxy) groups on the periphery have prepared by cyclotetramerization of a new precursor, namely 4-(4-pentylphenoxy)phthalonitrile **3** in the presence of the corresponding divalent metal salts [Zn(II), Co(II)]. The new compounds have been characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS spectra data. The new cobalt phthalocyanine **6** has tested as a catalyst for the oxidation of cyclohexene with different oxidants, such as *tert*-butylhydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), in organic solvent. It is seen that complex **6** can selectively oxidize cyclohexene to give 2-cyclohexen-1-one as major product, 2-cyclohexen-1-ol and cyclohexene oxide as minor product. Finally, because of the minimal destruction of the catalyst, higher selectivity and conversion, TBHP has found to be best oxidant.

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## 1. Introduction

The oxidation of hydrocarbons to oxygenic compounds is an important reaction in organic chemistry for basic research and industrial manufacturing [1,2]. Oxidation of olefins to give oxygen containing value-added products like alcohols, aldehydes, ketones, acids, and epoxides are immensely significant and useful reaction in chemical and industrial applications [3]. Today, much more attention has recently been focused on the aerobic catalytic oxidation of hydrocarbons to oxygen included compounds using metal catalysts. Catalyst containing d-block metals of the periodic table are widely used as in homogeneous and heterogeneous catalytic oxidations of different alkenes, alkynes, alcohols, halides, phenols, etc. [4,5].

2-Cyclohexen-1-one, 2-cyclohexen-1-ol and cyclohexene oxide are very useful synthetic intermediates on the catalytic oxidation of cyclohexene [6–9]. Because the synthetic metalloporphyrins are used as models of cytochrome P-450, they are highly efficient homogeneous and heterogeneous catalysts for cyclohexene oxidation by various oxidants, such as *tert*-butyl hydrogenperoxide [10], iodosylbenzene [11–13] and hydrogen peroxide [14–17]. The aerobic oxidation of olefins catalyzed by metalloporphyrins is

obtaining interest from economic and environmental viewpoints [18–20].

Synthetic metal porphyrin complexes have been extensively investigated as models for the catalytic activity of cytochrome P-450 [21–24]. But unfortunately, porphyrins often degrade during the catalytic reactions. One way to solve this problem, it has been created a more resistant porphyrin ring through ring substitution using electron withdrawing axial ligands [25–31]. Another way, phthalocyanine that are more stable than porphyrins (or other remarkable ligands such as macrocyclic compounds, Schiff base) can be used oxidation processes [32–35]. Especially, metallophthalocyanine complexes are attractive oxidation catalysts and can be prepared simply and cheaply for industrial applications. Phthalocyanines have been known for more than 70 years and have been extensively used as colorants [36–38]. Moreover, they have attracted interest for a variety of uses such as non-linear optics, liquid crystals, solar cells, catalysis, photosensitizers and in different chemical sensing applications [39–42].

Because Co(II) phthalocyanines are readily available oxidation catalysts and found to transfer oxygen from various oxygen donors to alkanes, alkenes, phenols and thiols, numerous studies are carried out [35,43–54]. In this work, we report the synthesis and characterization of 4-(4-pentylphenoxy) group-substituted metal-free **4** and metallophthalocyanines **5** and **6**. Additionally, it is also aimed that Co(II) phthalocyanine **6** is used as catalysts for the oxidation of cyclohexene, with the purpose of developing product selectivity and increasing the range of products.

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## 2. Experimental

### 2.1. Materials

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All chemicals, solvents and reagent were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by a reported procedure [55]. 4-Pentylphenol **1** [56], 4-nitrophthalonitrile **2** [57] were synthesized according to the literature.

### 2.2. Equipment

FT-IR spectra were obtained on a PerkinElmer 1600 FT-IR spectrophotometer with the samples prepared as KBr pellets. Optical spectra in the UV–visible region were recorded with a PerkinElmer Lambda 25 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl<sub>3</sub>, and chemical shifts were reported (δ) relative to Me<sub>4</sub>Si as internal standard. The MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe and Agilent 1100 Series spectrometer LC/MSD. Methanol, chloroform were used as solvents in mass analysis and all mass analysis were conducted in positive ion mode. Melting points were measured on an electrothermal apparatus. A domestic microwave oven was used for all syntheses of phthalocyanines. Optical spectra in the UV–vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. Agilent Technologies 7820A equipment (30m.0.32mm.0.50 mm DB Wax capillary column, FID detector) was used for gas chromatographic measurements.

### 2.3. Synthesis

#### 2.3.1. 4-(4-Pentylphenoxy) phthalonitrile (**3**)

4-Pentylphenol **1** (2 g, 2.04 mL, 12.20 mmol) was dissolved in dry DMF (40 mL) under N<sub>2</sub> atmosphere and 4-nitrophthalonitrile **2** (2.11 g, 12.20 mmol) was added to the solution. After stirring 10 min, finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> (5.05 g, 36.60 mmol) was added portion wise within 2 h with efficient stirring. The reaction mixture was stirred under N<sub>2</sub> at 50 °C for 3 days. Then the solution was poured into ice-water (100 mL). The precipitate formed was filtered off, washed first with water until the filtrate was neutral and then diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. The crude product was crystallized from ethanol. Yield: 2.65 g (75%), mp: 57–58 °C. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3078 (Ar-H), 2953–2866 (Aliph. C–H), 2234 (C≡N), 1589, 1564, 1485, 1467, 1373, 1313, 1282, 1249, 1202, 1167, 1083, 1018, 952, 851, 728. <sup>1</sup>H NMR. (CDCl<sub>3</sub>), (δ: ppm): 7.73 (d, 1H, ArH), 7.28–7.20 (m, 4H, ArH), 6.99 (d, 1H, ArH), 2.63 (t, 2H, CH<sub>2</sub>-Ar), 1.68 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>), 1.35 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>), 0.90 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), (δ: ppm): 162.40, 151.52, 141.53, 135.61, 130.74, 121.53, 121.47, 120.68, 117.75, 115.76, 115.32, 108.67, 35.54, 31.71, 31.43, 22.76, 14.30. MS (ESI), *m/z*: 308 [M + H<sub>2</sub>O]<sup>+</sup>.

#### 2.3.2. Synthesis of metal-free phthalocyanine (**4**)

The mixture of 4-(4-pentylphenoxy)phthalonitrile **3** (0.6 g, 2.06 mmol), *n*-pentanol (3 mL) and 12 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were placed in Schlenk tube at 130 °C, for 24 h. After cooling to room temperature the reaction mixture refluxed with ethanol (45 mL) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether and dried in vacuo. After that the crude product was purified by column chromatography which is placed silicagel using chloroform as eluent. Yield: 250 mg (43%). mp > 300 °C. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3290 (N–H), 3065 (Ar-H), 2925–2855 (Aliph. C–H), 1600, 1576, 1523, 1502, 1466,

1424, 1359, 1226, 1202, 1165, 1091, 1009, 926, 821, 742. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ: ppm): 7.26–7.08 (m, 28H, ArH), 2.61 (t, 8H, CH<sub>2</sub>-Ar), 1.58 (m, 8H, CH<sub>2</sub>-CH<sub>2</sub>), 1.39 (m, 16H, CH<sub>2</sub>-CH<sub>2</sub>), 0.90 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), (δ: ppm): 161.18, 157.39, 153.14, 141.19, 133.08, 132.49, 125.47, 122.55, 120.26, 113.92, 38.25, 34.61, 34.33, 25.56, 17.11. MS (ESI), *m/z*: 1094 [M-C<sub>5</sub>H<sub>11</sub>+2]<sup>+</sup>. UV–vis (chloroform),  $\lambda_{\max}(\log \epsilon)$  nm: 704 (5.01), 668 (4.94), 640 (4.51), 611 (4.33), 336 (4.85).

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

A mixture of 4-(4-pentylphenoxy)phthalonitrile **3** (0.6 g, 2.06 mmol), Zn(CH<sub>3</sub>COO)<sub>2</sub> (0.094 g, 0.51 mmol) and 2-(dimethylamino)ethanol (6 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After the mixture was being cooled to the room temperature, it was stirred by EtOH (30 mL) addition for overnight and filtered off. The crude product was also refluxed by EtOH (50 mL) for 6 h. The obtained dark-green product was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. After cooling to room temperature the reaction mixture was dropped in hot ethanol (40 mL), the product which was filtered off. The green solid product was purified by passing through silicagel column using CHCl<sub>3</sub>:MeOH (80:20) as eluting solvent system. Yield: 0.300 g (48%), mp > 300 °C. IR (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3031 (Ar-H), 2925–2855 (Aliph. C–H), 1602, 1504, 1468, 1393, 1335, 1260, 1226, 1161, 1082, 1043, 945, 891, 819, 743. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ: ppm): 7.71 (m, 4H, ArH), 7.33–7.22 (m, 20H, ArH), 7.02 (t, 4H, ArH), 2.74 (m, 8H, CH<sub>2</sub>-Ar), 1.63 (m, 8H, CH<sub>2</sub>-CH<sub>2</sub>), 1.36 (m, 16H, CH<sub>2</sub>-CH<sub>2</sub>), 0.93 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), (δ: ppm): 159.01, 152.31, 138.76, 130.47, 130.11, 123.50, 121.51, 120.71, 119.93, 35.74, 32.06, 31.78, 22.98, 14.50. MS (ESI), *m/z*: 1094 [M-Zn-C<sub>5</sub>H<sub>11</sub>+2]<sup>+</sup>. UV–vis (chloroform),  $\lambda_{\max}(\log \epsilon)$  nm: 681 (5.16), 613 (4.42), 353 (4.80).

#### 2.3.4. Synthesis of cobalt(II) phthalocyanine (**6**)

A mixture of 4-(4-pentylphenoxy) phthalonitrile **3** (0.6 g, 2.06 mmol), CoCl<sub>2</sub> (0.066 g, 0.51 mmol) and 2-(dimethylamino)ethanol (2.5 mL) was placed in a standard Schlenk tube under nitrogen atmosphere and degassed three times. Then temperature was increased up to 130 °C. The reaction system was stirred at 130 °C for 16 h. After the reaction mixture was cooled to room temperature, it was stirred by EtOH (30 mL) addition for overnight and filtered off. The crude product was also refluxed by EtOH (50 mL) for 6 h. The obtained dark-green product was filtered off, washed with hot EtOH–MeOH and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. After cooling to room temperature the reaction mixture was dropped in hot ethanol (40 mL), the product which was filtered off. The green solid product was purified by passing through silicagel column using CHCl<sub>3</sub>:MeOH (80:20) as eluting solvent system. Yield: 0.314 g (50%), mp > 300 °C. (KBr tablet)  $\nu_{\max}/\text{cm}^{-1}$ : 3030 (Ar-H), 2924–2854 (Aliph. C–H), 1602, 1524, 1504, 1466, 1405, 1333, 1263, 1228, 1162, 1115, 1090, 1056, 1015, 956, 875, 819, 750. UV–vis (chloroform),  $\lambda_{\max}(\log \epsilon)$  nm: 674 (4.93), 611 (4.33), 329 (4.66). MS (ESI), (*m/z*): 1094 [M-Co-C<sub>5</sub>H<sub>11</sub>+2]<sup>+</sup>.

## 3. Results and discussion

### 3.1. Synthesis and characterization

Scheme 1 shows a brief schematic for the synthesis of peripherally tetra-substituted metal-free **4**, zinc **5** and cobalt phthalocyanine **6** complexes. In dry DMF, using K<sub>2</sub>CO<sub>3</sub> as the base, phthalonitrile derivative **3** was synthesized through base-catalyzed aromatic displacement of 4-nitrophthalonitrile with 4-pentylphenol. Cyclotetramerization of the phthalonitrile compound **3** in a high-boiling solvent in the presence of a few drops

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