



# Synthesis characterization and metal sensing applications of novel chalcone substituted phthalocyanines



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## ABSTRACT

The synthesis of novel metallophthalocyanines (M = Zn, Co) bearing (E)-3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one as chalcone on four of the peripheral positions were achieved. These complexes have been characterized by a combination of FT-IR, <sup>1</sup>H NMR, HRMS and UV–vis spectroscopy techniques and all the new compounds are highly soluble in most common organic solvents. In addition, metal ion binding titration properties are investigated. Cu<sup>+2</sup> and Fe<sup>+3</sup> ions were used for titration. The titration results give us the opportunity for application of metal sensing studies of phthalocyanines.

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## 1. Introduction

Metallophthalocyanines (MPcs) have widespread applications in specific areas such as dyes and catalysts [1], organic photovoltaic devices [2–6], photodynamic therapy because of having strong absorption capacity of visible light between 600 and 850 nm [7–10] and electrochemical applications [11,12] arising from their conjugated macrocycle units. For all these applications phthalocyanines would be soluble either in common organic solvents or in water. For this purpose phthalocyanines (Pcs) are derivated on their peripheral or non-peripheral position via substitution with large groups [1,12,13].

Chalcones have gained attention due to their interesting anticancer, anti-inflammatory, antioxidant, cytotoxic, antimicrobial, analgesic and antipyretic properties [14–16]. Furthermore, many chalcone derivatives are subjected to sensor investigations and applications [17–21]. The most important parameter affecting the physical and chemical properties of phthalocyanines is substituents that present in the phthalocyanine structure. In the content of this project, it is first time in the literature to investigate metal sensing ability of designed phthalocyanines containing chalcone groups with vinylphenoxy group directly attached to peripheral position of phthalocyanine ring. Recently, Pcs having chalcone moiety with methoxy acetophenone group substituted

on phthalocyanine ring has been reported by some other groups. However none of them have investigated the metal sensing properties [14,22].

It is well known from the literature that bulky peripheral substituents can be used for enhancing solubility in organic media and can prevent the aggregation [1,20]. Furthermore chalcone derivatives are not explored so much as substituent on phthalocyanines. The potential usage of chalcone as sensor is an applicable area. The derivatization of metallo Pcs with chalcones will not only give solubility to Pcs, but also gives favorable characteristic for sensing [18–22].

The newly designed MPcs having chalcone moiety on their peripheral position were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MALDI-TOF, and UV/vis spectra. Here in, we report the preparation and characterization of new chalcone substituted phthalocyanines and study their metals sensing properties. The newly designed MPcs having chalcone moiety on their peripheral position were characterized by <sup>1</sup>H NMR, IR, MALDI-TOF and UV/vis spectra.

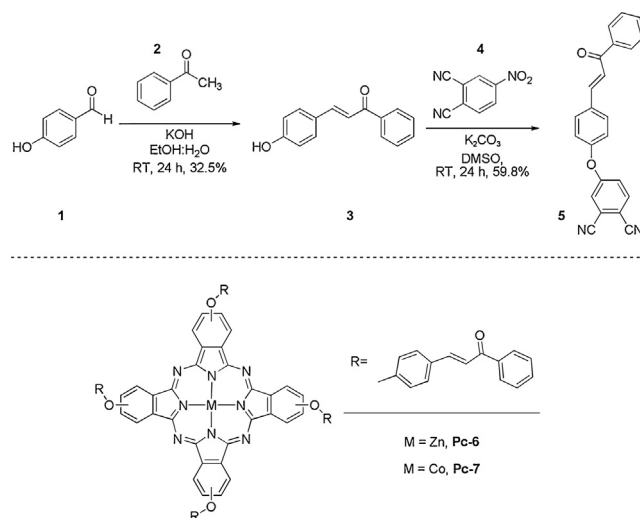
## 2. Experimental

### 2.1. General

All experiments were carried out in pre-dried glassware (1 h, 150 °C). The following reaction solvents were distilled from the indicated drying agents: DMAE (CaH<sub>2</sub>), DMF (CaH<sub>2</sub>). All other chemicals were purchased from commercial suppliers and used without further purification. Melting points were obtained on a Barnstead Electrothermal 9200 model melting point apparatus.

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**Scheme 1.** Synthesis of (E)-4-(4-(3-oxo-3-phenylprop-1-enyl)phenoxy) phthalonitrile **5** and target Pcs scaffolds.

Flash column chromatography was performed by using thick-walled glass columns with flash grade silica (Merck Silica Gel 60). The reactions were monitored by thin layer chromatography using pre-coated silica gel plates (Merck Silica Gel PF-254), visualized by UV-light and polymolybdenum phosphoric acid in ethanol as appropriate. All extracts were dried over anhydrous magnesium sulfate and solutions were concentrated under vacuum by using a rotary evaporator.

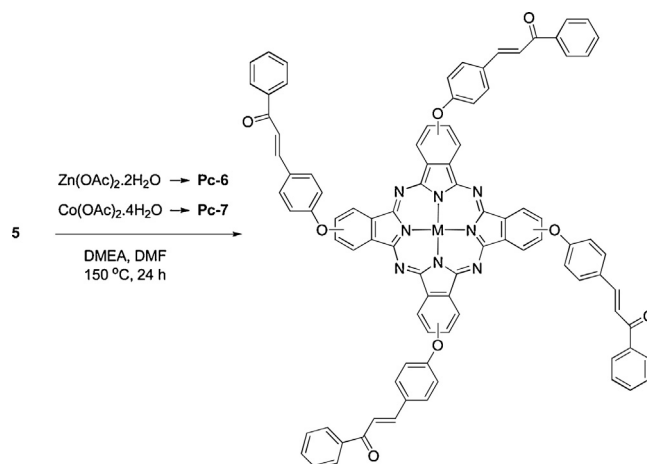
## 2.2. Spectroscopy

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  on a VARIAN Infinity Plus 300 MHz NMR spectrometer. Chemical shifts were expressed in ppm relative to  $\text{CDCl}_3$  ( $\delta$  7.26 and 77.0 for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively) and TMS as the internal standards. Infrared spectra were recorded on Perkin Elmer Spectrum Two FT-IR spectrometer. HRMS and MALDI-TOF spectra were taken on Bruker Daltonics flex Analysis. UV-vis spectroscopy was measured on a Shimadzu UV 2600 model Spectrophotometer.

## 2.3. Synthesis

### 2.3.1. (E)-3-(4-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one), **3**

4-hydroxybenzaldehyde (41.0 mmol, 5 g) was added to a stirred solution in which KOH (9.20 g) was solved in 60 mL of water-ethanol (1:1) mixture. After acetophenone (4.78 mL) was added as dropwise to this solution. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 24 h and poured in a beaker. The HCl (aq) Solution was added for neutralizing the medium. Solid was filtered in a sintered funnel, and recrystallized in ethanol. Light greenish yellow solid was obtained (mp 191 °C, 2.99 g, 32.5% chemical yield). FT-IR (ATR System,  $\text{cm}^{-1}$ ): 3164, 3019, 1647, 1598, 1579, 1555, 1509, 1373, 1348, 1322, 1282, 1216, 1183, 1166, 1108, 1040, 1020, 1001, 993, 976, 941, 896, 861, 832, 778;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.13 (s, 1H), 8.13 (d,  $J=7.32$ , 2H), 7.79–7.70 (m, 4H), 7.67–7.63 (m, 1H), 7.61–7.53 (m, 2H), 6.85 (d,  $J=8.49$ , 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ )  $\delta$  189.6, 160.8, 145.2, 138.6, 131.7 (overlapped 2C signals), 129.3 (overlapped 2C signals), 129.0 (overlapped 2C signals), 126.4 (overlapped 2C signals), 119.1, 116.5 (overlapped 2C signals). Exact mass: 224.08. HRMS:  $m/z$  [M] calcd. For  $\text{C}_{15}\text{H}_{12}\text{O}_2$ : 224.25; found [M + 2H] 226.0



**Scheme 2.** Synthesis of target phthalocyanines **Pc-6** and **Pc-7**.

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