



Synthesis of Novel Chalcone Substituted Metallophthalocyanines: Electrochemistry, Spectroelectrochemistry, and Catalytic Oxidation of 2-mercaptoethanol

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Abstract Novel metallophthalocyanines (M = Zn, Co) carrying four (E)-1-(furan-2-yl)-3-(4-hydroxyphenyl)prop-2-en-1-one (chalcone) at the peripheral positions were synthesized. These complexes have been characterized by a combination of infrared spectroscopy (FT-IR), proton NMR (¹H-NMR), high resolution mass spectroscopy (HRMS), and ultraviolet visible (UV-Vis) spectrophotometry techniques. Also, cyclic voltammograms of these phthalocyanines were recorded and zinc phthalocyanine has one and cobalt phthalocyanine has two reduction reactions. Spectroelectrochemical investigation shows the ring-based reduction of MPcs. **Pc-7** cobalt(II) phthalocyanine was investigated as a catalyst in the catalytic oxidation of 2-mercaptoethanol. Turnover number, initial reaction rate, and the oxygen consumption were found in the catalytic oxidation of 2-mercaptoethanol as 16.6, 0.29, 2.52, respectively.

Keywords: Chalcone, phthalocyanine, UV-Visible spectrophotometry, cyclic voltammetry, 2-mercaptoethanol.

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INTRODUCTION

Dyes and catalysts (1-4), organic photovoltaic devices (5-10), photodynamic therapy (11-14), and electrochemical applications (15-18) are phthalocyanines' widespread applications stemmed from peripheral functionalization of them. New properties of phthalocyanines arise from their conjugated macrocyclic units. The phthalocyanines should be soluble in water or in organic solvents in order to be used in these applications. Solubility could be improved by deriving on the peripheral or non-peripheral position of the phthalocyanines via substitution with large groups and by changing the metal on the core of the phthalocyanines (19-23).

Chalcones have the following characteristics: Anticancer, anti-inflammatory, antioxidant, cytotoxic, antimicrobial, analgesic and antipyretic (24,25). In recent years, chalcones are investigated as sensors and biological activities. The substituents on the periphery of phthalocyanines effect the physical and chemical properties. In this paper, the chalcone group with furan is directly attached to the phthalonitrile and then newly designed phthalocyanines were obtained (24-30). Chalcone group is electron-rich and has a high absorption property. It is estimated that the electron flow is realized from the chalcone groups located in the peripheral structure towards the phthalocyanine ring. Therefore, this gives usability to these molecules when they are used in dye sensitized solar cells as sensitizer. In addition, it is thought that electron-rich structure of chalcones positively contribute to the catalytic effect of phthalocyanine.

Mercaptans are thiol compounds and have environmental pollutant properties. The removal of mercaptans is not only important in terms of preventing environmental pollution. In addition, the mercaptan eliminates the effects of catalysts added to petroleum products such as petroleum and diesel to improve performance. So the mercaptan oxidation process is used to remove the thiols. Mercaptan oxidation occurs by means of oxygen in the air through catalysts. Both homogeneous and heterogeneous catalysts have been used for the oxidation of thiols (37-40).

In this study, novel MPcs having four chalcone moiety on their peripheral positions were synthesized and characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FTIR, MALDI-TOF, and UV/Vis spectra. These phthalocyanines have potential for applications as a multifunctional material in future studies.

EXPERIMENTAL

General

All experimental runs of this work were carried out with a pre-dried glass substrate heated at 150 °C for 1 hour and then cooled under an inert nitrogen atmosphere. Then the reaction solvents are distilled from the specified drying agents: 2-Dimethylaminoethanol, DMAE, N,N-Dimethylformamide, DMF (CaH₂). All fine chemicals were 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.

The thick-walled glass columns were used for flash column chromatography with flash grade silica (Merck Silica Gel 60). The reaction monitoring was achieved by thin layer chromatography (TLC) using pre-coated silica gel plates (Merck Silica Gel PF-254), visualized under UV-light and polymolybdenum phosphoric acid in ethanol as appropriate. All extracts obtained were dried over anhydrous magnesium sulfate and solvents was evaporated under vacuum by using a rotary evaporator.

Spectroscopy

The NMR spectra, ¹H NMR and ¹³C NMR were taken in deuterio chloroform (CDCl₃) and deuterio DMSO (DMSO-d₆) on a VARIAN Infinity Plus 300 MHz NMR spectrometer. Chemical shifts were expressed in ppm relative to CDCl₃ (δ7.26 and 77.0 for ¹H and ¹³C NMR, respectively) and DMSO-d₆ 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.

Catalytic oxidation of 2-mercaptoethanol

A CyberScan DO 300 model dissolved oxygen meter was used to achieve catalytic oxidation of 2-mercaptoethanol. 0.152 micromole (μmol) Co(II) phthalocyanine (Co(II)Pc) (**Pc-7**) was dissolved in 50 mL of THF. The reaction vessel was bubbled with air in order to obtain oxygen saturation in the solution. 7,3 μL (1.52 millimole (mmol)) 2-mercaptoethanol was added. The molar ratio 2-mercaptoethanol as substrate to Co(II)phthalocyanine as catalyst was 10000:1. Then 1 mL of 0.25 wt% aqueous sodium hydroxide solution was added to the reaction vessel. The recording of the oxygen in the reaction mixture was started at the same time. Then time-dependent oxygen consumption was calculated. The catalytic activity of Co(II) phthalocyanine **Pc-7** is characterized by turnover number TON (conversion of mol oxygen per mol phthalocyanine), initial reaction rate (μmol oxygen consumption per second) and the oxygen consumption (μmol/min) (31-33).

Synthesis

Synthesis of (E)-1-(furan-2-yl)-3-(4-hydroxyphenyl)prop-2-en-1-one, (chalcone), 3

KOH solution (16 mL, 10%) and ethanol (32 mL) were mixed in a round-bottomed flask. 2 g of 4-hydroxybenzaldehyde (16.4 mmol) was added into the prepared solution and stirring was continued for 15 minutes. 1.9 g of 1-(furan-2-yl)ethanone **2** (17.2 mmol) was added into the stirring solution. The reaction mixture was continued to stir under nitrogen atmosphere for 24 h. The reaction mixture was poured in a beaker, dilute aqueous HCl solution was added for neutralizing. Solid was filtered over a sintered funnel, recrystallized in ethanol and chromatographed by eluting with ethyl acetate:hexane (ratio is 1:3). Greenish yellow solid (2.99 g, 21.9% chemical yield). Soluble in ethylacetate, acetonitrile and tetrahydrofuran. FT-IR (ATR, cm^{-1}): 3379, 3193, 3174, 3132, 3025, 2971, 2821, 1739, 1643, 1609, 1574, 1508, 1549, 1461, 1379, 1343, 1275, 1225, 1171, 1156, 1086, 1049, 1014, 988, 926, 881, 824, 766, 737. ^1H NMR (300 MHz, DMSO-d_6) δ 8.04 (dd, $J=1.76$, $J=0.59$, 1H), 7.75 (dd, $J=3.51$, $J=0.59$, 2H), 7.73-7.68 (m, 2H), 7.65 (s, 1H), 7.50 (d, $J=15.82$, 1H), 6.86-6.82 (m, 2H), 6.79-6.76 (m, 1H), ^{13}C NMR (75 MHz, DMSO-d_6) δ 177.4, 160.8, 158.1, 153.8, 148.7, 143.9, 131.6, 126.2, 119.5, 119.0 (overlapped 2C signals), 116.5, 113.3. Exact mass: 214.06. HRMS: m/z [M] calcd. For $\text{C}_{13}\text{H}_{10}\text{O}_3$: 214.06; found $[\text{M}+\text{H}]^+$ 215.7 and $[\text{M}+\text{Na}]^+$ 237.6

Synthesis of chalcone-substituted phthalonitrile, 5

Compound **3** (670 mg, 3.1 mmol) and 4-nitrophthalonitrile (540 mg, 3.1 mmol) were dissolved in 12 mL of DMSO in a round-bottomed flask and stirred under nitrogen atmosphere. Potassium carbonate (861 mg, 6.2 mmol) was added and stirring was continued for 24 h. The reaction was monitored by TLC. The mixture was poured into 50 mL cold water. The grey solid obtained was filtered through a sintered funnel, washed with methanol, and dried under vacuum, then separated by column chromatography by eluting with ethyl acetate : hexane (ratio is 1:3, v:v). (421 mg, 39.7% chemical yield). FT-IR (ATR, cm^{-1}): 3146, 3132, 3108, 3073, 3043, 2227, 1661, 1605, 1588, 1561, 1507, 1483, 1465, 1411, 1397, 1341, 1294, 1281, 1248, 1219, 1201, 1181, 1168, 1158, 1117, 1085, 1053, 1016, 983, 954, 930, 894, 884, 870, 854, 831, 826, 816, 764. ^1H NMR (300 MHz, CDCl_3) δ 8.13 (d, $J=8.49$, 1H), 8.07 (s, 1H), 7.98 (d, $J=7.91$, 2H), 7.87 (d, $J=12.59$, 2H), 7.80-7.67 (m, 2H), 7.48 (d, $J=9.08$, 1H), 7.27 (d, $J=8.20$, 2H), 6.80 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 177.9, 161.2, 155.6, 153.8, 147.0, 142.4, 140.0, 135.8, 133.0, 131.1 (overlapped 2C signals), 122.3, 122.1 (overlapped 2C signals), 122.0, 121.1, 118.1 (overlapped 2C signals), 115.5, 113.0, 109.8, Exact mass: 340.08. HRMS: m/z [M] calcd. For $\text{C}_{21}\text{H}_{12}\text{N}_2\text{O}_3$: 340.33; found $[\text{M}+\text{H}]^+$ 341.4 and $[\text{M}+\text{Na}]^+$ 363.5

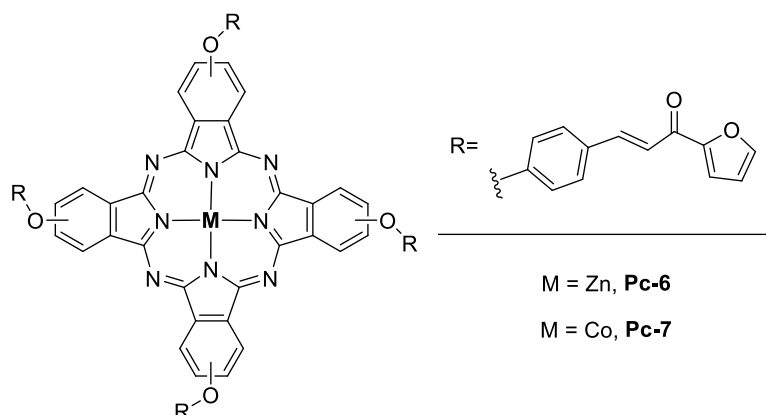
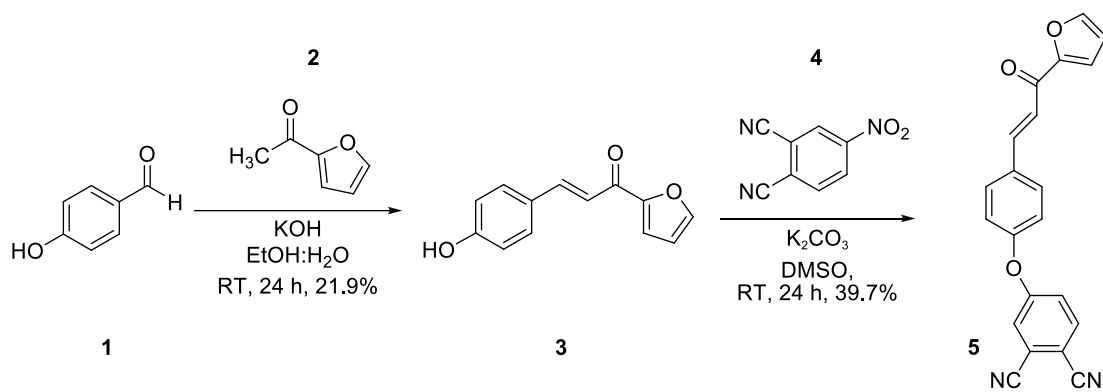
Synthesis of chalcone substituted zinc phthalocyanine, Pc-6

Compound **5** (200 mg, 0.59 mmol) was dissolved in the 6 mL mixture of DMAE/DMF (1:2 v:v). Zinc acetate dihydrate (32.6 mg, 0.15 mmol) was added to this stirring mixture, and then

refluxed under nitrogen atmosphere for 24 h. After finishing the reaction, methanol:water (ratio is 1:1 v:v) was used to stop the reaction and to obtain the precipitate. The obtained dark green solid was centrifuged. The solid was dried in a vacuum incubator and purified by column chromatography (elution with ethyl acetate : hexane (ratio is 1:3)). Dark green solid, mp >300 °C, (162.7 mg, 76.3% chemical yield). FT-IR (ATR, cm^{-1}):3125, 3063, 2924, 2853, 1768, 1713, 1657, 1591, 1504, 1464, 1387, 1358, 1333, 1310, 1292, 1259, 1228, 1165, 1086, 1044, 1013, 986, 943, 923, 883, 830, 759, 746. ^1H NMR (300 MHz, DMSO-d_6) δ 8.11-8.08 (m, 5H), 8.02-7.95 (m, 13H), 7.88-7.83 (m, 8H), 7.78-7.71 (m, 8H), 7.46-7.41 (m, 5H), 7.36-7.33 (m, 3H), 7.28-7.23 (m, 6H), 6.84-6.79 (m 4H). MALDI-TOF MS: m/z $[\text{M}]^+$ calcd. For $\text{C}_{84}\text{H}_{48}\text{N}_8\text{O}_{12}\text{Zn}$: 1422.78; found $[\text{M}+4\text{H}]^+$ 1426.8. Anal. Calc. for C, 70.71; H, 3.39; N, 7.85; O, 13.46; Zn, 4.58, Found: C, 70,7; H, 3.4; N, 7.8 %.

Synthesis of chalcone substituted Cobalt phthalocyanine, Pc-7

Compound **5** (220 mg, 0.65 mmol) was dissolved in a 6 mL mixture of DMAE/DMF (1:2). Cobalt(II) acetate tetrahydrate (41.4 mg, 0.16 mmol) was added to this stirring mixture then refluxed under the nitrogen atmosphere for 24 h. After finishing the reaction, methanol/water mixture (1:1 v:v) was used to stop the reaction and to obtain the precipitate. The obtained dark green solid was centrifuged. The solid was dried in a vacuum incubator and column chromatography was applied by eluting with ethyl acetate : n-hexane (ratio is 1:3 v:v). Dark green solid, mp >300 °C, (163 mg, 71.2% chemical yield). FT-IR (ATR System, cm^{-1}):3124, 2922, 1713, 1657, 1591, 1503, 1463, 1393, 1328, 1290, 1229, 1163, 1117, 1087, 1043, 1011, 955, 922, 882, 824, 751. MALDI-TOF MS: m/z $[\text{M}]^+$ calcd. For $\text{C}_{84}\text{H}_{48}\text{N}_8\text{O}_{12}\text{Co}$: 1424.3; found $[\text{M}-5\text{H}]^+$ 1419.2., Anal. Calc. For C, 71.04; H, 3.41; Co, 4.15; N, 7.89; O, 13.52., Found: C, 71.0; H, 3.4; N, 7.9 %.



Scheme 1. Synthesis of (E)-4-(4-(3-(furan-2-yl)-3-oxoprop-1-enyl)phenoxy)phthalonitrile **5** and target Pc scaffolds.

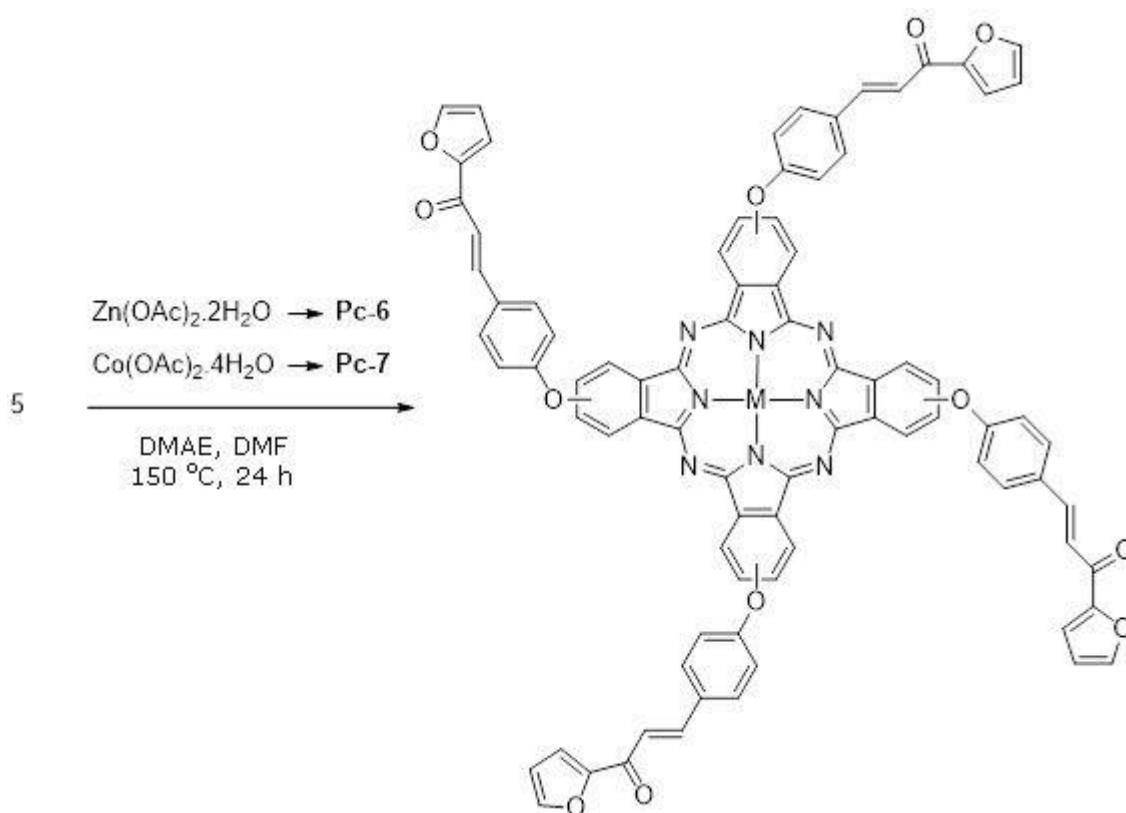
RESULTS AND DISCUSSION

Synthesis

The literature about phthalocyanine shows us that in order to enhance solubility and to prevent aggregation in organic media or water, bulky substituents could be used as peripheral or non-peripheral substituents of phthalocyanines. Furthermore, changing the metal in the phthalocyanine center affects the solubility of the phthalocyanines (1,26). We used chalcone **3** in this research as a bulky substituent synthesized from 4-hydroxybenzaldehyde and 2-acetylfuran in the mixture of ethanol and water by using KOH as the harsh alkaline media. The reaction has given 21.9% yield. Then the novel chalcone-derived phthalonitrile **5** was obtained from the nucleophilic aromatic substitution (**S_NAr**) type substitution reaction between chalcone **3** and 4-nitro-2,6-dicyanobenzonitrile **4**, after the column chromatographic isolation chemical yield was calculated as 39.7% (Scheme 1). Moreover, chalcone-derived phthalocyanines are newly discovered for synthesis and application. Chalcones have metal sensing potential along with biological activity. So, deriving metallo Pcs with chalcones will give solubility and these phthalocyanines will be mentioned in the new researches about biologic activity of Pcs and characteristics for sensing (25-30).

The molecular structures of **3** and **5** are described on the basis of ^1H and ^{13}C NMR spectra and approved by FT-IR spectra. The obtained phthalonitrile **5** was used for the synthesis of metallophthalocyanines **Pc-6** and **Pc-7**. In the synthetic routes of Pcs, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ salts were used to give center ions to Pcs respectively Zn^{2+} and Co^{2+} in the cyclotetramerization reaction of **5**, using DMEA as the catalyst at high temperature, an isomeric mixture of the desired metallo-Pcs **Pc-6** and **Pc-7** as expected (Scheme 2). The ^1H NMR spectra of **Pc-6** was recorded in DMSO-d_6 .

Pc-6 is soluble in DMSO, so the ^1H NMR spectra for **Pc-6** was carried out in DMSO-d_6 . **Pc-7** is well soluble in both DMSO and DMF. Both phthalocyanines are soluble in the mixture of DMSO-water. The structures of novel Pc compounds **Pc-6** and **Pc-7** were characterized by FTIR, UV-Vis, ^1H and ^{13}C NMR, and MALDI-TOF techniques.



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

Structure Elucidation

The FT-IR spectrum of all synthesized species clearly shows that the products desired in all steps are obtained as intended.

The C=O carbonyl bonds stretching vibrations can be attributed to the bands appearing at 1661 cm^{-1} for compound **5**. After the cyclotetramerization of phthalonitrile **5**, this band shifts to 1713 cm^{-1} for both **Pc-6** and **Pc-7**. The band observed at 1605 cm^{-1} for compound **5** was assigned to C=C bonds stretching vibration. After the synthesis of phthalocyanines this band

shifts to 1657 cm^{-1} for both **Pc-6** and **Pc-7**. The FT-IR spectra of **5** gives us the specific information on the synthesis of chalcone-derived phthalonitrile shows the disappearance of the characteristic broad band at 3193 cm^{-1} which can be referred to hydroxyl on the chalcone **3**. Additionally, the strong characteristic single band at 2227 cm^{-1} can be referred to as the CN vibration which was observed clearly. The disappearance of this characteristic signal at 2227 cm^{-1} in the FT-IR spectrum of both **Pc-6** and **Pc-7** have been accepted as a proof of cyclotetramerization of the monomer **5**. The other bands under 2000 cm^{-1} do not have considering changes. Absorption bands at 3125, 3063, 2924, 2853, 1768, 1713, 1657, 1652, 1591, 1504, 1464, 1387, 1358, 1333, 1310, 1292, 1259, 1228, 1165, 1086, 1044, 1013, 986, 943, 923, 883, 830, 759, and 746 cm^{-1} are observed for **Pc-6**; these can be attributed to phthalocyanine's skeletal vibrations (31). **Pc-7** also shows very similar peaks between $751\text{--}3124\text{ cm}^{-1}$. Because of having aromatic structures for **3** and **5**, the NMR spectra of **3** and **5** have peaks in between 6-8 ppm, similar to starting phthalonitriles. The ^1H -NMR spectra of the phthalocyanines show the peaks in the aromatic region with small chemical shift differences (Figure 1).

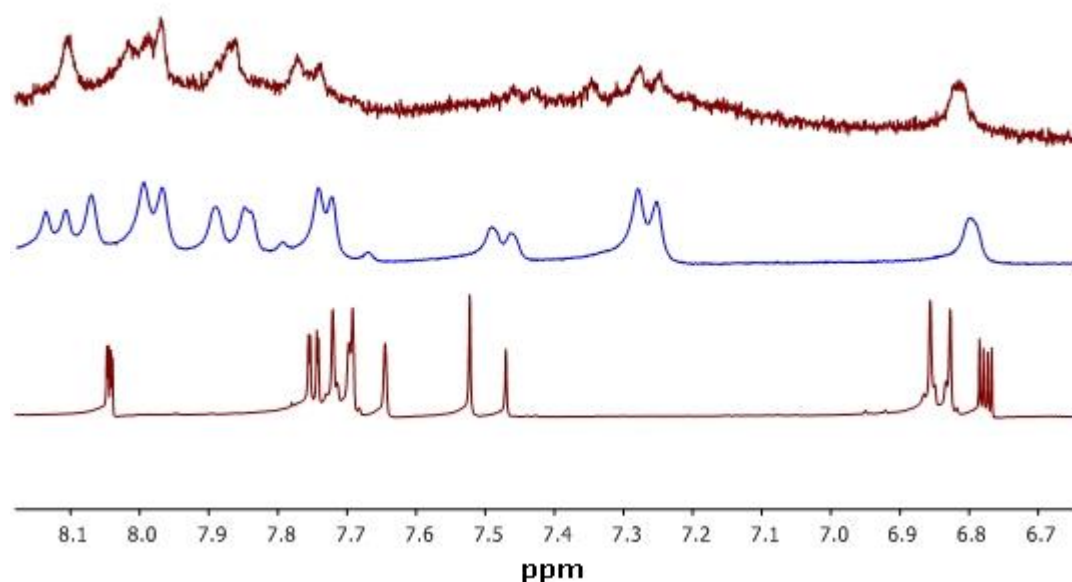


Figure 1. Expanded ^1H NMR spectrum of compounds **3** (bottom), **5** (middle) and **Pc-6** (top).

The mass spectra of phthalocyanines **Pc-6** and **Pc-7** were also acquired. Molecular ion peaks are identified as 1426.8 for $[\text{M}+4\text{H}]^+$ for **Pc-6** and as 1419.2 for $[\text{M}+4\text{H}]^+$ for **Pc-7**.

UV-Vis absorption spectra

The UV-Visible spectra of **Pc-6** and **Pc-7** are recorded in a mixture of DMSO: water (1: 4 ratio, v:v) in DMSO and a wide range of 10^{-6} M and 10^{-5} M . The electronic absorption spectrum in between 300 nm and 750 nm for both solvent systems can be seen in Figures 2 and 3, respectively. All of the absorption spectra show about 330 nm typical Soret band for **Pc-6** and **Pc-7**. Figures 2 and 3 show typical non-aggregated phthalocyanines. Figure 2a shows that **Pc-6** has a strong Q band at 678 nm in DMSO, having a shoulder at 641 nm with a vibronic band

at 611 nm and also a Soret band peaking at 334 nm. Figure 2b, on the other hand, shows that **Pc-6** has a strong Q band at 684 nm in the mixture of DMSO:water (1:4, v:v) with a vibronic band at 637 nm and also a Soret band peaking at 335 nm. Figure 3a shows **Pc-7** gives a weaker but clear Q band at 668 nm, having a shoulder at 617 nm and a Soret band at 332 nm. Figure 3b shows that **Pc-7** has a strong Q band at 679 nm in the mixture of DMSO:water (1:4) having a shoulder at 622 nm and also a Soret band at 329 nm. Non-aggregation behavior of both **Pc-6** and **Pc-7** phthalocyanines can be seen clearly in the insets of Figures 2 and 3. So both Pcs are able to use for water soluble applications.

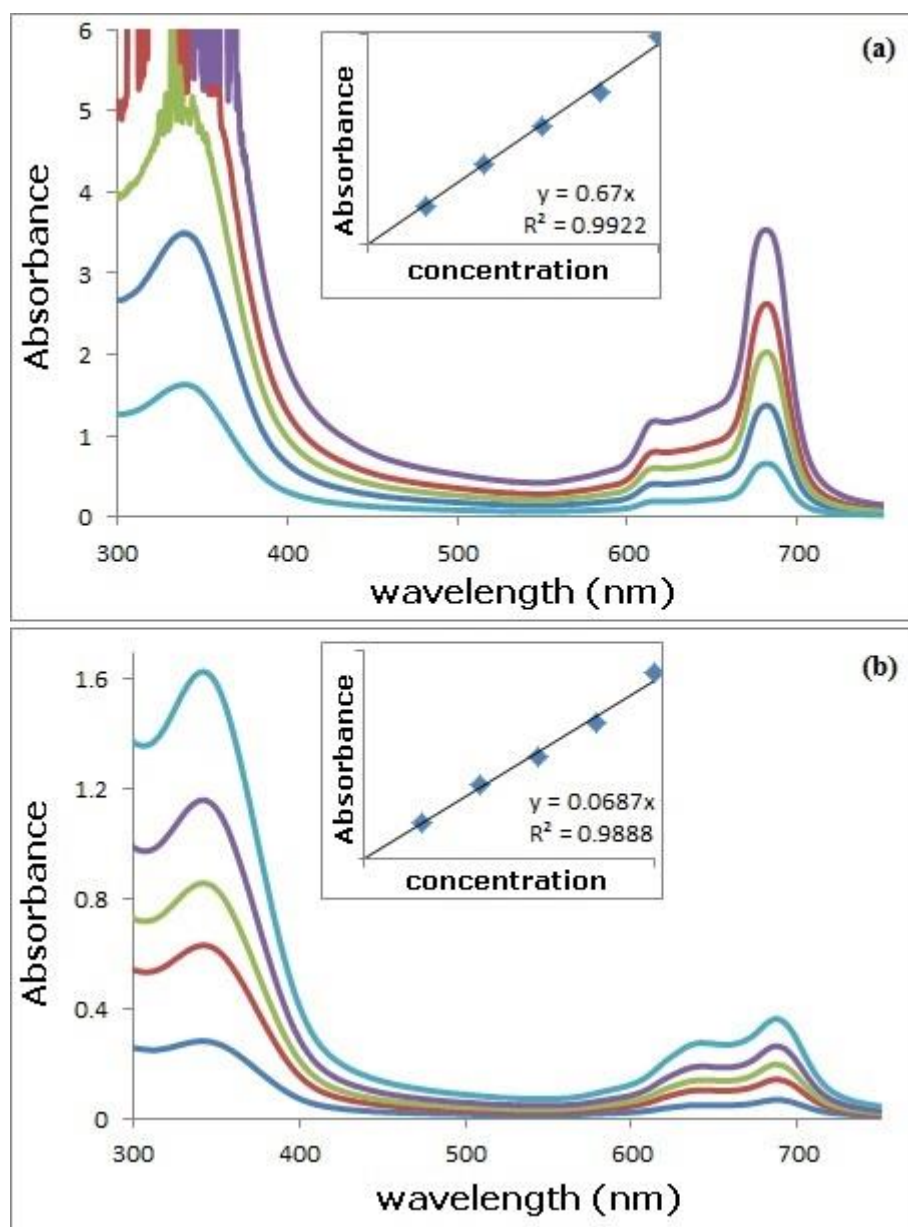


Figure 2. Comparison of the electronic absorption spectra in different concentration (from 10^{-6} M to 10^{-5} M) in the range of 400-750 nm for **Pc-6** (a) in DMSO, (b) in DMSO:water (1:4 ratio).

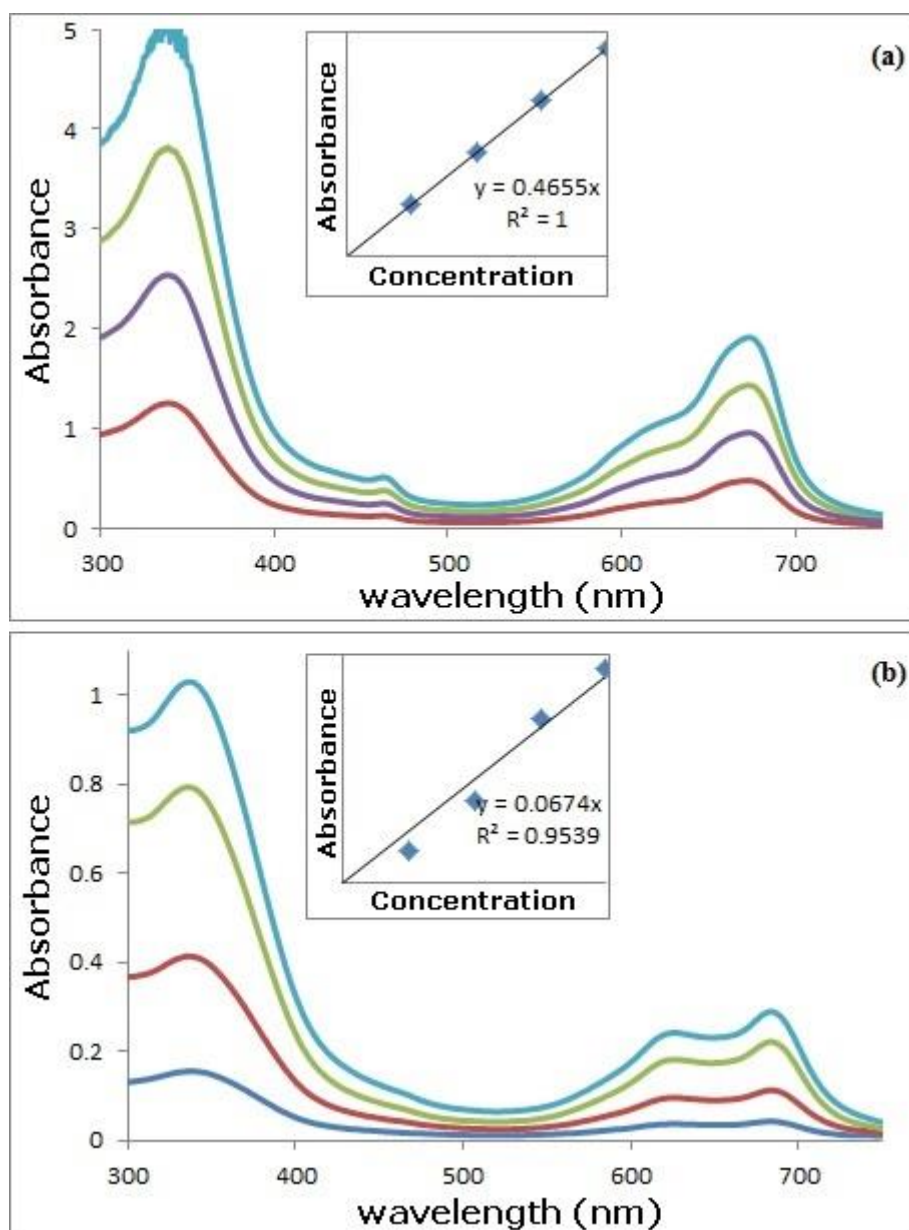


Figure 3. Comparison of the electronic absorption spectra in different concentration (from 10^{-6} M to 10^{-5} M) in the range of 400-750 nm for **Pc-7** and (a) in DMSO (b) in DMSO:water (1:4 ratio)

Cyclic voltammetric measurements

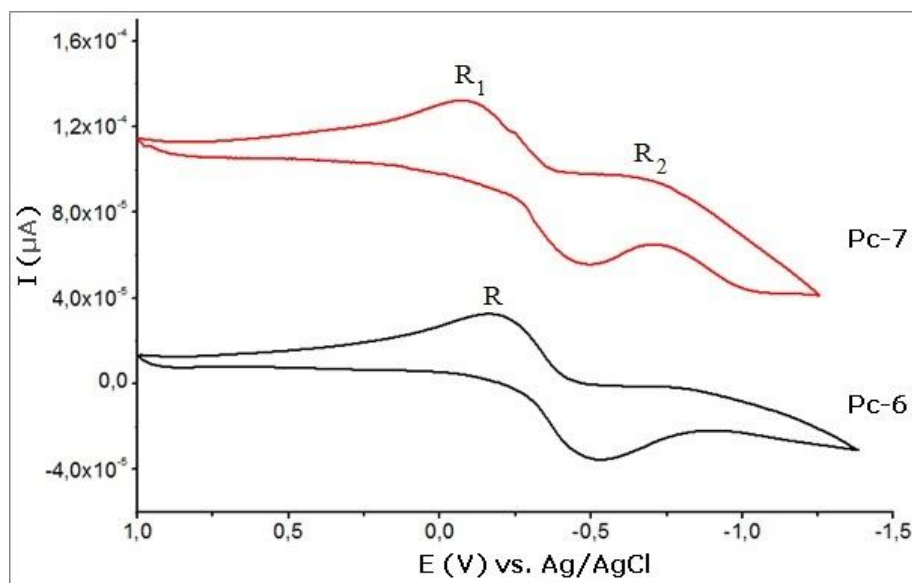


Figure 4. CVs of Zinc phthalocyanine, **Pc-6** and cobalt(II)phthalocyanine, **Pc-7** recorded at 100 mV/s scan rate on a Pt working electrode in DMSO/TBAP for Zinc phthalocyanine, **Pc-6**, DMF/TBAP for cobalt(II)phthalocyanine, **Pc-7**.

Cyclic voltammograms (CVs) were taken with Parstat 2273 potentiostat/galvanostat. A three electrode system having a Pt working electrode, Pt counter electrode, and a Ag/AgCl reference electrode was used. Extra pure dimethylsulfoxide and N,N-dimethylformamide were used to dissolve the phthalocyanines and 0.1 mol/L tetrabutylammonium perchlorate (TBAP) was used as electrolyte.

Figure 4 shows CV responses in DMSO/TBAP for **Pc-6** and DMF/TBAP **Pc-7**. It can be seen clearly from Figure 4 **Pc-6** while zinc phthalocyanine, **Pc-6**, having one reversible reduction, R at -0.22 V, cobalt phthalocyanine, **Pc-7**, has two reversible reductions, R₁ at -0.11 V and R₂ at -0.72 V. The difference that having one and two reduction reaction is coming from metal ions in the cavity of phthalocyanine.

Spectroelectrochemistry

Optically transparent thin-layer electrode cell kit was used cell in order to determine the nature of the redox processes in spectroelectrochemical studies.

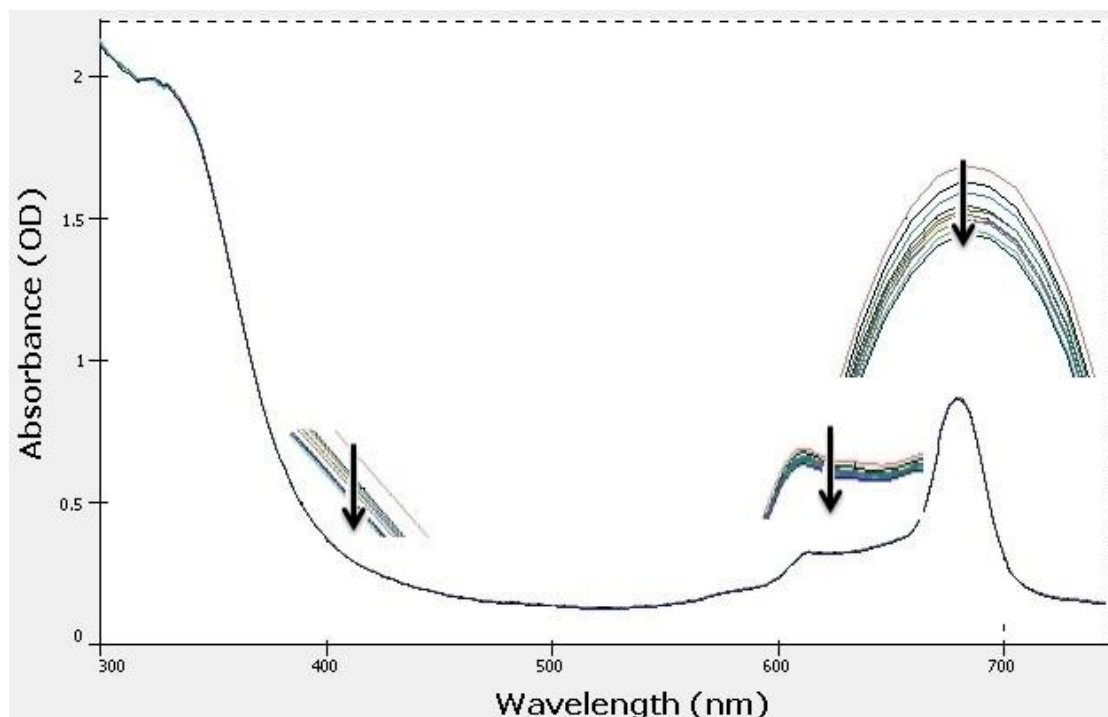


Figure 5. UV-Vis spectral changes of complex **Pc-6** in DMSO containing 0.1 M TBAP observed during application of controlled potential at -0.25 V.

Figure 5 shows UV-Visible spectral changes when the reduction potential at -0.25 V for **Pc-6** with a slight decrease in absorption of whole range and there is no isosbestic point and shift of Q band. It is well known that an isosbestic point occurs when the spectrum collected is overlaid, and it indicates that there is a change from one state to another. The absence of isosbestic point would be interpreted in two ways; the decomposition of the molecule or there is not a change in the structure of the molecule. Decomposition is eliminated because the reduction process is renewable (Fig 4). So the molecule is not decomposing and not undergoing a structural change.

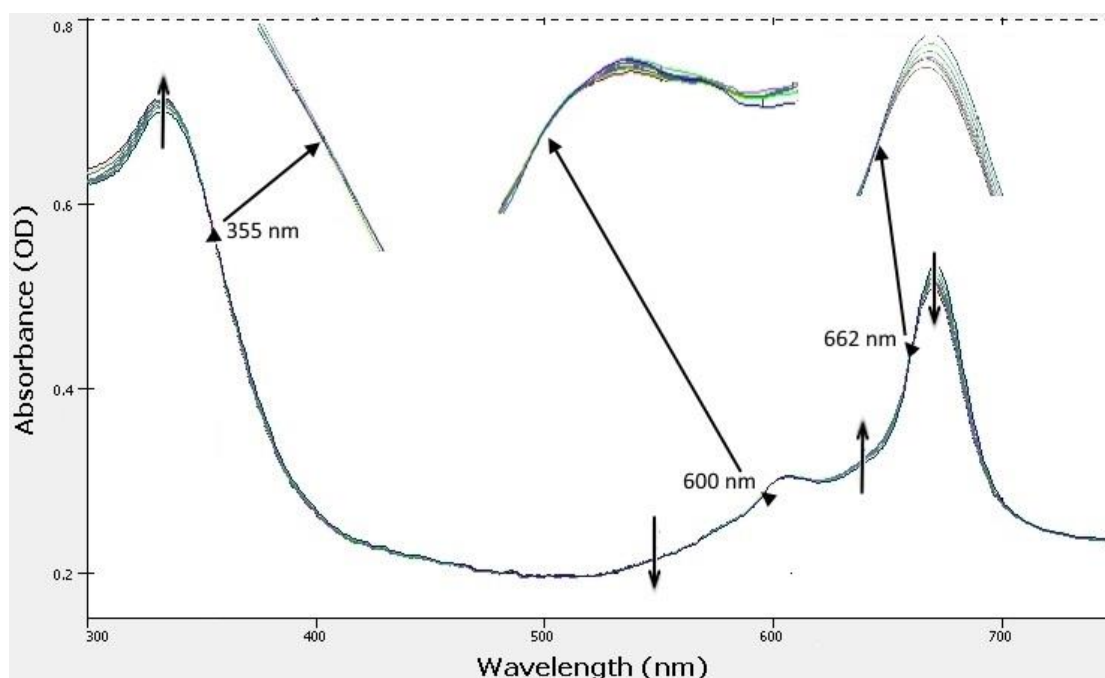
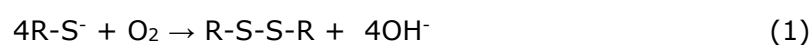


Figure 6. UV-Vis spectral changes of complex **Pc-7** in DMF containing 0.1 M TBAP observed during application of controlled potential at -0.25V.

Figure 6 shows the UV-Visible spectral changes when the reduction potential at -0.25V for **Pc-7**. There is no shift of the Q band. This spectroelectrochemical investigation was done for **Pc-7** R₁ process (Figure 4). It is agreed that there is no change to Co^IPc or Co^{II}Pc from the absence of Q band shift. Isosbestic points were observed at 355 nm, 600 nm and 662 nm. Further reduction at the potential of process R₁ (Figure 4) showed the spectral changes typical of ring-based processes. There is a decrease in the absorbance of Q band with isosbestic points mentioned above. That the Q band is not shifting is due to stabilization of the highest occupied molecular orbital (HOMO) in MPc complexes relative to the lowest unoccupied molecular orbital (LUMO) (35).

Catalytic oxidation of 2-mercaptoethanol

The catalytic activity of Co(II) phthalocyanines on the oxidation of 2-mercaptoethanol is well known application (36-40). **Pc-7** is well soluble and non-aggregated as seen in the sections above. RS⁻ ion generated by NaOH and O₂ coordinate to two axial sides of the central Co(II) in **Pc-7**. Then the electron transfer from the thiolate to oxygen via central Co(II) occurs and disulfide forms. The reaction between 2-mercaptoethanol and oxygen can be seen in equation (1).



The catalytic ratio of 2-mercaptoethanol and phthalocyanine (thiol/catalyst=10000). This reaction needs a basic media. When a small amount of NaOH solution was added to the

reaction mixture, the thiol (RSH) will immediately produce thiolate (RS^-). Then the Co(II)Pc will start to catalyze the oxidation of 2-mercaptoethanol by oxygen. TON (mol oxygen per mol phthalocyanine), initial reaction rate ($\mu\text{mol}/\text{sec}$) and the oxygen consumption ($\mu\text{mol}/\text{min}$) was calculated as 16.6, 0.29, and 2.52 respectively and oxygen consumption over time is seen on Figure 7.

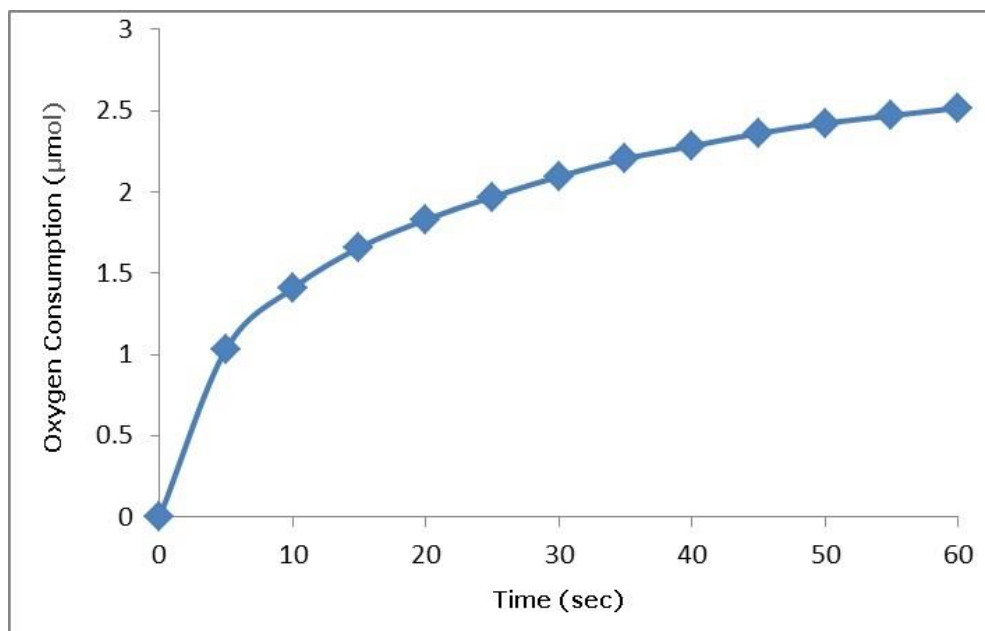


Figure 7. Oxygen consumption in the reaction of catalytic oxidation of 2-mercaptoethanol by Co(II)Pc, **Pc-7**, as catalyst in THF.

CONCLUSION

In conclusion, novel Zn(II) and Co(II) phthalocyanines which are substituted with chalcone bearing furyl moiety have been synthesized and characterized. In our synthetic route, in the presence of KOH as catalyst the chalcone group that is carrying one hydroxyl was synthesized first in the mixture of ethanol and water. Then 4-nitrophthalonitrile was derived with synthesized chalcone group via **SnAr** type substitution reaction. Widespread Pc synthetic approach was used for the direct synthesis of both **Pc-6** and **Pc-7** phthalocyanines. The synthesized chalcone in this study is newly designed and synthesized by our group. The structures of all compounds synthesized have been fully characterized by using FT-IR, ^1H NMR, ^{13}C NMR, MALDI-TOF MS, and UV-Vis spectroscopic techniques. Electronic absorption spectra showed that both Pcs are nonaggregated and also well soluble in DMSO and in the mixture of DMSO : water (1 : 4 ratio). **Pc-7** is also well soluble in DMF. Cyclic voltammograms give one reduction for **Pc-6** and two reduction for **Pc-7**. The spectroelectrochemical investigation shows the ring based reduction potential for MPC's. **Pc-7** cobalt(II) phthalocyanine was investigated as a catalyst in the catalytic oxidation of 2-mercaptoethanol. The catalytic oxidation of 2-mercaptoethanol is a widely studied reaction for the detection of catalytic activity. Turnover

number, initial reaction rate and the oxygen consumption was found in the catalytic oxidation of 2-mercaptoethanol as 16.6, 0.29, 2.52, respectively.

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