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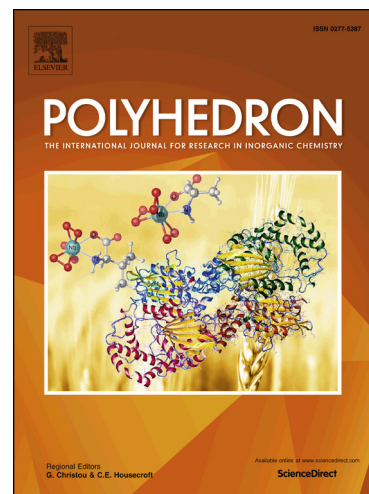
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Novel peripherally and non-peripherally hydrobenzoin substituted optically active phthalocyanines: Synthesis, characterization, aggregation, electrochemical properties and catalytic applications

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Abstract

The novel optically active two zinc(II) phthalocyanines and two cobalt(II) phthalocyanines with four chiral hydrobenzoin moieties at the non-peripheral (**4** and **5**) and peripheral positions (**6** and **7**) of the phthalocyanine ring have been synthesized. The structures of the synthesized compounds are characterized by ¹H NMR, IR, UV-Vis, Circular Dichroism (CD) and MALDI-TOF MS spectral data. The comparative studies of the spectral, aggregation properties, voltammetry and catalytic applications of novel zinc(II) and cobalt(II) phthalocyanines, tetra-substituted with hydrobenzoin at peripheral and non-peripheral positions, were investigated. All synthesized phthalocyanines are highly soluble in most common organic solvents. In the enantioselective addition of diethylzinc to aldehydes, the best catalytic activity was obtained with

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3-methoxybenzaldehyde in the presence of non-peripherally hydrobenzoin substituted zinc(II) phthalocyanine **4** and afforded the corresponding chiral secondary alcohol with the yield of 38% and the enantiomeric excess of 33%. In the oxidation of benzyl alcohol, the highest conversion of benzyl alcohol to benzaldehyde was obtained with non-peripherally substituted cobalt(II) phthalocyanine **5** as 91% with the highest selectivity of 83%.

Keywords: Optically active phthalocyanine; Catalysis; Electrochemistry; C_2 -symmetric; Chiral diol

1. Introduction

Phthalocyanines (Pcs) and their metal complexes are one of the most studied functional molecular materials in the literature due to their high thermal and chemical stability along with their unique properties such as strong UV-Vis light absorption, high molar absorption coefficients, and electron transfer abilities [1, 2]. A goal of research on the chemistry of phthalocyanines is to achieve control over the structure of synthetic molecules in order to improve their application capabilities in scientific and technological areas. For these purposes, by adding various substituents to the non-peripheral and peripheral positions of the benzene rings, numerous Pcs have been prepared with almost all metal ions in the periodic table [3-9].

Optically active compounds are ubiquitous and play a fundamental role in life, especially in the area of pharmaceutical and agricultural industries [10]. The design and synthesis of new optically active compounds is one of the most important goals in modern chemistry [11]. In spite of large academic interest, the first optically active phthalocyanines were reported in 1993 and since then, limited number of reports have explored in the synthesis of phthalocyanine bearing optically active groups [12]. Most of studies have concentrated on combining chiral binaphthol

groups with a phthalocyanine core and most of chiral substituents have been attached to the β positions of the phthalocyanine ring [13-16]. Studies on combining different chiral groups with a phthalocyanine core are still limited and spectral properties of these molecules are unknown.

Although phthalocyanines have a wide range of applications, they have not received attention for the usage in enantioselective reactions yet, which is one of the most studied areas in chemistry [17]. Enantioselective diethyl zinc addition to aldehydes is one of the most studied catalytic reactions in the field of asymmetric catalysis. The alkylation of aldehydes with organometallic reagents in the presence of a catalytic amount of a chiral molecule gives a new C-C bond in an enantioselective manner [18]. Enantioselective addition of organozinc reagents to aldehydes gives optically active pure secondary alcohols [16, 17]. These alcohols are both key compounds in the preparation of pharmaceuticals and agrochemicals and important intermediates in the synthesis of many substrates such as esters, amides, and ethers [19].

Selective oxidation of benzyl alcohol to benzaldehyde is an important organic transformation as well as the alkylation of aldehydes in organic chemistry. Benzaldehyde is a very valuable chemical which has widespread applications in perfumery, dyestuff and agrochemical industries [20, 21]. Normally, benzyl alcohol can be traditionally oxidized to benzaldehyde with various stoichiometric inorganic oxidants such as chromium reagents (pyridinium chlorochromate or dipyridine chromium(IV) oxide) and permanganates. Unfortunately, the use of these reagents is limited since they are relatively expensive, generates equal amounts of metal waste, or requires large excess of reagent be used. Therefore, the selective oxidation of benzyl alcohol using different types of oxidants such as hydrogen peroxide, tert-butylhydroperoxide or 3-chloroperbenzoic acid has been proposed to replace the present oxidation processes that use stoichiometric quantities of inorganic oxidants. Besides that, synthesis of new efficient and effective catalysts for selective catalytic oxidation of benzyl alcohol to benzaldehyde is still demanding for the industrial applications.

In this study, we report, for the first time, the synthesis, characterization, aggregation and electrochemical properties of peripheral and non-peripheral chiral C_2 -symmetric diol substituted phthalocyanine complexes, and investigation of their catalytic efficiency in the enantioselective addition of diethylzinc to aldehydes and the oxidation of benzyl alcohol. It is noteworthy that there has been no example of optically active phthalocyanines used in the enantioselective diethylzinc addition to aldehydes so far to the best of our knowledge.

2. Experimental

2.1. Materials and Equipment

(1*R*,2*R*)-1,2-diphenylethane-1,2-diol **1** was prepared according to the literature [22]. 3-nitrophthalonitrile and 4-nitrophthalonitrile were synthesized following the procedure given in the published paper [23]. All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [24]. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 400-630 mesh).

FTIR spectra were measured on a Perkin Elmer Spectrum 65 spectrometer using KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using CDCl_3 and THF-d_8 (99.9%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV-Vis region with a PG-T80+ spectrophotometer using 1 cm path length cuvettes at room temperature. Circular dichroism (CD) measurements were performed with a JASCO J-810 spectropolarimeter. Optical rotations were measured with a Rudolph Autopol-I series polarimeter. GC separations were performed on Shimadzu GC-2010 Plus. Cyclic voltammetry

and square wave voltammetry measurements were performed with the three-electrode technique using a Gamry (Interface 1000) Electrochemical Analyzer under computer control. Elemental analyses were obtained with a LECO Elemental Analyser (CHNS 0932) spectrophotometer. Melting points were determined with an electrothermal apparatus and are reported uncorrected.

2.2. Synthesis

2.2.1. 3-((1*R*,2*R*)-2-hydroxy-1',2'-diphenylethoxy)phthalonitrile (**2**, Scheme 1)

(1*R*,2*R*)-1,2-diphenylethane-1,2-diol **1** (1.5 g, 7.0 mmol) and 22.5 mL of DMSO were placed in two-neck flask under a nitrogen atmosphere at room temperature. To this reaction mixture was added 3-nitrophthalonitrile (1.2 g; 7.0 mmol) and stirred for 15 min under inert atmosphere. Finely ground anhydrous K₂CO₃ (0.97 g; 7.0 mmol) was then added to the resulting mixture at room temperature. The reaction was monitored by thin layer chromatography and completed in 2 h. The reaction mixture was poured into water-ice (1:3 v/v) resulting in the formation of light-yellow precipitate and then extracted with dichloromethane. The combined organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure to give a crude product that was purified by silica gel chromatography. The elution was carried out with dichloromethane–ethylacetate (95:5). The product was obtained as a white solid. Yield: 1.55 g, (65%); mp: 128-130 °C. Found: C, 77.34; H, 4.58; N, 8.19%; 'molecular formula C₂₂H₁₆N₂O₂' requires C, 77.63; H, 4.74; N, 8.23%. $[\alpha]_D^{20} = +237.67$ ($c = 1$, CHCl₃); retention time 15.93 min, Chiral ART Amylose-C, 30:70 *n*-hexane-*i*PrOH, flow rate of 0.5 mL/min, 254 nm, $t = 40$ °C; IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3500 (OH), 3064, 3033, 2910, 2232 (C≡N), 1734, 1579, 1462, 1285, 1043, 793, 764, 701; ¹H-NMR (400 MHz, CDCl₃, ppm) δ : 7.43 (t, $J = 8.3$ Hz, H), 7.29 (dd, $J = 7.8$ Hz, $J = 0.8$ Hz, H), 7.25-7.20 (m, 6H), 7.11 (m, 2H), 7.05 (m, 3H), 5.27 (d, $J = 7.5$ Hz, H),

5.10 (d, $J = 7.5$ Hz, H), 3.09 (br, OH); ^{13}C -NMR (100 MHz, CDCl_3 , ppm) δ : 160.3, 137.9, 135.0, 134.3, 128.9, 128.7, 128.4, 128.2, 127.3, 127.1, 121.1, 125.7, 119.0, 117.0, 115.2, 113.1, 105.8, 87.4, 77.9; MS (ESI) MS calculated $[\text{M}+\text{Cl}]^-$ for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2\text{Cl}$: 375.1 found: 375.2

2.2.2. 4-((1*R*,2*R*)-2-hydroxy-1',2'-diphenylethoxy)phthalonitrile (**3**, Scheme 1)

Synthesis of **3** was performed by following the procedure for **2** by using 4-nitrophthalonitrile (0.89 g, 4.67 mmol), **1** (1 g, 4.67 mmol) and K_2CO_3 (0.64 g, 4.67 mmol). Yield: 0.81 g, (51%); mp: 59-60 °C. Found: C, 76.89; H, 4.56; N, 7.96%; 'molecular formula $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ ' requires C, 77.63; H, 4.74; N, 8.23%. $[\alpha]_D^{20} = +9.99$ ($c = 1$, CHCl_3); retention time 17.49 min, Chiral ART Amylose-C, 30:70 *n*-hexane-*i*PrOH, flow rate of 0.5 mL/min, 254 nm, $t = 40$ °C; IR (KBr disc) $\nu_{\text{max}}/\text{cm}^{-1}$: 3472 (OH), 3063, 3034, 2909, 2231 ($\text{C}\equiv\text{N}$), 1730, 1596, 1562, 1492, 1315, 1291, 1250, 11998, 1007, 838, 764, 699; ^1H -NMR (400 MHz, CDCl_3 , ppm) δ : 7.59 (d, $J = 8.8$ Hz, H), 7.26-7.24 (m, 7H), 7.16 (dd, $J = 8.8$ Hz, $J = 2.5$ Hz, H), 7.10 (dd, $J = 7.8$ Hz, $J = 1.25$ Hz, 2H), 7.01 (dd, $J = 7.8$ Hz, $J = 1.25$ Hz, 2H), 5.21 (d, $J = 7.3$ Hz, H), 5.01 (d, $J = 7.3$ Hz, H), 2.35 (br, OH); ^{13}C -NMR (100 MHz, CDCl_3 , ppm) δ : 160.9, 138.0, 135.1, 134.9, 129.0, 128.8, 128.5, 128.3, 127.2, 127.0, 121.1, 120.7, 117.4, 115.4, 115.0, 107.9, 86.5, 78.1; MS (ESI) MS calculated $[\text{M}+\text{Cl}]^-$ for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2\text{Cl}$: 375.1 found: 375.2

2.2.3. 1(4), 8(11), 15(18), 22(25)-Tetrakis-((1*R*,2*R*)-2-hydroxy-1',2'-diphenylethoxy)phthalocyaninato zinc(II) (**4**)

3-((1*R*,2'*R*)-2-hydroxy-1',2'-diphenylethoxy)phthalonitrile **2** (0.2 g; 0.59 mmol) was reacted with anhydrous $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ (0.055 g; 0.29 mmol) in *n*-pentanol (2.5 mL) at 140 °C for 24 h in a Schlenk tube under nitrogen in order to obtain zinc(II) phthalocyanines **4**. At the end of this

period, the reaction mixture was cooled to room temperature. Solvent of the reaction mixture was evaporated under reduced pressure to give a crude product. The crude product was purified by chromatography over silica gel column with a solvent mixture hexane-diethyl ether (7:3) followed by methanol and chloroform solvents as eluents. The yield was 0.025 g (10%). mp: 222-223 °C. Found: C, 74.59; H, 4.57; N, 7.92%; 'molecular formula $C_{88}H_{64}N_8O_8Zn$ ' requires C, 74.07; H, 4.52; N, 7.85%. IR (KBr disc) ν_{max}/cm^{-1} : 3451, 3271 (OH), 3064, 3034, 2923, 1767, 1723, 1609, 1560, 1482, 1455, 1382, 1275, 1155, 1055, 749, 701. 1H -NMR (400 MHz, d_8 -THF, ppm) δ : 10.1-8.83 (m, 12H), 7.88-6.95 (m, 40H), 6.01-5.40 (m, 8H); UV-Vis (DMF): λ_{max} , nm (log ϵ): 322 (4.71), 634 (4.60), 704 (5.31); MS (MALDI-TOF) (m/z): calculated $[M+H]^+$ for $C_{88}H_{65}N_8O_8Zn$: 1425.7 found: 1425.7.

2.2.4. 1(4), 8(11), 15(18), 22(25)-Tetrakis-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]* phthalocyaninato cobalt(II) (5)

Synthesis of **5** was performed by following the procedure for **4**. Except $CoCl_2$ instead of $Zn(CH_3CO_2)_2$ was employed. The amounts of all the reagents were the same except for $CoCl_2$ (0.035 g). The crude product was purified by chromatography over silica gel column with a solvent mixture hexane-diethyl ether (5:5) followed by chloroform-methanol (98:2) solvent system as eluents. The yield was 0.43 g (21%). mp: 221-222 °C. Found: C, 74.26; H, 4.40; N, 7.61%; 'molecular formula $C_{88}H_{64}N_8O_8Co$ ' requires C, 74.71; H, 4.54; N, 7.89%. IR (KBr disc) ν_{max}/cm^{-1} : 3342 (OH), 3061, 3031, 2925, 1721, 1608, 1483, 1458, 1271, 1029, 757, 699; UV-Vis (DMF): λ_{max} , nm (log ϵ): 304 (4.54), 634 (4.18), 700 (4.72); MS (MALDI-TOF) (m/z): calculated $[M]^+$ for $C_{88}H_{64}N_8O_8Co$: 1419.4 found: 1419.4.

2.2.5. 2(3), 9(10), 16(17), 23(24)-Tetrakis-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]* phthalocyaninato zinc(II) (**6**)

Synthesis of **6** was performed by following the procedure for **4**. Except 4-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]*phthalonitrile **3** instead of 3-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]*phthalonitrile **2** was employed. The amounts of all the reagents were the same. The crude product was purified by chromatography over silica gel column with methanol followed by chloroform as the eluting solvents. The yield was 0.056 g (22%). mp: > 300 °C. Found: C, 73.77; H, 4.42; N, 7.81%; 'molecular formula C₈₈H₆₄N₈O₈Zn' requires C, 74.07; H, 4.52; N, 7.85%. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3419 (OH), 3029, 2924, 1715, 1608, 1485, 1452, 1398, 1335, 1277, 1225, 1092, 1046, 766, 746, 698; ¹H-NMR (400 MHz, d₈-THF, ppm) δ : 9.13 (m, 6H), 8.86 (m, 6H), 7.50-6.89 (m, 40H), 5.88 (m, 4H), 5.29 (m, 4H); UV-Vis (DMF): λ_{\max} , nm (log ϵ): 354 (5.03), 614(4.67), 684 (5.35); MS (MALDI-TOF) (*m/z*): calculated [M+2H]⁺ for C₈₈H₆₆N₈O₈Zn: 1426.4 found: 1426.4.

2.2.6. 2(3), 9(10), 16(17), 23(24)-Tetrakis-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]* phthalocyaninato cobalt(II) (**7**)

Synthesis of **7** was performed by following the procedure for **4**. Except 4-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]*phthalonitrile **3** (0.4 g; 1.18 mmol) and CoCl₂ (0.075 g; 0.58 mmol) instead of 3-*[(1R,2R)-2-hydroxy-1',2'-diphenylethoxy]*phthalonitrile (**2**) and Zn(CH₃CO₂)₂ respectively were employed. The crude product was purified by chromatography over silica gel column with a mixture hexane-diethyl ether (3:7) followed by chloroform-methanol (99:1) as the eluting solvents. The yield was 0.093 g (22%). mp: 297-298 °C. Found: C, 74.99; H, 4.64; N, 7.78%; 'molecular formula C₈₈H₆₄N₈O₈Co' requires C, 74.71; H, 4.54; N,

7.89%. IR (KBr disc) $\nu_{\max}/\text{cm}^{-1}$: 3552, 3436 (OH), 3062, 3033, 2903, 1709, 1612, 1524, 1477, 1411, 1343, 1275, 1230, 1137, 1064, 1013, 751, 699; UV-Vis (DMF): λ_{\max} , nm (log ϵ): 330 (5.31), 670 (5.43); MS (MALDI-TOF) (m/z): calculated $[\text{M}]^+$ for $\text{C}_{88}\text{H}_{64}\text{N}_8\text{O}_8\text{Co}$: 1419.4 found: 1419.4.

2.2.7. General procedure for the oxidation of benzyl alcohol with cobalt(II) phthalocyanines 5 and 7

A schlenk tube containing magnetic stir bar was charged with benzyl alcohol, catalyst and solvent. The schlenk tube was capped with a rubber septum and was purified with bubbling nitrogen gas to remove the oxygen for ten minutes. The oxidant was then added and the reaction mixture was stirred for the desired time. All the products and conversion of benzyl alcohol were determined by gas chromatography analysis. The catalytic reactions were monitored by GC-FID chromatograph equipped with a $30\text{ m} \times 0.25\ \mu\text{m} \times 0.25\ \mu\text{m}$ capillary column (Rxi-5ms, 95% diphenyl, 95% dimethyl polysiloxane) by comparison standards (benzaldehyde, benzoic acid and 1,4-benzoquinone).

2.2.8. General procedure for the enantioselective diethylzinc addition to aromatic aldehydes

Under an argon atmosphere, chiral ligand (0.1 mmol) was dissolved in dry solvent, $\text{Ti}(\text{OiPr})_4$ (0.94 mmol) was added and stirred for 1 h for the Ti-mediated reactions. Et_2Zn (2 mmol, 1 M in hexane) was added, and the resulting yellow solution was stirred for 20 min at rt. Aldehyde (1 mmol) was then added dropwise in 10 min. and the reaction was stirred for another 24 h at room temperature. After quenching with 1 mL saturated NH_4Cl solution, 25 mL of H_2O was added and then extracted with CH_2Cl_2 ($3 \times 25\text{ mL}$). The combined organic phases were dried over Na_2SO_4

and evaporated in vacuo. The crude product was purified by flash chromatography to give the corresponding alcohol. Enantiomeric excesses were determined by GC analysis with chiral HP-CHIRAL-B20 column.

3. Result and Discussion

3.1. Synthesis and Characterization

(1*R*,2*R*)-1,2-diphenylethane-1,2-diol substituted chiral phthalonitriles **2-3** and their optically active phthalocyanine derivatives **4-7** were synthesized according to the route shown in Scheme 1.

The reaction of 3-nitrophthalonitrile or 4-nitrophthalonitrile with (1*R*,2*R*)-1,2-diphenylethane-1,2-diol (**1**) in the presence of potassium carbonate as the base in DMSO gave the desired products 3-((1'*R*,2'*R*)-2-hydroxy-1',2'-diphenylethoxy)phthalonitrile **2** and 4-((1'*R*,2'*R*)-2-hydroxy-1',2'-diphenylethoxy)phthalonitrile **3** with moderate yields, respectively. In the IR spectrum of **2** and **3**, the presence of an intense C≡N stretching band at 2232 and 2231 cm⁻¹, the disappearance of the strong NO₂ stretching vibrations at 1350 and 1550 cm⁻¹ [25], the appearance of an OH stretching vibration at 3500 and 3472 cm⁻¹, respectively, confirmed the formation of compounds **2** and **3**. The IR spectrum of **3** is very similar to that of **2**, but with small shifts in wavenumbers. To determine the exact structure of **2** and **3**, the ¹H NMR spectrum was acquired in CDCl₃. The presence of significant resonance of OH group as broad singlet at δ = 3.09 for **2** and 2.35 for **3** ppm is agreement with the proposed structures. The aliphatic CH protons were observed as two doublets at δ = 5.27, 5.10 ppm for **2** and 5.21, 5.01 ppm for **3** with a coupling constant of *J* = 7.5 and 7.3 Hz, respectively. The other sets of protons were appeared between about 7.6-7.0 ppm as expected. The ¹³C NMR spectrum of the same compounds clearly indicated

the expected carbon resonances. The nitrile carbons were observed at $\delta = 115.2, 113.1$ ppm for **2** and $115.4, 115.0$ ppm for **3**. The carbon resonances concerning hydroxyl-connected CH and the oxygen connected CH at $\delta = 87.4, 77.9$ ppm for **2** and $86.5, 78.1$ ppm for **3** are in good agreement with the proposed structures. In addition to the elemental analysis results, the molecular ion peak at $m/z = 375.2$ $[M+Cl]^-$ in the ES/MS mass spectra of both **2** and **3** also confirms the proposed structures.

The zinc(II) phthalocyanines **4** and **6** were synthesized directly by cyclotetramerization of the phthalonitrile compounds **2** and **3** in the presence of the anhydrous metal salt $Zn(CH_3CO_2)_2$ in a Schlenk system in n-pentanol, respectively. The blue green phthalocyanines were isolated by column chromatography on silicagel. In the IR spectrum of **4** and **6**, the disappearance of the sharp $C\equiv N$ vibration at around 2230 cm^{-1} and appearance of new resonance at 1609 for **4** and 1608 cm^{-1} for **6** corresponding to $C=N$ vibration in phthalocyanine core of **4** and **6** confirmed cyclotetramerization of the phthalonitrile derivatives. The vibration for the OH group was observed at 3451 for **4** and 3419 cm^{-1} for **6**. In the 1H NMR spectrum of **4** and **6**, the aromatic protons appeared at $\delta = 10.1-8.83$ (m, 12H), $7.88-6.95$ (m, 40H) ppm for **4** and 9.13 (m, 6H), 8.86 (m, 6H), $7.50-6.89$ (m, 40H) ppm for **6**. The aliphatic CH protons were observed at $\delta = 6.01-5.40$ (m, 8H) ppm for **4** and 5.88 (m, 4H), 5.29 (m, 4H) ppm for **6**. The molecular ion peaks at m/z : 1425.7 $[M+H]^+$ for **4** and 1426.4 $[M+2H]^+$ for **6** were easily identified. These results confirm that the complexes have been synthesized successfully.

Cobalt(II) phthalocyanines **5** and **7** were obtained from dicyano derivative **2** and **3** and the anhydrous metal salt $Co(CH_3CO_2)_2$ in a Schlenk system in n-pentanol at $140\text{ }^\circ\text{C}$ for 24 h, respectively. The disappearance of the strong $C\equiv N$ stretching vibration in the IR spectra of **2** and **3** can be taken as a clear evidence for the formation of phthalocyanine complexes **5** and **7**. The rest of the IR spectra of the cobalt(II) phthalocyanines **5** and **7** are very similar to that of zinc(II) phthalocyanines **4** and **6**. The 1H NMR spectra of cobalt(II) phthalocyanines **5** and **7** could not be

acquired due to the paramagnetic cobalt(II) center. In the mass spectra of **5** and **7**, the presence of molecular ion peaks at $m/z = 1419.4 [M]^+$ for both **5** and **7** confirmed the proposed structures.

3.2. UV-Vis and CD absorption spectra

The UV-Vis absorption spectra of metallophthalocyanines **4-7** in THF are shown in Fig. 1. The phthalocyanines show typical electronic spectra with two absorption bands. One of them is in UV region at about 300-500 nm (B band) and the other one is in the visible region at 600-800 nm (Q band) [1]. Metal complexes of substituted and unsubstituted phthalocyanines with D_{4h} symmetry show an intense single Q band in the visible region [26]. Zinc(II) phthalocyanines **4** and **6** shows characteristic absorptions in the Q band region at 704 and 680 nm without splitting, with weaker absorptions at 634 and 612 nm and in the B band region at 320 and 350 nm, respectively. Cobalt(II) phthalocyanines **5** and **7** exhibit the characteristic absorption in the Q band region at 694 and 668 nm with weaker absorptions at 628 and 604 nm and in the B band region at 372 and 338 nm, respectively. It is well known that α substitution of benzene rings in the phthalocyanine skeleton results in red shifting of the spectra in metallophthalocyanines [27, 28]. This is due to the electron density enhancement caused by the substitution at the non-peripheral position in the case of **4** and **5**.

The aggregation behaviors of phthalocyanine complexes **4-7** were investigated in different solvents such as diethyl ether, DMF, THF, CH_2Cl_2 , $CHCl_3$ (Fig. 2. for complex **5** and **7**, see Supplementary info S-Fig. 1. for complex **4**, S-Fig. 2. for complex **6**). The cobalt(II) phthalocyanines **5** and **7** show solvent-dependent spectra. The broadening of the Q band in the UV-Vis spectra of **5** and **7** in diethyl ether, dichloromethane and chloroform can be attributed to the monomeric and oligomeric phthalocyanine species for **5** and **7**. Changes in the solvent from diethylether to DMF (thereby raising the dielectric constant of the medium) moved the monomer-

dimer equilibrium toward higher monomer ratios. It has been shown that the tendency of the phthalocyanine to dimerize is greater in solvents of low dielectric constant [29]. Zinc(II) phthalocyanine complexes **4** and **6** did not show aggregation in these solvents.

The aggregation behaviors of phthalocyanine complexes **4-7** were also investigated at different concentrations in THF and DMF. The Beer-Lambert law was obeyed for phthalocyanine complexes **4-7** in THF and DMF from concentrations between 10×10^{-6} and 2×10^{-6} mol dm⁻³. As the concentration increased, the intensity of the absorption of the Q band also increased, and there were no new bands shifted to the higher energy region due to the presence of aggregated species for all phthalocyanines (Fig. 3. for **4**, Supplementary info S-Fig. 3. for CoPc **5**, S-Fig. 4. for ZnPc **6** and S-Fig. 5. for CoPc **7**).

Non-peripherally substituted phthalocyanines **4** and **5** and peripherally substituted phthalocyanines **6** and **7** have four chiral hydrobenzoin substituents. Because of these chiral substituents, they are expected to have circular dichroism (CD) activity. The CD spectra of these chiral phthalocyanines were recorded in THF at room temperature. Fig. 4. shows the CD spectrum of **4** in range 300-800 nm (See supplementary info S-Fig. 6. for the CD spectra of complexes **5-7**). The CD spectra of **4-7** have negative CD signal over the entire spectrum with the intense Q and B bands corresponding to the electronic absorption spectra of the phthalocyanines. It is known that negative CD signal is observed in the CD spectra of right-handed conformer, while positive CD signal is observed in the CD spectra of left-handed conformer [12, 30]. In the case of all synthesized phthalocyanines **4-7**, the appearance of the negative CD signal in the B and Q band absorption spectra of **4-7** indicates that all compounds are right-handed. This also proves that due to the existence of the chiral (1*R*,2*R*)-1,2-diphenylethane-1,2-diol group at peripheral and non-peripheral positions of the phthalocyanine complexes **4-7**, the effective chiral information transfer to the phthalocyanines at the molecular level [31].

3.2. Electrochemical Measurements

Glassy carbon electrode (0.071 cm² surface area), a platinum plate (0.5 cm² surface area) and an Ag/AgCl electrode were used as the working, counter and the reference electrodes, respectively. Cyclic voltammograms were obtained at different scan rates at room temperature. Square wave voltammograms were studied with pulse size of 100 mV and frequency of 25 Hz. The electrochemical analyses were done in DCM / TBAPF₄ containing 0.50 mM solution of phthalocyanine complexes **4-7**. The data of the voltammetry analyses are given in Table.1. Non-peripheral substituent causes the steric effect on the structure. So, these substituents may impose some conformational stress on phthalocyanine complexes **4** and **5**. According to the given redox couples in Table 1, the peripheral substituent slightly shifted the potentials more negative. Electrochemical properties of non-peripherally substituted phthalocyanines complexes **4** and **5** were slightly different from peripherally substituted phthalocyanines complexes **6** and **7** [32, 33].

The cyclic voltammogram (CV) shown in Fig. 5a was obtained with glassy carbon electrode at various scan rates (250, 100, 75, 50, 25 mV s⁻¹) in DCM/ TBAPF₄ electrolyte containing 0.50 mM solution of zinc(II) phthalocyanine **4** (See supplementary info S-Fig. 7-9. for the cyclic voltammogram (CV) of complexes **5-7**). Peak current densities of each molecule increased with increasing scan rate. In order to be able to decide that a redox reaction is reversible, it is necessary to follow the steps given below.

- The voltage separation between the current peaks (ΔE) should be equal to $59/n$ mV,
- Peak potential should not change with scan rate,
- The ratio of anodic and cathodic peak currents should be equal to 1,
- Peak currents must be proportional to the square root of the scan rate.

The reaction is not reversible if one of these conditions is not met.

Hereby, potentials became more positive both anodic and cathodic directions at 100 and 250 mV s^{-1} scan rates. The potential shifts at higher scan rates are indicated that redox reactions have quasi-reversible systems. In the backward scan, formed species in the oxidation reactions in the forward scan, were reduced.

The reversibility of the complex was also checked with the square wave voltammogram (SWV) given in Fig.5b. Peak current ratios and symmetry of the peaks of a redox couple were used to characterize reversibility or irreversibility of a redox process. Voltammograms were analyzed using different parameters, which were half wave peak potential ($E_{1/2}$), peak to peak potential separation (ΔE_p), the difference between the first oxidation and first reduction processes ($\Delta E_{1/2}$). I_{pa}/I_{pc} ratios for reduction and I_{pc} / I_{pa} for oxidation reactions.

Fig. 5c shows the dependence of cathodic and anodic peak current densities on the square root of the scan rate ($I - \nu^{1/2}$). The linear curves indicate that the oxidation reactions are processing with diffusion control at the glassy carbon electrode in DCM / TBAPF₄ electrolyte containing 1.00 mM solution of zinc(II) phthalocyanine **4**.

The difference between the first anodic peak to first cathodic peak is directly refers to the HOMO-LUMO gap of complex. A large HOMO-LUMO gap implies high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electrons to a high-lying LUMO, to extract electrons from a low-lying HOMO, and so to form the activated complex of any potential reaction [34]. When compared with the complexes, it is seen that the non-peripheral and peripheral substituents of phthalocyanine complexes **4** and **6** influence the band gap, but it did not cause any change at phthalocyanine complexes **5** and **7**. Since zinc redox is an inactive as central metal, the redox reactions of the structures are directly affected by the positions of the hydrobenzoin groups at phthalocyanine skeleton. It can be seen that the band gaps of the zinc(II) phthalocyanine complexes **4** and **6** varied according to the position of hydrobenzoin substituted to the benzene rings of phthalocyanine. However, since cobalt redox is an active center, the change

in the position of the hydrobenzoin substituents in the case of phthalocyanine complexes **5** and **7** did not directly affect the redox reactions and the band gap did not change.

3.3. Catalytic Studies

3.3.2. Enantioselective diethyl zinc addition to aromatic aldehydes

Enantioselective induction of optically active novel phthalonitriles **2** and **3**, and their zinc(II) phthalocyanine derivatives **4** and **6** were investigated in the addition of diethylzinc to aromatic aldehydes (Table 2). This reaction is a known method for the formation of carbon–carbon bonds. Reactions were carried out using 2 equiv. of diethylzinc (1M solution in hexane) at room temperature for 24 h in the presence of 0.1 equiv. of the developed ligands in various solvents. We started with 2-methoxybenzaldehyde as test substrate in order to examine the efficiency of the chiral ligands. 2-Methoxybenzaldehyde gives the corresponding secondary alcohol with poor enantioselectivities and yields in both dichloromethane and toluene catalyzed by phthalonitrile **2** (Table 2, entries 1 and 2). Titanium mediated reactions are reported to give more efficient and selective results [35-37]. Considering these literature data, we also explored the reactivity and selectivity of the addition of diethylzinc to aromatic aldehydes in the presence of titanium isopropoxide as additive. Addition of the titanium species did not make any sense in catalytic activity with chiral ligand **2** (Table 2, entry 3). When the reaction was performed under the catalysis of **3** in both solvents, we observed parallel outcome (Table 2, entries 4-6). While Zn-Pc **4** showed some enantioselective induction, disappointed results were obtained with Zn-Pc-**6** (Table 2, entries 7-10). The reactions were then carried out with another test substrate having an electron-releasing substituent on the phenyl ring, 3-methoxybenzaldehyde under the catalysis of all synthesized ligands (Table 2, entries 11-22). Although we obtained some conversions, we

could not observe any enantioselectivity except using Zn-Pc **4** as catalyst. It is noteworthy that Zn-Pc **4** catalyzed the reaction and led to increase in both enantioselectivity and yield (Table 2, entry 17). The electronic nature of the substituent on the phenyl ring was also investigated. Thus, using aldehyde with electron-withdrawing chlorine at the 3-position gave some conversion but any enantioselectivity under the catalysis of all chiral ligands exception of Zn-Pc **4** (Table 2, entries 23-33). Using benzaldehyde gave unsatisfactory results (Table 2, entries 34-43). No enantioselective induction was observed on the ethylation of sterically hindered 1-naphthaldehyde using phthalonitriles **2** and **3** and Zn-Pc **6**. Remarkably, moderate yield and enantioselectivity were observed when using Zn-Pc **4** (Table 2, entry 50). Adding an extra metal Ti (IV) led to a slight decrease in both the enantioselectivity and yield (Table 2, entry 51).

3.3.2. Oxidation of benzyl alcohol with cobalt(II) phthalocyanines **5** and **7**

The catalytic activities of cobalt(II) phthalocyanines **5** and **7** were explored for the oxidation of benzyl alcohol. Benzyl alcohol can be turned into various organic compounds in oxidation reactions. In this work, three fragments (benzaldehyde as major product, benzoquinone and benzoic acid as minor products) were determined due to the attack by catalytically active species (Scheme 2) [21].

Initially, to examine the catalytic activity of cobalt(II) phthalocyanines **5** and **7**, the oxidation of benzyl alcohol was carried out under two different temperatures (25 and 80°C) in two different solvents (dimethyl formamide (DMF) and acetonitrile (ACN)) with several oxidants (tert-butyl hydroperoxide (TBHP), m-chloroperoxybenzoic acid (m-CPBA), and hydrogen peroxide (H₂O₂)). The molar ratio of benzyl alcohol, oxidant and catalyst **5** was 115/300/1 and reaction time was (12 hours for 25 °C and 5 hours for 80 °C) kept constant. The results are presented in Table 3. Although the oxidation of benzyl alcohol to the benzaldehyde was found to be very slow

at room temperature in acetonitrile with TBHP (Table 3, entry 6) and m-CPBA (Table 3, entry 8) as an oxidant almost full conversion was obtained in DMF when using m-CPBA as an oxidant, but the benzaldehyde selectivity of the products was poor (20%) (Table 3, entry 3). Besides that, in the presence of H₂O₂ as an oxidant, the catalyst **5** showed only 8% conversion in DMF (Table 3, entry 5) even when the temperature is raised to 80 °C. On the other hand, the best benzaldehyde selectivity (91%) was achieved with TBHP as an oxidant in acetonitrile solvent but in relatively low conversion (22%) at 80 °C (Table 3, entry 7) with catalyst **5**. These studies showed that high temperature was needed to get best benzaldehyde selectivity for the oxidation of benzyl alcohol. Therefore, the efficiency of the catalyst **7** was studied at 80 °C with the same oxidants in DMF and ACN solvents. According to the results on Table 3, catalyst **7** was showed best selectivity (89%, entry 14) with TBHP in acetonitrile as in the catalyst **5**. In the presence of m-CPBA as oxidant, the catalyst activity and selectivity are moderate in both DMF (Table 3, entry 12) and ACN (Table 3, entry 15) solvents and also the use of H₂O₂ as oxidant in ACN very poor benzaldehyde selectivity (15%, Table 3, entry 16) was obtained. Based on the results, TBHP in ACN solvent medium was the most efficient oxidant source to oxidation of benzyl alcohol to benzaldehyde for our catalytic system. The influence of cation and bromine anion to the oxidation of benzyl alcohol was also investigated with different additives in the presence of catalyst **5** (Table 3, Entry 17-19). While using any additive gave 22% conversion (entry 7), the addition of KBr and (Bu)₄NBr leads to a substantial increase in conversion of benzyl alcohol to 46% and 64%, respectively (Table 3, entry 17 and 19). However, the benzyl alcohol conversion is increased up to 94% with 82% selectivity when *N*-Bromosuccinimide (NBS) used as an additive (Table 3, entry 18). For comparison, a blank experiment was carried out under the optimized conditions without catalyst and we did not observe benzaldehyde in the reaction mixture (Table 3, entry 20).

To extend catalytic applications of catalyst **5** and **7**, the effect of oxidant amount for the benzyl alcohol oxidation was studied by varying the oxidant to catalyst ratio from 100/1 to 900/1 at 80 °C (Table 4, Fig. 6). For both catalysts **5** and **7**, the conversion of benzyl alcohol was completed for the oxidation process with increasing oxidant to catalyst molar ratio but the selectivity for benzaldehyde did decrease when greater than 300/1 oxidant/catalyst ratio was used. The higher oxidant ratio presumably affects coordination the cobalt ion and leads to the generation of inactive intermediate species [38-42]. Besides, the formation of benzoic acid in small yields when oxidant to catalyst ratio of 300/1.

The effect of substrate/catalyst ratio on the performance of the oxidation reactions using catalyst **5** and **7** was then examined (Table 5, Fig. 7). The reaction rate and conversion normally depended on the amounts of CoPc catalyst used. At a substrate to catalyst ratio of 300:1 the oxidation of benzyl alcohol can be carried out to 65% (91% benzaldehyde selectivity) and 87% (81% benzaldehyde selectivity) conversion with catalyst **5** and **7**, respectively. On further increasing the substrates/catalyst ratio, the catalytic activity decreases to such extent that for the oxidation of benzyl alcohol in 5h.

So far, many of cobalt(II) phthalocyanine catalysts have been reported for oxidation of benzyl alcohol. A few related studies among these are summarized in the following lines. Çakır et al. have synthesized and characterized (2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy) substituted Co(II) phthalocyanine and investigated their catalytic activity for benzyl alcohol oxidation. They found that TBHP is the best oxidant in acetonitrile at 70°C with high total conversion (89%) and 78% selectivity [43]. Aktaş and coworkers reported the selective oxidation of benzyl alcohol to benzaldehyde with Co(II) phthalocyanine complex which has halogenated (-CF₃) substituent. This study showed that higher temperature (90°C) and 600/1:substrate/catalyst ratio was needed to reach an optimum conversion of benzyl alcohol to benzaldehyde in the presence of TBHP as an oxidant. They also reported that a small amount of benzyl benzoate was

formed as by-product during the oxidation reactions [44]. In another report, Saka et al. prepared 2-(2-(4-allyl-2-methoxyphenoxy)ethoxy)ethoxyphthalonitrile and then its new peripherally tetra substituted Co(II) complex to investigate in benzyl alcohol oxidation. Based on benzyl alcohol, 91% total conversion and 82.4% benzaldehyde selectivity was obtained at 90°C for 3 hours when 400/800/1 substrate/oxidant/catalyst ratio was used [45]. In this work, we achieved the high conversion (up to 91%) and selectivity (up to 84%) at 80°C with our peripheral and non-peripheral diol substituted phthalocyanine Co(II) complexes.

4. Conclusion

In the present study, four novel peripherally and non-peripherally hydrobenzoin substituted optically active phthalocyanine derivatives were synthesized. The structural characterization was done by a combination of ^1H NMR, IR, UV-Vis and MS spectral data. All phthalocyanines are highly soluble in common organic solvents. The Q-band of non-peripherally substituted phthalocyanine complexes **4** and **5** was red-shifted relative to that of peripherally substituted phthalocyanine complexes **6** and **7**. The negative CD signals for all phthalocyanines at the CD spectra of **4-7** prove that the chiral information from the hydrobenzoin substituent at α and β position of the phthalocyanine skeleton transferred to phthalocyanines **4-7** at molecular level. The solvent and concentration effects on the aggregation properties of the phthalocyanines were determined. The metallophthalocyanines demonstrated no aggregation behavior in DMF and THF from concentrations between 10×10^{-6} and 2×10^{-6} mol dm $^{-3}$. Enantioselective catalytic activity of optically active phthalonitriles **2** and **3**, and their zinc(II) phthalocyanines **4** and **6** was evaluated in diethylzinc addition to aldehydes. The enantioselective addition of diethylzinc to 3-methoxybenzaldehyde in the presence of non-peripherally hydrobenzoin substituted zinc(II) phthalocyanine **4** gave the corresponding chiral secondary alcohol with the yield of 38% and the

enantiomeric excess of 33%. The catalytic activity of cobalt(II) phthalocyanines **5** and **7** was investigated in the oxidation of benzyl alcohol by using different oxidants. The highest conversion of benzyl alcohol to benzaldehyde was obtained with non-peripherally substituted cobalt(II) phthalocyanine **5** as 91% with the highest selectivity of 83%. These results showed that the functional phthalocyanines derived from C_2 -symmetric diols can be interesting in enantioselective catalytic systems and the oxidation of benzyl alcohol. Further study in this direction is currently in progress and the results will be reported in due course.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at:

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Figure captions:

Scheme 1. Synthetic pathway of phthalonitriles and zinc(II) and cobalt(II) phthalocyanine derivatives. Reagents and conditions: (i) DMSO, K_2CO_3 , rt; (ii) $Zn(CH_3COO)_2$, n-pentanol, DBU, 140 °C, (iii) $CoCl_2$, n-pentanol, DBU, 140 °C,

Scheme 2. Oxidation of benzyl alcohol using cobalt(II) phthalocyanines **5** and **7** as catalysts

Fig. 1. UV–Vis spectra of zinc(II) phthalocyanines (**4** and **6**), and cobalt(II) phthalocyanines (**5** and **7**) in THF (Concentration: 2×10^{-6} M)

Fig. 2. UV–Vis spectra of cobalt(II) phthalocyanine **5** and **7** in different solvents (Concentration: 10×10^{-6} M)

Fig.3. Aggregation properties of zinc(II) phthalocyanine **4** at different concentrations (Concentration: 2×10^{-6} , 4×10^{-6} , 8×10^{-6} , 10×10^{-6} M). Inset: Beer-Lambert plot.

Fig.4. (a) CD and (b) electronic spectra of zinc(II) phthalocyanine **4** in THF (concentration: 10×10^{-6} M)

Fig. 5. (a) Effect of the various scan rates (250, 100, 75, 50, 25 $mV s^{-1}$) on electrooxidation of 0.50 mM solution of **4** in DCM/TBAPF₄ electrolyte at the glassy carbon electrode at 298 K. (b) Square wave voltammetry at 100 $mV s^{-1}$ scan rate. (c) Dependence of anodic peak current densities during the forward and backward scan on the square roots of scan rate.

Table 1. Voltammetric data of the phthalocyanines. All voltammetric data were given versus Ag/AgCl

Table 2. Enantioselective addition of diethylzinc to various aldehydes catalyzed by chiral phthalonitriles (**2**, **3**)^a and zinc(II) phthalocyanines (**4**, **6**)^b.

Table 3. The effect of temperature, solvent and oxidant on benzyl alcohol oxidation with cobalt(II) phthalocyanines **5** and **7**^a

Table 4. Amount of oxidant effect on benzyl alcohol oxidation with cobalt(II) phthalocyanines **5** and **7**^a

Table 5. The effect of substrate/catalyst ratio on benzyl alcohol oxidation with cobalt(II) phthalocyanines **5** and **7**^a

Table 1. Voltammetric data of the phthalocyanines. All voltammetric data were given versus Ag/AgCl

Molecule	Redox processes	Mechanism	$E_{1/2}$ ^a	ΔE_p (mV) ^b	I_{pa}/I_{pc} ^c	$\Delta E_{1/2}$ ^d
ZnPc (4)	R ₁	Zn ^{II} Pc ⁻⁴ /Zn ^{II} Pc ⁻³	-0.77	23	1.05	1.42
	O ₁	Zn ^{II} Pc ⁻¹ /Zn ^{II} Pc ⁰	0.65	0	0.44	
	R ₂	Zn ^{II} Pc ⁻⁵ /Zn ^{II} Pc ⁻⁴	-1.17	10	0.82	
	O ₂	Zn ^{II} Pc ⁻² /Zn ^{II} Pc ⁻¹	-0.37	-	-	
CoPc (5)	R ₁	Co ^{II} Pc ⁻² /Co ^I Pc ⁻²	-0.10	25	1.64	0.67
	O ₁	Co ^{III} Pc ⁻² /Co ^{II} Pc ⁻²	0.57	80	0.50	
	R ₂	Co ^I Pc ⁻³ /Co ^I Pc ⁻²	-1.16	9	0.77	
ZnPc (6)	R ₁	Zn ^{II} Pc ⁻² /Zn ^{II} Pc ⁻¹	-0.69	51	1.17	1.17
	O ₁	Zn ^{II} Pc ⁻¹ /Zn ^{II} Pc ⁰	0.48	24	0.45	
	R ₂	Zn ^{II} Pc ⁻⁴ /Zn ^{II} Pc ⁻³	-0.96	4	0.93	
	R ₃	Zn ^{II} Pc ⁻⁵ /Zn ^{II} Pc ⁻⁴	-1.31	5	0.86	
	R ₁	Co ^{II} Pc ⁻² /Co ^I Pc ⁻²	-0.21	45	0.62	
CoPc (7)	O ₁	Co ^{III} Pc ⁻² /Co ^{II} Pc ⁻²	0.46	45	0.44	0.67
	R ₂	Co ^{II} Pc ⁻² /Co ^{II} Pc ⁻¹	-0.62	246	1.00	
	R ₃	Co ^I Pc ⁻³ /Co ^I Pc ⁻²	-1.30	20	0.76	

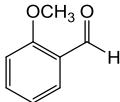
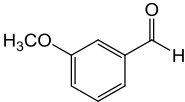
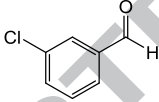
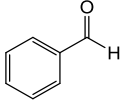
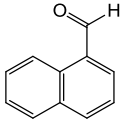
^aThe potential at the half-diffusion current ($(i_{\text{initial}} + i_{\text{peak}})/2$) is $E_{1/2}$ at 0.100 V s⁻¹ scan rate.

^b $\Delta E_p = E_{pa} - E_{pc}$.

^c $I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation processes.

^d $\Delta E_{1/2} = E_{1/2}(\text{first oxidation}) - E_{1/2}(\text{first reduction})$

Table 2. Enantioselective addition of diethylzinc to various aldehydes catalyzed by chiral phthalonitriles (**2**, **3**)^a and zinc(II) phthalocyanines (**4**, **6**)^b.

Entry	Aldehydes	Ligand	Solvent	Yield (%) ^c	ee (%) ^{d,e}
1		2	Dichloromethane	21	7 (<i>R</i>)
2		2	Toluene	28	11 (<i>R</i>)
3 ^f		2	Toluene	20	5 (<i>R</i>)
4		3	Dichloromethane	28	9 (<i>R</i>)
5		3	Toluene	36	11 (<i>R</i>)
6 ^f		3	Toluene	30	rac
7		4	Dichloromethane	34	17 (<i>R</i>)
8 ^f		4	Dichloromethane	25	10 (<i>R</i>)
9		6	Dichloromethane	36	rac
10 ^f		6	Dichloromethane	15	rac
11		2	Dichloromethane	17	rac
12		2	Toluene	20	rac
13 ^f		2	Toluene	10	rac
14		3	Dichloromethane	10	rac
15		3	Toluene	15	rac
16 ^f		3	Toluene	10	rac
17		4	Dichloromethane	38	33 (<i>R</i>)
18		4	Toluene	28	rac
19 ^g		4	Dichloromethane	36	30 (<i>R</i>)
20 ^f		4	Dichloromethane	20	rac
21		6	Dichloromethane	24	rac
22 ^f		6	Dichloromethane	15	rac
23		2	Dichloromethane	30	rac
24		2	Toluene	28	rac
25 ^f		2	Toluene	10	rac
26		3	Dichloromethane	14	rac
27		3	Toluene	25	rac
28 ^f		3	Toluene	10	rac
29		4	Dichloromethane	37	26 (<i>R</i>)
30 ^f		4	Dichloromethane	25	15 (<i>R</i>)
32		6	Dichloromethane	23	rac
33 ^f		6	Dichloromethane	10	rac
34		2	Dichloromethane	18	rac
35		2	Toluene	25	rac
36 ^f		2	Toluene	10	rac
37		3	Dichloromethane	10	rac
38		3	Toluene	15	5 (<i>R</i>)
39 ^f		3	Toluene	15	rac
40		4	Dichloromethane	20	rac
41 ^f		4	Dichloromethane	15	rac
42		6	Dichloromethane	12	rac
43 ^f		6	Dichloromethane	10	rac
44		2	Dichloromethane	10	rac
45		2	Toluene	12	rac
46 ^f		2	Toluene	10	rac
47		3	Dichloromethane	30	rac
48		3	Toluene	15	rac
49 ^f		3	Dichloromethane	25	rac
50		4	Dichloromethane	66	26 (<i>R</i>)
51 ^f		4	Dichloromethane	50	20 (<i>R</i>)
52		6	Dichloromethane	28	rac
53 ^f		6	Dichloromethane	20	rac

^a Reaction conditions: 1 equiv. aldehyde, 2 equiv. Et₂Zn, 10 mol% ligand, rt, 24 h. ^b 2.5 mol% **4**. ^c Isolated yield.
^d Determined by GC analysis with chiral HP-CHIRAL-20B. ^e Determined by comparison of optical rotations with the literature. ^f Reaction with 0.94 equiv. Ti(OiPr)₄. ^g 5 mol% **4**.

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Table 3. The effect of temperature, solvent and oxidant on benzyl alcohol oxidation with cobalt(II) phthalocyanines **5** and **7**^a

Entry	Catalyst	Solvent	Temp. (°C)	Oxidant	Additive	Total conversion (%) ^b	Benzaldehyde (%)	Benzoic acid (%)	1,4-benzoquinone (%)	Selectivity (%)	TON	TOF (h ⁻¹)
1	5	DMF	25	TBHP	-	<5	<5	-	-	-	-	-
2	5	DMF	80	TBHP	-	19	7	-	-	36	22	4
3	5	DMF	25	m-CPBA	-	98	20	54	-	20	113	23
4	5	DMF	80	m-CPBA	-	24	14	10	-	58	28	6
5	5	DMF	80	H ₂ O ₂	-	8	<5	-	-	-	9	2
6	5	ACN	25	TBHP	-	9	6	-	-	67	10	2
7	5	ACN	80	TBHP	-	22	20	-	-	91	25	5
8	5	ACN	25	m-CPBA	-	22	12	9	-	54	25	5
9	5	ACN	80	m-CPBA	-	91	31	40	-	34	105	21
10	5	ACN	80	H ₂ O ₂	-	<5	<5	-	-	-	-	-
11	7	DMF	80	TBHP	-	23	12	-	-	52	26	5
12	7	DMF	80	m-CPBA	-	20	18	<5	-	90	23	5
13	7	DMF	80	H ₂ O ₂	-	45	25	-	-	55	52	10
14	7	ACN	80	TBHP	-	44	39	<5	-	89	51	10
15	7	ACN	80	m-CPBA	-	100	41	36	-	41	115	23
16	7	ACN	80	H ₂ O ₂	-	74	11	-	-	15	85	17
17	5	ACN	80	TBHP	KBr	46	38	7	<5	82	53	11
18	5	ACN	80	TBHP	NBS	94	76	6	9	82	105	21
19	5	ACN	80	TBHP	(Bu) ₄ NBr	64	51	12	<5	80	74	15
20	-	ACN	80	TBHP	NBS	0	-	-	-	-	-	-

^aReaction conditions: benzyl alcohol (1.61x10⁻⁴ mol), oxidant (4.20x10⁻⁴ mol), catalyst (1.40x10⁻⁶ mol), solvent 10.0 mL, ^bConversions were determined by GC based on benzyl alcohol. Reactions were conducted for 5 and 12 hours when carried out 25°C and 80°C, respectively. TON: Mole of substrate converted per mole of metal in the catalyst. TOF: TONxh⁻¹.

Table 4. Amount of oxidant effect on benzyl alcohol oxidation with cobalt(II) phthalocyanines **5** and **7**^a

Entry	Catalyst	Oxidant/catalyst	Total conversion (%) ^b	Benzaldehyde (%)	Benzoic acid (%)	1,4-benzoquinone (%)	Selectivity (%)	TON	TOF (h ⁻¹)
1	5	100/1	77	51	26	-	66	89	18
2	7	100/1	95	45	40	5	47	109	22
3	5	200/1	76	51	23	<5	67	87	17
4	7	200/1	100	55	40	5	55	115	23
5	5	300/1	91	76	7	10	83	105	21
6	7	300/1	87	73	7	7	84	100	20
7	5	500/1	100	59	33	5	59	115	23
8	7	500/1	100	47	41	7	47	115	23
9	5	700/1	99	57	31	7	57	114	23
10	7	700/1	100	47	37	11	47	115	23
11	5	900/1	100	54	30	9	54	115	23
12	7	900/1	100	46	36	10	46	115	23

^aReaction conditions: benzyl alcohol (1.61×10^{-4} mol), oxidant (TBHP), catalyst (1.40×10^{-6} mol), solvent (acetonitrile, 10.0 mL), 80°C, 5h. ^bConversions were determined by GC based on benzyl alcohol. TON: Mole of substrate converted per mole of metal in the catalyst. TOF: $\text{TON} \times \text{h}^{-1}$.

Table 5. The effect of substrate/catalyst ratio on benzyl alcohol oxidation with cobalt(II) phthalocyanines **5** and **7**^a

Entry	Catalyst	Substrate/catalyst	Total conversion (%) ^b	Benzaldehyde (%)	Benzoic acid (%)	1,4-benzoquinone (%)	Selectivity (%)	TON	TOF (h ⁻¹)
1	5	300/1	65	59	3	2	91	195	39
2	7		87	71	11	6	81	264	53
3	5	600/1	45	42	2	1	93	270	54
4	7		64	47	4	2	73	384	77
5	5	900/1	22	20	1	1	91	198	40
6	7		51	46	2	2	90	459	92
7	5	1200/1	26	25	1	1	96	312	62
8	7		27	24	2	2	89	324	65
9	5	1500/1	19	18	1	-	95	285	57
10	7		23	21	1	1	91	345	69
11	5	2000/1	13	12	-	-	92	260	52
12	7		14	12	-	1	85	280	56

^aReaction conditions: benzyl alcohol, oxidant (TBHP, 4.2×10^{-4} mol), catalyst (1.40×10^{-6} mol), solvent (acetonitrile, 10.0 mL), 80°C, 5h, ^bConversions were determined by GC based on benzyl alcohol. TON: Mole of substrate converted per mole of metal in the catalyst. TOF: TONxh⁻¹.

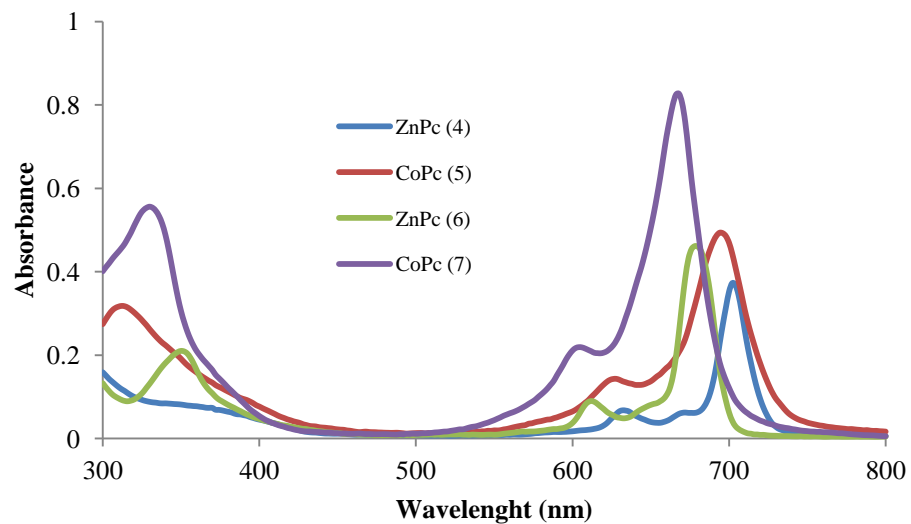


Fig. 1. UV-Vis spectra of zinc(II) phthalocyanines **4** and **6**, and cobalt(II) phthalocyanines **5** and **7** in THF

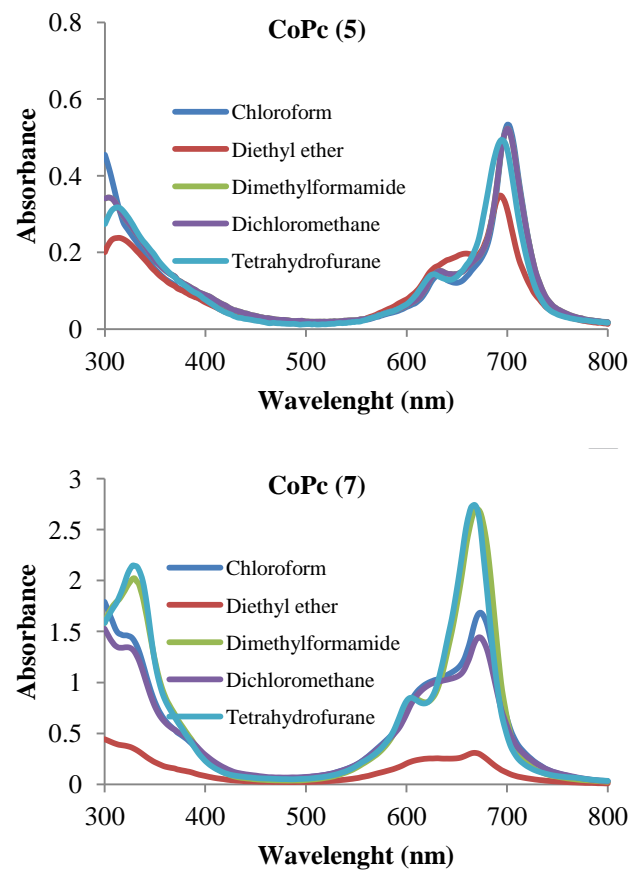


Fig.2. UV–Vis spectra of cobalt(II) phthalocyanine **5** and **7** in different solvents (Concentration: 10×10^{-6} M)

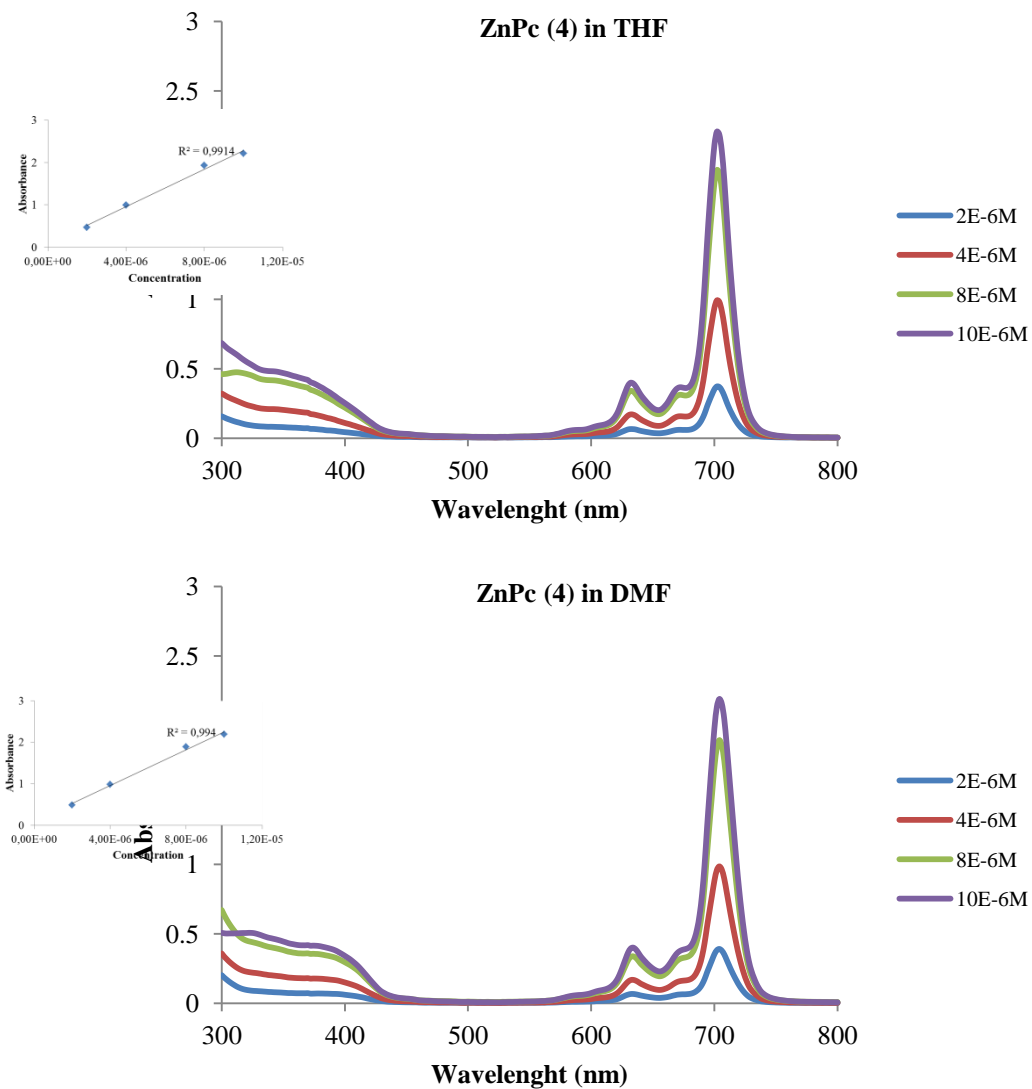


Fig.3. Aggregation properties of zinc(II) phthalocyanine **4** at different concentrations (Concentration: 2×10^{-6} , 4×10^{-6} , 8×10^{-6} , 10×10^{-6} M). Inset: Beer-Lambert plot.

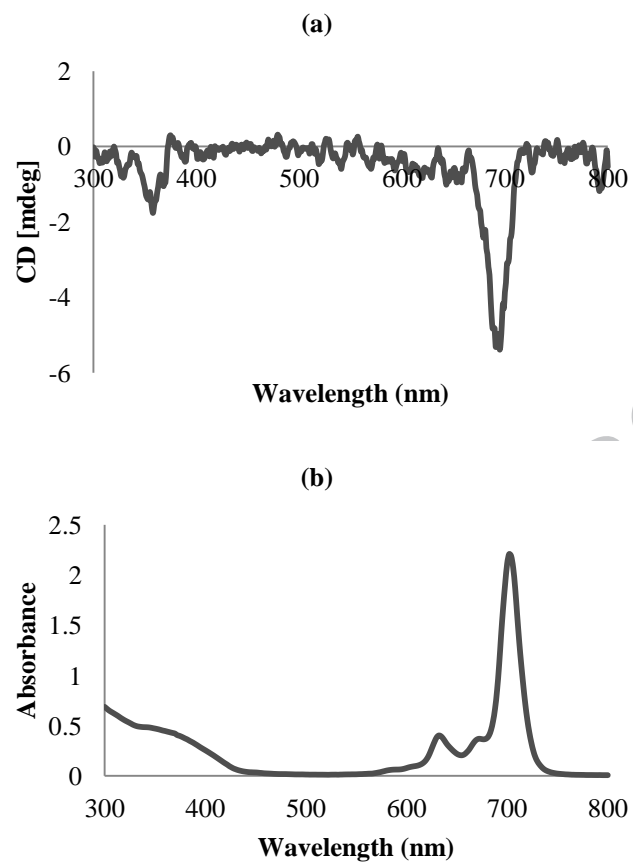
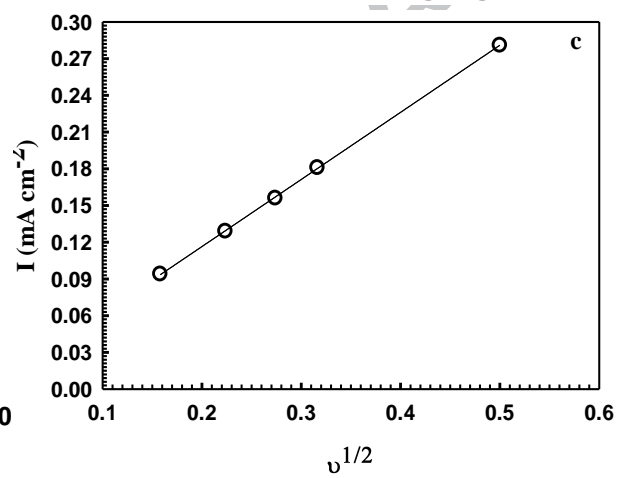
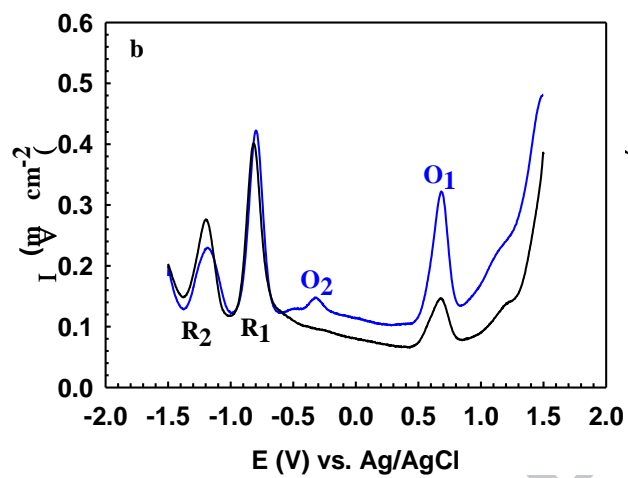
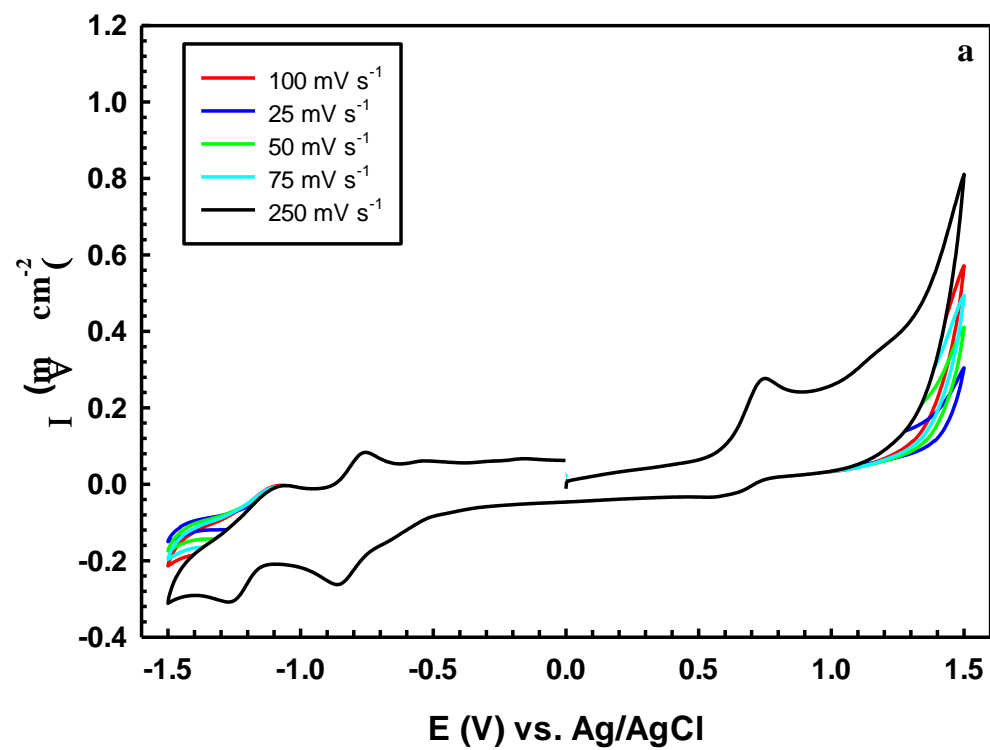
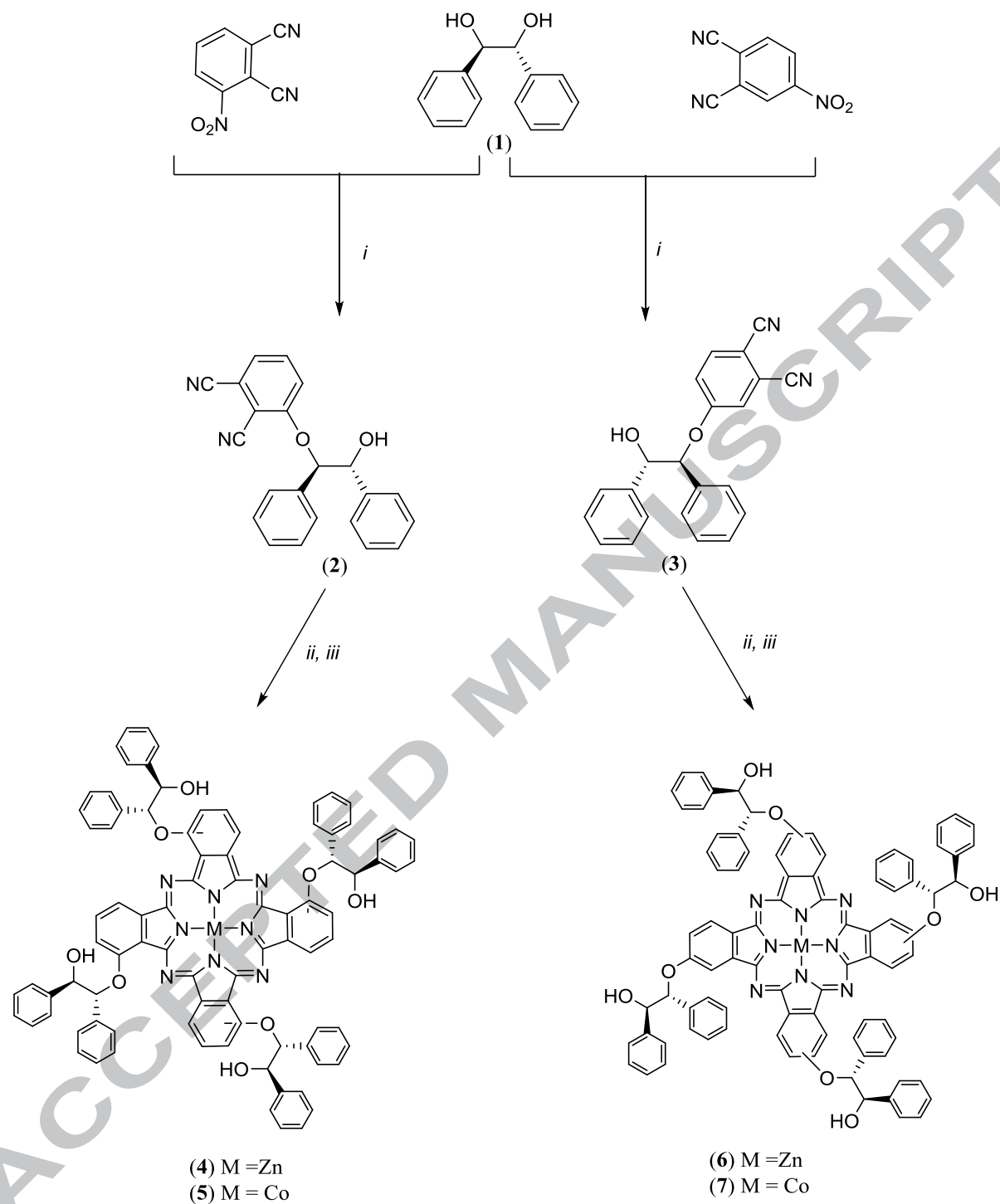


Fig.4. (a) CD and (b) electronic spectra of zinc(II) phthalocyanine **4** in THF (concentration: 10×10^{-6} M)

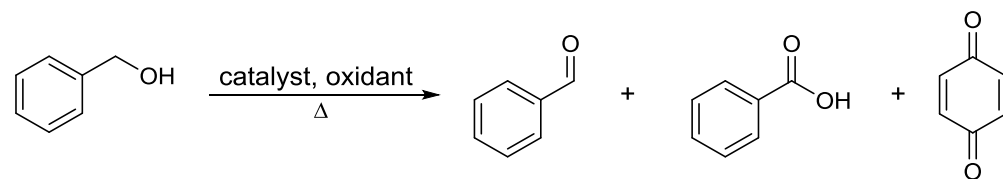


.50 mM solution of **4** in DCM/TBAPF₄
mV s⁻¹ scan rate. (c) Dependence of anodic peak



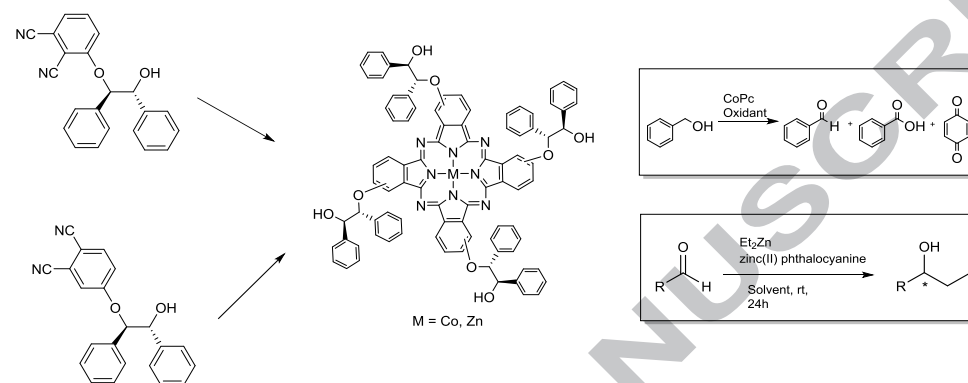
Scheme 1. Synthetic pathway of phthalonitriles, and zinc(II) and cobalt(II) phthalocyanine derivatives. Reagents and conditions: (i) DMSO, K_2CO_3 , rt; (ii) $\text{Zn}(\text{CH}_3\text{COO})_2$, n-pentanol, DBU, 140 °C, (iii) CoCl_2 , n-pentanol, DBU, 140 °C,

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Scheme 2. Oxidation of benzyl alcohol using cobalt(II) phthalocyanines **5** and **7** as catalysts

Graphical Abstract-Pictogram



Graphical Abstract-Synopsis

- Four novel optically active phthalocyanine derivatives were synthesized.
- Aggregation and electrochemical properties of phthalocyanines were investigated.
- ZnPc derivatives were tested as catalysts in asymmetric catalysis.
- CoPc derivatives were tested in oxidation of benzyl alcohol.

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