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SYNTHESIS, CHARACTERIZATION, AGGREGATION AND ELECTROCHEMICAL PROPERTIES OF PERIPHERAL OCTA-2-{[4-(2-BENZYLPHENOXY)BENZYL]THIO} ETHOXY GROUP SUBSTITUTED COBALT(II) PHTHALOCYANINE**

Meltem B. SAĞLAM* and Zekeriya BIYIKLIOĞLU

Department of Chemistry, Faculty of Science, Karadeniz Technical University, Trabzon, Turkey

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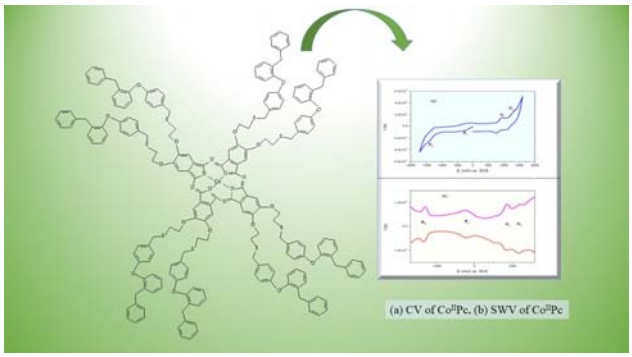
We were reported here, the synthesis, characterization, aggregation and electrochemical properties of 4,5-bis(2-{[4-(2-benzyl)phenoxy)benzyl]thio}ethoxy)phthalonitrile and 2,3,9,16, 17,23,24-octa[(2-{[4-(2-benzyl)phenoxy)benzyl]thio}ethoxy)] phthalociyaninatocobalt(II). CoPc were prepared by the reaction of 4,5-bis(2-{[4-(2-benzyl)phenoxy)benzyl]thio}ethoxy) phthalonitrile with the corresponding anhydrous metal salt in n-pentanol and DBU. The structures of the original compounds were identified by using elemental analysis, ^{1}H-NMR, ^{13}C-NMR, IR, mass and UV-vis spectroscopic data. Electrochemical redox characteristics of the compounds were determined by electroanalytical techniques such as cyclic voltammetry, square wave voltammetry. The aggregation tendencies and electrochemical redox properties of all phthalocyanines were investigated on the basis of central metal, solvent medium and substituent effects, using UV-Vis spectral.



INTRODUCTION

Phthalocyanines (Pcs) are planar aromatic organic compounds with 18π electron system and consist of four isoindoline units. Their colors are ranging from blue to brown, and so they can be used as dyes, paints, color for metal surfaces, fabrics, and plastics. In recent years Pcs have been studied extensively because they are useful materials in many applications such as metal sensors,[1] electro chromic display devices,[2,3] liquid crystals,[4,5] photovoltaic cells,[6] non-linear optical applications,[7,8] blue and green,[9,10] photodynamic therapy,[11,12] ladder polymers,[13] catalytic applications,[14] and Langmuir-Blodgett films.[15]

The practicability of Pcs compounds in the interest of technological areas strongly depends on both their solubility and electron transfer properties. On the other hand, these properties are directly related to π–π interaction between the Pc molecules, which affects aggregation and solubility leanings in most organic solvents. Strong intermolecular π–π interactions between the metalophthalocyanines (MPcs) molecules lead to their stacking as aggregation and, thus, decrease insolubility.[16] Therefore, the solubility of Pcs can be raised by the addition of appropriate functional groups for exp.: alkyl, alkoxyl, phenoxyl and other bulky groups onto their substitutional positions, as a result of the decrease in the intermolecular interactions.[17]

* Corresponding author: meltemkilicaslan@hotmail.com
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The occurrence of aggregation phenomenon in Pcs solutions can be detected by electronic spectroscopy. The Q-band corresponding to the π-π* electronic transitions of Pcs molecules is broadened or split into two bands if the aggregated species are present in the solution. Splitting points out strong intermolecular interactions while the weak interactions are usually reflected by the broadening of the electronic absorption signals, especially the Q-band absorption. Similar reflections are also observed in the electrochemical redox signals since the redox processes of Pcs compounds are affected and thus, can be arranged by many factors, including the nature of the central metal ions in the Pcs core, the binding positions of the substitution form, the molecular interactions like axial coordination and aggregation.[18,19] Therefore, the consequence of the aggregation phenomenon on the electrochemical redox processes of Pc compounds can also be detected and investigated. The combination of electronic absorption spectroscopy with voltammetry as *in situ* UV-Vis spectra electrochemistry provides a good illustration of the effect of aggregated species on the redox electrochemistry of these compounds. On the other hand, the tendency of aggregation depends on both the concentration of the Pc compound in the solution medium and the solvent polarity. Thus, the monitoring of the electronic absorption spectra at different concentrations in a broad window and different solvent media is practical to identify the presence of aggregated species.

Pcs bearing huge substituents usually do not aggregate and possess high solubility. This makes their purification and characterization easy, and this type of compounds receives considerable attention compared to others. The non-aggregation of these compounds can be provided by different ways such as; (i) the binding positions of the substitution form, (ii) the use of surfactants, (ii) and introduction of dendrimers on the phthalocyanine macrocycle.[20–22] Easily modifiable structure of Pc compounds and their technological applicability in various areas motivated us to design new examples and study their electrochemical properties. As a continuation of our efforts, in this study, 2,3,9,16,17,23,24-octa[(2-{[4-(2-benzyl)phenoxy)benzyl]thio}ethoxy)] phthalociyaninatocobalt(II) (Scheme 1) has been synthesized and characterized. Furthermore, electrochemical and aggregation features of these compounds displayed by electrochemical measurements. This case has shown a complete assignment of the redox processes to the Pc ring or metal center possible. [23]

EXPERIMENTAL

1. Materials and methods

All chemicals purchased from Aldrich and all solvents were dried and purified as described in the literature.[24] Elemental analyses were performed on a Costech ECS 4010 Elemental Analyzer. The UV-Vis spectra of the solutions were recorded by using a UV mini-1240 UV Spectrophotometer. The IR spectra of the solutions were monitored on a Perkin Elmer 1600 FT-IR Spectrophotometer. ^{1}H and ^{13}C-NMR spectra were measured on a Bruker Advance III 400 MHz NMR Spectrometer in $CDCl_3$, and chemical shifts (δ) were stated relative to Me_4Si as an internal standard. Mass spectra were measured on a Bruker microflex LT MALDI-TOF MS Spectrometer. Melting points were measured on an electro thermal apparatus. Electrochemical measurements carried out with Gamry Interface 1000 potentiostat/galvanostat.

2. Synthesis of compounds

2.1. 2-{[4-(2-benzylphenoxy]benzyl]thio}ethanol **(1):** 2-benzylphenol (1.33 g, 7.22 mmol) dissolved in 30 mL absolute ethanol, and the mixture refluxed for 4-5 h. And then, the reaction mixture cooled at room temperature, dry Na_2CO_3 (1.92 g, 18.13 mmol), and dry NaI (0.27 g, 1.81 mmol) added. The mixture heated at 50°C, and 4-chloroylbenzyl-2-hydroxyethylsulfide (1.46 g, 7.22 mmol (%98, d=1g/mL)) and 15 mL absolute ethanol added drop wise for 2 hours to maintain. Then, the reaction mixture refluxed for 7 days under an inert atmosphere. Finally, the mixture cooled to room temperature, filtered, evaporated under vacuum, and viscous liquid product afforded. This product redissolved in chloroform (80 mL) after washed with water while neutral. The combined organic extracts dried with anhydrous $MgSO_4$ and evaporated to dryness. The dark brown oily product isolated. Yield: 2.28 g (90 %). Anal. cal. for, $C_{22}H_{22}O_2S$: C, 75.35; H, 6.30; O, 9.16 %. Found: C: 75.42; H: 6.28; O: 9.10 %. IR, $\nu_{max/cm}^{-1}$: 3321 (-OH), 3061-3027(Ar-H), 2921 (Aliph.-CH), 1901(C=C), 1594, 1489(Ar-C=C), 1238(Ar-O-Ar), 1091, 821. ^{1}H-NMR ($CDCl_3$), (δ: ppm): 7.28 (m, 10H, Ar-H), 7.15 (t, 1H, Ar-H), 6.91 (t, 1H, Ar-H), 6.81 (d, 1H, Ar-H), 5.42 (s, 1H, OH), 4.03 (s, 2H, -CH_2), 3.72 (s, 4H, -CH_2), 2.65 (t, 2H, -CH_2). ^{13}C-NMR ($CDCl_3$), (δ: ppm): 153.88, 151.31, 140.14, 136.60, 130.31, 128.79, 127.75, 120.80, 115.65, 60.35, 42.00, 36.25, 35.16, 34.29. MS (FAB) (m/z): 351 $[M+H]^+$.

2.2. 4,5-bis(2-{[4-(2-benzyl)phenoxy)benzyl]thio} ethoxy) phthalonitrile **(2):** 2-{[4-(2-benzylphenoxy]benzyl]thio}ethanol **(1)** (1.24 g, 3.54 mmol), 4,5-dichloro-1,2-dicyanobenzene (0.52 g, 2.65 mmol), and 30 mL dry DMF stirred about for 15 min., at 25ºC, dry K_2CO_3 (1.24 g, 8.85 mmol) added portion-wise within 2 hours. The reaction mixture stirred under an inert atmosphere at 70ºC for about 4 days. Then, it emptied into ice-water, and the oily product extracted with chloroform. The combined organic extracts dried with anhydrous $MgSO_4$, and evaporated to dryness. The dark green oily product obtained. This product treated with hot ethanol

and allowed to stand overnight in a refrigerator. It filtrated, and the filtrate evaporated to dryness. The brown oily product obtained. Yield: 1.45 g (%87). Anal. cal. for, $C_{52}H_{44}O_4S_2N_2$: C, 75.70; H, 5.38; N, 3.40; O, 7.76 %. Found: C, 75.65; H, 5.34; N, 3.44; O, 7.83 %. IR, $\nu_{max/cm}^{-1}$: 3026(Ar-H), 2954-2850(Aliph.-CH), 2231 (C≡N), 1728(C=C), 1587, 1487(Ar-C=C), 1275(Ar-O-Ar), 1092(Ar-O-C), 859. ^{1}H-NMR ($CDCl_3$), (δ: ppm): 7.78 (d, 1H, Ar-H), 7.19 (m, 25H, Ar-H), 6.65 (s, 1H, Ar-H), 6.43 (s, 1H, Ar-H), 4.23 (m, 2H, -CH_2), 3.94 (m, 4H, -CH_2), 3.72 (s, 6H, -CH_2), 2.87 (ddd, 2H, -CH_2), 2.69 (m, 2H, -CH_2). ^{13}C-NMR ($CDCl_3$), (δ: ppm): 157.64, 151.94, 130.29, 128.81, 126.39, 121.49, 120.43, 119.39, 116.63, 109.45(C≡N), 70.63, 45.50, 36.84. MS (FAB) (m/z): 848 $[M+K]^+$.

2.3. 2,3,9,16,17,23,24-Octa[(2-{[4-(2-benzyl)phenoxy) benzyl]thio}ethoxy)] phthalociyaninato cobalt(II) **(3):** Compound **2** (0.26 g, 0.315 mmol), anhydrous $CoCl_2$ (0.027 g, 0.21 mmol), 5 mL of dry n-pentanol and 0.05 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under an inert atmosphere. It degassed several times, and then the mixture stirred at 138ºC for 18 h. After cooling to the room temperature, the reaction mixture refluxed with ethanol (40 mL) to precipitate the product. Then it washed with respectively; hot ethanol, hot methanol, hexane, petroleum ether, and dried under vacuum. The solid blue-green product is soluble in acetone, ethyl acetate, chloroform, DMF, DMSO, and THF. It refined by column chromatography with silica gel, using ethyl acetate/acetone (9:1) solvent system. Yield: 128 mg (%49). m.p:>300ºC. Anal. cal. for, $C_{208}H_{176}O_{16}S_8N_8Co$: C, 74.37; H, 5.28; N, 3.34; O, 7.62 %. Found: C, 74.41; H, 5.32; N, 3.39; O, 7.57 %. IR, $\nu_{max/cm}^{-1}$: 3059-3025(Ar-H), 2899(Aliph.-CH), 1716(C=C), 1582, 1486 (Ar-C=C), 1440, 1244 (Ar-O-Ar), 1094 (Ar-O-C), 886. UV-vis (Toluene): $\lambda_{max/nm}$: 669 (5.31), 605 (4.78), 342 (5.22). MS (FAB) (m/z): 3355 $[M]^+$.

3. Electrochemical measurements

All electrochemical measurements carried out with Gamry Interface 1000 potentiostat/galvanostat utilizing a three-electrode configuration at 25°C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire served as the counter electrode and a saturated calomel electrode (SCE) employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabuthylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

4. Aggregation studies

The aggregation behavior of the phthalocyanine complex **3** investigated at different concentrations (was changed from $12x10^{-6}$-$2x10^{-6}$ M) in THF and at different solvents, such as: DMF, DMSO, ethyl acetate, chloroform, THF, toluene. The Q band position changed with the solvent. In general, the redshift of the Q band increased with a refractive index of the solvent. The electronic absorption spectra of in these solvents analyzed by using the method described by Babyliss.[25]

RESULTS AND DISCUSSION

2-{[4-(2-benzylphenoxy]benzyl]thio}ethanol **(1)** and 4,5-bis(2-{[4-(2-benzyl)phenoxy)benzyl] thio}ethoxy) phthalonitrile **(2)** synthesized according to literature.[26] The synthetic pathways for the preparation of **1-3** shown in Scheme 1.

The stretching vibrations of -OH band at 3321 cm^{-1} and Ar-O-Ar groups at 1238 cm^{-1} seemed to shift in the IR spectrum of **1**. The ^{1}H-NMR spectrum of **1** (Fig. 1) indicated aromatic protons at δ values of 7.28, 7.15, 6.61, 6.81 ppm, aliphatic protons at δ values of 4.03, 3.72, 2.65 ppm , -OH proton at δ value of 5.42 ppm respectively, and -OH proton signals disappeared with deuterium exchange. The ^{13}C NMR spectrum of **1**; Ar-O-Ar at δ=153.88 ppm, CH_2-OH at δ=60.35 ppm, CH_2-S at δ=42.00 ppm, Ar-CH_2 at δ=36.25 ppm, SCH_2 at δ=34.29 ppm, indicated the presence of carbon resonance.

Compound **2** prepared by the reaction of 2-{[4-(2-benzylphenoxy]benzyl]thio}ethanol **(1)**, and 4,5-dichloro-1,2-dicyanobenzene carried out by a base-catalyzed nucleophilic displacement reaction in dry DMF at 70ºC and the yield %87. In the IR spectrum of compound **2**, stretching vibrations of -OH band at 3321 cm^{-1} disappeared, and C≡N groups at 2231 cm^{-1} observed.

The ^{1}H-NMR spectrum of compound **2** (Fig. 2), belonging to -OH groups signals δ=5.42 ppm disappeared to proposed for the structure. ^{1}H-NMR spectrum of compound **2** indicates aromatic protons at δ values of 7.78, 7.19, 6.65, 6.43 ppm, and aliphatic protons at values of 4.23, 3.94, 3.72, 2.87, 2.69 ppm. The ^{13}C NMR spectrum of compound **2** indicated the presence of nitrile carbon atoms (C≡N) at 109.45 ppm.

The result of cyclotetramerization of dinitrile **2**, which obtained CoPc **3** supported by the absence of the sharp -C≡N vibration at 2231 cm^{-1}. ^{1}H-NMR spectrum of CoPc **3** not be obtained because of cobalt have paramagnetic properties. The MS spectrum of compound **3** showed molecular ion peaks at m/z=3055 $[M]^+$, confirming the proposed structure. The UV-Vis absorption spectra of CoPc **3** (Fig. 3) in THF show intense Q absorption at λ_{max} = 665 nm, respectively, with weaker absorption at 597 nm, respectively. The Q band absorption of **3** observed as a single band, which is typical of substituted and unsubstituted metal complexes of Pcs with D_{4h} symmetry.[27] B band absorptions of **3** are observed at λ_{max} = 340 nm, as expected.

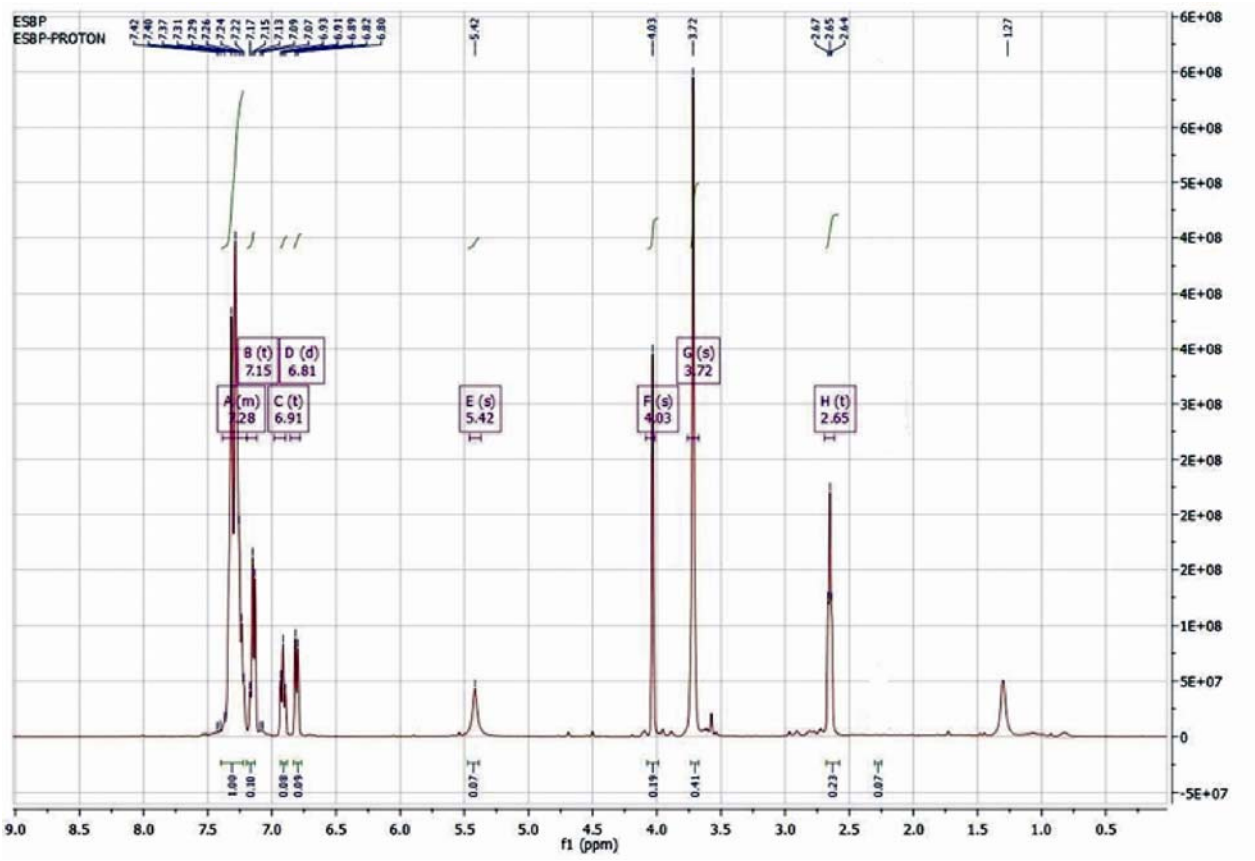


Fig. 1 – The ^{1}H-NMR spectrum of **1** in chloroform.

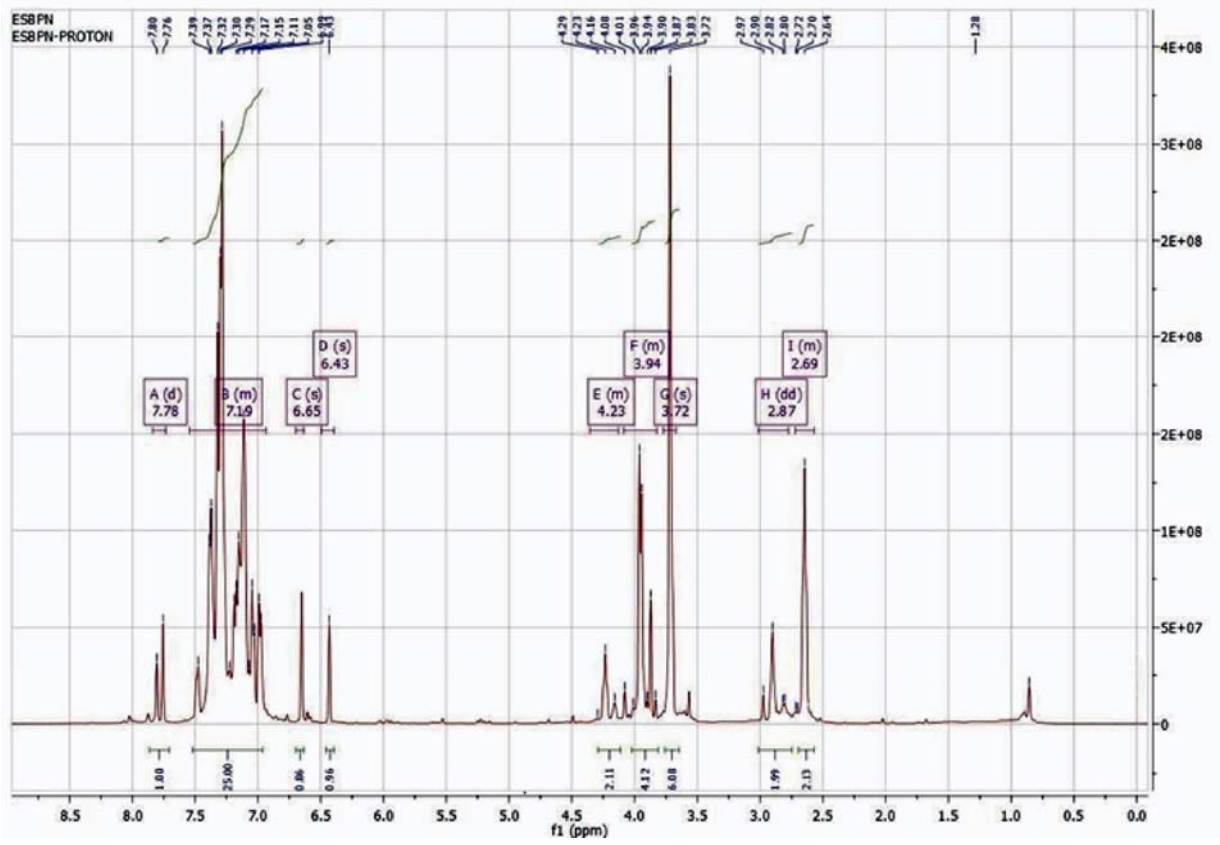
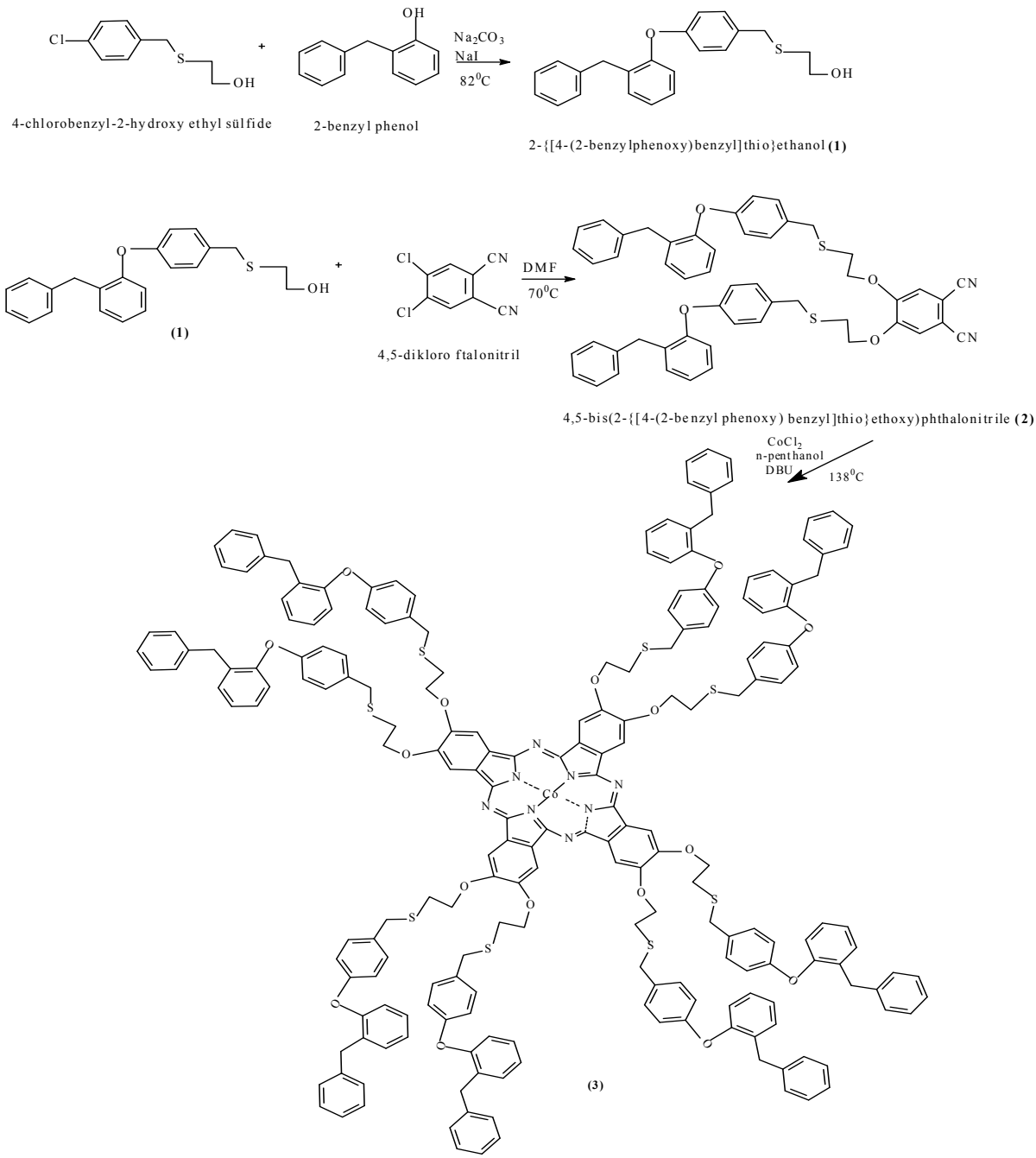


Fig. 2 – The ^{1}H-NMR spectrum of **2** in chloroform.



Scheme 1 – The synthesis of compounds **1-3**.

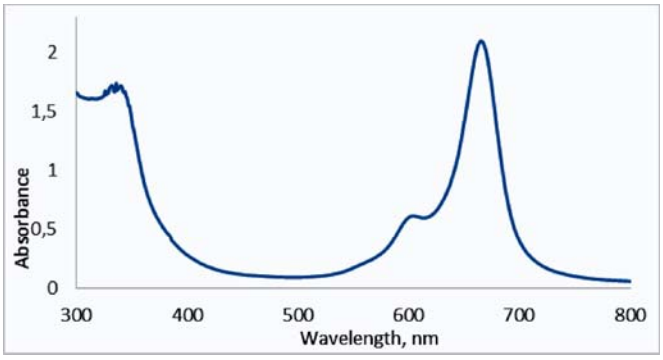


Fig. 3 – Uv-vis spectra of phthalocyanine **3** in Toluene ($1x10^{-5}$M).

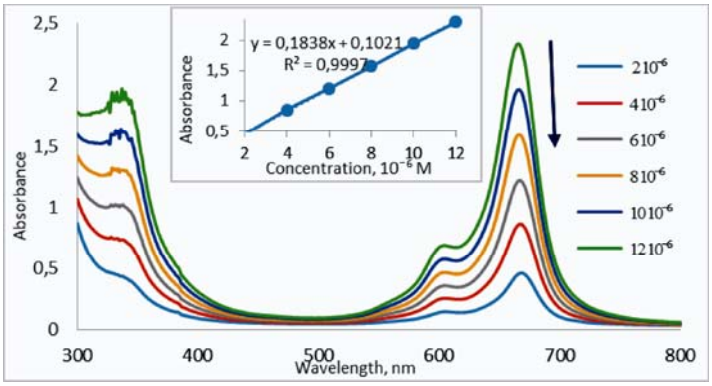


Fig. 4 – The aggregation behavior of phthalocyanine 3 in THF at different concentrations.

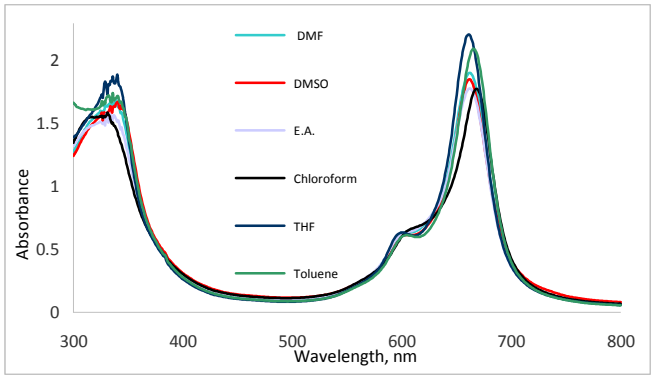


Fig. 5 – The aggregation behavior of phthalocyanine 3 in different solvents ($1x10^{-5}$M).

The mass spectrum of 2-{[4-(2-benzylphenoxy]benzyl]thio}ethanol **(1)**, 4,5-bis(2-{[4-(2-benzyl)phenoxy)benzyl]thio}ethoxy)phthalonitrile **(2)** and 2,3,9,16,17,23,24-Octa[(2-{[4-(2-benzyl)phenoxy)benzyl]thio}ethoxy)]phthalociyaninato cobalt(II) **(3)** showed molecular ion peaks at m/z=351 $[M+H]^+$, 848 $[M+K]^+$, 3355 $[M]^+$, respectively providing support for the structure.

1. Aggregation properties

The aggregation behavior of compound **3** searched by their UV-Vis spectra recorded at different concentrations in THF (Fig. 4). The broad split band and also the presence of a remarkably broad shoulder in 600-660 nm region at all concentrations within the range of $12x10^{-5}$-$2.0x10^{-5}$ M pointed out the presence of aggregated species of compound **3**. Although the amount of the aggregated species of compound **3** relatively decreases with dilution, these species are still present in the solution, even at 2.0 x 10^{-5} M concentration (Fig. 4). As clearly shown in Fig.4, CoPc **(3)** do not form aggregated species at different concentrations. And so, non-aggregated species are well confirmed by linear variation of the absorption with the concentration, as shown by the spectra in Fig. 4.

The aggregation behavior of compound **3** also investigated different solvents, such as DMF, DMSO, ethyl acetate, chloroform, THF, and toluene (Fig. 5). The formation of aggregated species at these different solvents reflected by the appearance of considerably broad shoulders within the range of 600-660 nm at a concentration of 1.0 x 10^{-5} M, as shown in Fig. 5. However, the Q band position slightly changes due to the solvent polarity effect, as shown for compound **3** in Fig. 5. In general, the redshift of the Q band increases with a refractive index of the solvent. CoPc **(3)** do not form aggregated species in all different solvents, as shown by the spectra in Fig.5. The electronic absorption spectra of in these solvents analyzed by using the method described by Babyliss.[25]

2. Electrochemical studies

All electrochemical measurements carried out with Gamry Interface 1000 potentiostat/galvanostat utilizing a three-electrode configuration at 25°C. The working electrode was a Pt disc with a surface

area of 0.071 cm^2. A Pt wire served as the counter electrode, and a saturated calomel electrode (SCE) employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabuthylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

Voltammetric analyses of $Co^{II}Pc$ carried out in dichloromethane (DCM)/tetrabutylammoniumperchlorate (TBAP) electrolyte system on a Pt working electrode with (CV) and (SWV) techniques. The results of the voltammetric data is given in Table 1.

Figures 6a and 6b show the CV and SWV responses of $Co^{II}Pc$ in DCM/TBAP on a Pt working electrode. $Co^{II}Pc$ exhibits two quasi-reversible reduction (R_1= -0.26 V, R_2= -1.34 V) and one reversible oxidation (O_1= 0.84 V), one quasi-reversible oxidation (O_1= 1.18 V) process with respect to ΔE_p values. Cobalt phthalocyanines generally shows a metal-based reduction process at around 0 V due to the electron gaining to the empty d orbitals of Co^{II} center located between the HOMO and LUMO orbitals of the Pc ring.[28] For this reason, R_1 processes could assigned to the cobalt-based redox couple and the remaining redox couple (R_2) to the ring based redox couple.

Table 1

Voltammetric data of the $Co^{II}Pc$. All voltammetric data given *versus* SCE

Phthalocyanine	Redox processes	[a]$E_{1/2}$	[b]ΔE_p (mV)	[c]$\Delta E_{1/2}$
$Co^{II}Pc$	**R_1**	-0.26[d]	152	
	R_2	-1.34 [e]	140	
	O_1	0.84	88	1.10
	O_2	1.18	145	

[a]: $E_{1/2}$ values ((E_{pa}+E_{pc})/2) were given *versus* SCE at 0.100 Vs^{-1} scan rate. **[b]:** $\Delta E_p = E_{pa}-E_{pc}$. **[c]**: $\Delta E_{1/2}$ = $E_{1/2}$ (first oxidation)-$E_{1/2}$ (first reduction). **[d]:** This process is assigned to $[Co^{II}Pc^{2}]/[Co^{I}Pc^{2-}]^{1-}$. **[e]:**This process is assigned to $[Co^{I}Pc^{2-}]^{1-}/[Co^{I}Pc^{3-}]^{2-}$.

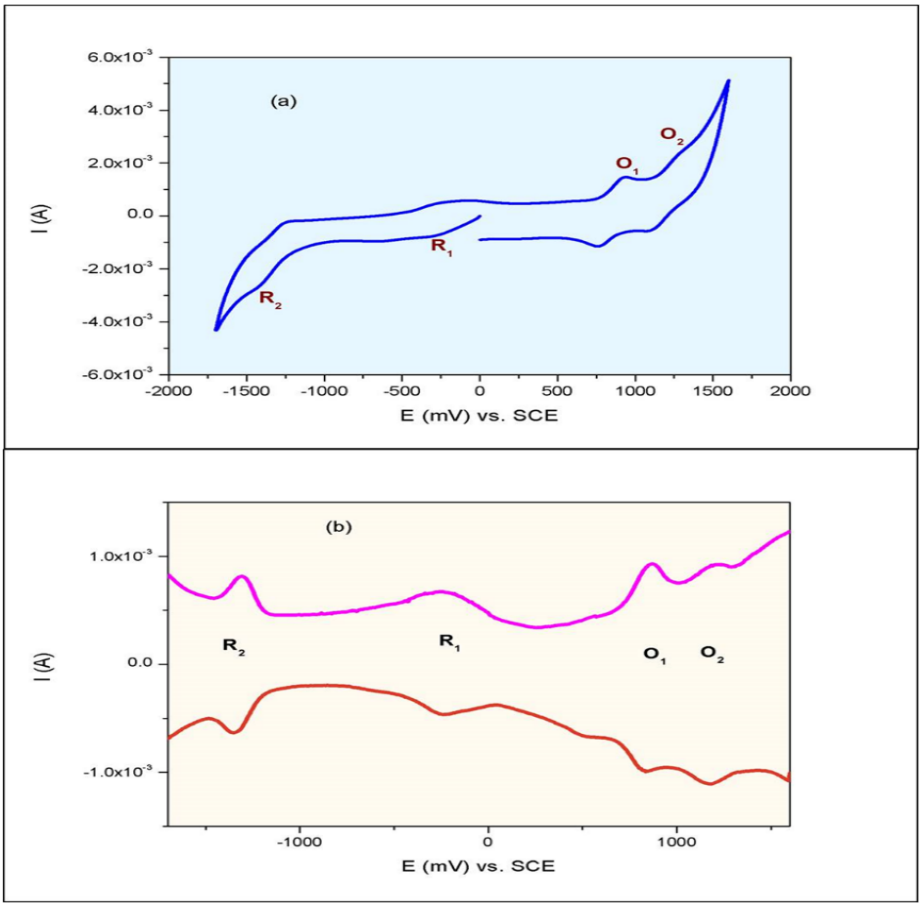


Fig. 6 – (a) CV of $Co^{II}Pc$**.** (b) SWV of $Co^{II}Pc$.

CONCLUSIONS

The syntheses of new Pc compound **3** has been achieved by the tetramerization of phthalonitrile derivative, 2-{[44,5-bis(2-{[4-(2-benzyl)phenoxy) benzyl]thio} ethoxy) phthalonitrile **2** in n-pentanol at 140°C. The newly prepared compounds were characterized by classical spectroscopic methods. Aggregation behaviors of the Pc compound was investigated by their UV-Vis spectra in different solvents and concentrations. 2,3,9,16,17,23,24-Octa[(2-{[4-(2-benzyl)phenoxy)benzyl]thio} ethoxy)] phthalociyaninato cobalt(II) **3** do not display aggregation behavior, due to the axial coordinating ability of the central metal. CoPc has excellent solubility in various organic solvents such as: DMSO, $CHCl_3$, DMF, and THF. The electrochemical properties of $Co^{II}Pc$ studied in solution with voltammetric measurements. According to the results, which enrich the possible usage of the complex in various electrochemical technologies, $Co^{II}Pc$ display rich electrochemical redox behavior including both ligand and/or metal-based, usually reversible or quasi-reversible one-electron redox processes. Electron transfer processes of the compounds, especially CoPc was found to be associated with net color changes, and thus, usable as electro chromic materials. It was found to be able to catalyze reduction of dioxygen to water via a process including both 4-electrons transfer and two 2-electrons transfer steps to form directly water in one step and first hydrogen peroxide and then water in two steps, respectively. Therefore, it appeared as a good candidate for preparing high-performanced ORR electrocatalysts for fuel cell applications.

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