






New octa-benzothiazole substituted metal-free and metallophthalocyanines: Synthesis, characterization and electrochemical studies

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Abstract

The synthesis of novel phthalonitrile (3) and synthesis, spectroscopic and electrochemical properties of the following octa-benzothiazole substituted metal-free (4), cobalt(II) (5), and zinc(II) (6) phthalocyanines are reported for the first time in this work. The novel phthalonitrile (3) has been characterized by FT-IR, ¹H NMR, ¹³C NMR, and mass spectroscopy and the novel phthalocyanines (4-6) have been characterized by FT-IR, electronic spectroscopy, and mass spectroscopy. Voltammetric analysis of benzothiazole group substituted phthalocyanines (MPc) were determined by cyclic voltammetry (CV) and square wave voltammetry (SWV). According to the results, phthalocyanines revealed metal and ligand-based quasi-reversible reduction and oxidation processes. While the CoPc 5 showed one metal-based and one Pc-based reduction reactions, H₂Pc 4 and ZnPc 6 gave two Pc-based reduction reactions.

Keywords: Phthalocyanine, zinc, electrochemistry, squarewave, cyclic voltammetry

1. Introduction

Phthalocyanines, planar aromatic macrocycles constituted by four isoindole units linked together through nitrogen atoms, were serendipitously discovered in 1928. These synthetic analogs of the naturally occurring porphyrins have been the subject of extensive research in many different fields such as lithium batteries, optical data storage, solar energy conversion, catalysis, and so on [1-6]. Apart from the use in materials science, phthalocyanines are also highly promising for their applications as magnetic resonance imaging (MRI) and photodynamic therapy (PDT) [7-9].

Many functions of metallophthalocyanine derivatives resulted from electron transfer occurring in these macromolecules. Determination of electrochemical behavior is required for the development of functional materials carrying metallophthalocyanine. MPc having Pc²⁻, phthalocyanine dianion, does not show redox activity at the ring. Two successive one-electron oxidations may happen by the removal of electrons from *a_{1u}* forming Pc⁻¹ and Pc⁰ species. Reductions happen by adding electrons to *e_g* to form Pc³⁻, Pc⁴⁻, Pc⁵⁻ and Pc⁶⁻ species. Each oxidation and reduction species has a definite spectrum that can be employed for its characterization. The presence of the electroactive

central metal causes additional redox processes to occur, resulting in unique electronic spectral behavior [10].

Also, phthalocyanines can be used as electrochemical sensors. The use of metallophthalocyanines as electrochemical sensors has become widespread and new sensors are being produced day by day [11,12].

In our previous papers, we reported electrochemical and spectroelectrochemical properties of various tetra substituted metal-free and metallophthalocyanines which have electroactive and non-electroactive centers. [13-16]. As seen in the literature, the electrochemical properties of tetrasubstituted metal-free and metallophthalocyanines have worked in recent years [17-19], but there is not much work on the electrochemical properties of octa-substituted metal-free and metallophthalocyanines [20-22]. So in this study, the electrochemical properties of the octa-substituted metal-free phthalocyanine (4) and zinc(II) phthalocyanine (6) having the non-electroactive center, and cobalt(II) phthalocyanine (5) carrying an electroactive center have been investigated.

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2. Experimental

The used materials and equipment were provided as supplementary information.

2.1. Synthesis

2.1.1. Synthesis of 4,5-bis(2-(benzo[d]thiazol-2-yl)phenoxy)phthalonitrile (3)

The mixture of 2-(benzo[d]thiazol-2-yl) phenol (1) (2.00 g, 8.80 mmol) and 4,5-dichlorophthalonitrile (2) (0.86 g, 4.40 mmol) were dissolved in dry DMF (30 ml) under nitrogen atmosphere and this mixture was stirred at 65 °C for 10 min. After stirring, finely ground anhydrous K₂CO₃ (2.42 g, 17.60 mmol) was added over a period of 2 h and it was stirred under the nitrogen atmosphere at 65 °C for 3 days. The reaction mixture was added crushed ice. The forming white precipitate was filtered off, washed with distilled water, and then dried in vacuo. Yield: 1.33 g (52%), m.p.: 109.2-110.3 °C. C₃₄H₁₈N₄O₂S₂. FT-IR $\nu_{\max}/\text{cm}^{-1}$: 3061 (Ar-H), 2237 (C≡N), 1482, 1381, 1270, 1197, 1010, 969, 757, 727, 694. ¹H NMR (CDCl₃) (δ ppm): 8.57-8.56 (d, H, Ar-H), 8.07-8.05 (d, H, Ar-H), 8.02-8.00 (d, H, Ar-H), 7.93 (s, H, Ar-H), 7.91-7.88 (m, 2H, Ar-H) 7.72-7.70 (d, H, Ar-H), 7.65-7.62 (t, H, Ar-H), 7.53-7.50 (m, 3H, Ar-H), 7.45-7.40 (m, 3H, Ar-H), 7.19-7.17 (d, H, Ar-H), 7.14-7.12 (d, H, Ar-H), 7.09 (s, H, Ar-H), 7.00-6.96 (t, H, Ar-H). ¹³C NMR (CDCl₃) (δ ppm): 169.39, 160.68, 157.94, 157.29, 152.61, 151.84, 150.42, 135.62, 135.54, 132.80, 132.66, 131.39, 129.84, 128.45, 127.55, 126.73, 126.61, 125.75, 125.59, 123.49, 122.20, 121.72, 121.56, 121.50, 119.94, 119.57, 117.87, 116.79, 115.62, 114.28, 114.22, 110.36. MS (ES⁺), m/z : Calc.: 578.68; Found: 578.66 [M]⁺.

2.1.2. Synthesis of metal-free phthalocyanine H₂Pc (4)

Compound 3 (0.20 g, 0.34 mmol) and three drops of DBU were stirred in dry *n*-pentanol (3 mL) under reflux in a nitrogen atmosphere at 160 °C in a sealed glass tube for 24 h. Then, the mixture was degassed several times before it was left to cool to room temperature. 20 mL of ethanol was added to the mixture to be precipitated the green crude product and filtered off. The obtained green product was filtered off again after the refluxing with 40 mL of ethanol for 4 h. The solid product was successively washed several times with hot ethanol, distilled water, and diethyl ether to removing the organic impurities. Column chromatography using chloroform-methanol (96:4) solvent system as eluent was applied to purification of the product after it dried in vacuo. Yield: 70 mg (35%), m.p.: >300 °C. C₁₃₆H₇₄N₁₆O₈S₈. FT-IR $\nu_{\max}/\text{cm}^{-1}$: 3286 (N-H), 3061 (Ar-H), 1497, 1422, 1239, 1100, 1012, 871, 749, 726. UV/vis (chloroform): λ , nm (log ϵ): 712 (5.40), 675 (5.26), 645 (4.79), 611 (4.62), 384 (4.92). MS

(ES⁺), m/z : Calc.: 2316.72; Found: 1550.480 [M-6C₇H₄NS+K]⁺.

2.1.3. General procedures for metallophthalocyanine derivatives (5, 6)

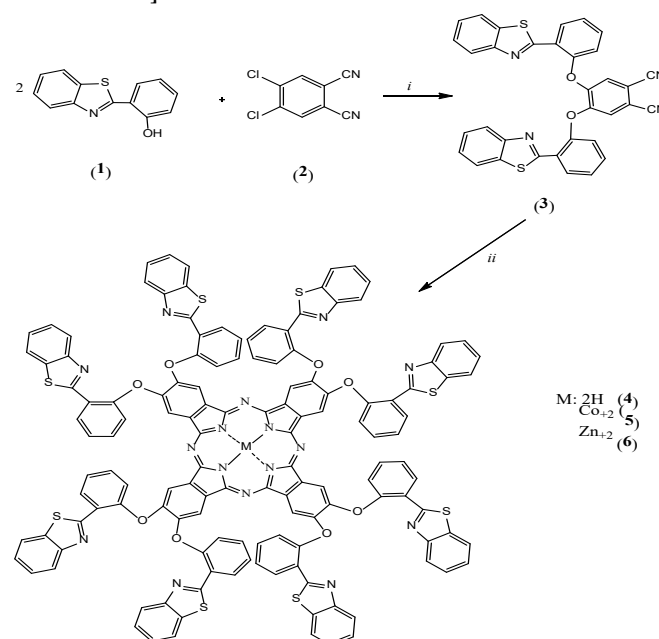
The mixture of compound 3 (0.40 g, 0.68 mmol), anhydrous metal salt [CoCl₂ (88 mg, 0.68 mmol) or Zn(CH₃COO)₂ (124 mg, 0.68 mmol)] and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene was stirred at 160 °C with dry *n*-pentanol (3 mL) in a sealed tube for 24 h. Then, the mixture was left to cool to room temperature. The green crude product was precipitated with 10 mL of ethanol and then filtered off. The green-colored product was filtered off again after refluxing with 40 mL of ethanol for 4 h. It was successively washed several times with hot ethanol, distilled water, and diethyl ether to remove the organic impurities. Column chromatography using a chloroform-methanol (96:4) solvent system as eluent was applied to purify the product after it dried in vacuo.

2.1.3.1. Cobalt (II) phthalocyanine (5)

Yield: 27 mg (7%), m.p.: >300 °C. C₁₃₆H₇₂N₁₆O₈S₈Co. FT-IR $\nu_{\max}/\text{cm}^{-1}$: 3058 (Ar-H), 1497, 1432, 1399, 1242, 1195, 1098, 1004, 967, 888, 750, 725. UV/vis (chloroform): λ , nm (log ϵ): 682 (5.15), 613 (4.48), 305 (5.15). MS (ES⁺), m/z : Calc.: 2373.63; Found: 1607.901 [M-6C₇H₄NS+K]⁺.

2.1.3.2. Zinc (II) phthalocyanine (6)

Yield: 102 mg (25%), m.p.: >300 °C. C₁₃₆H₇₂N₁₆O₈S₈Zn. FT-IR $\nu_{\max}/\text{cm}^{-1}$ (KBr pellet): 3061 (Ar-H), 1727, 1428, 1388, 1239, 1195, 1094, 990, 877, 753, 744. UV/vis (chloroform): λ , nm (log ϵ): 691 (5.25), 619 (4.52), 358 (4.86), 317 (5.06). MS (ES⁺), m/z : Calc.: 2380.09; Found: 1614.725 [M-6C₇H₄NS+K]⁺.



Scheme 1. Synthesis of 3, 4, 5 and 6. *i*: K₂CO₃, DMF, 50 °C, 5 days. *ii*: 1-pentanol, DBU, related metal salts (CoCl₂, Zn(ac)₂), 24h, 160 °C

3. Results and discussion

3.1. Synthesis and characterization

The octa-benzothiazole substituted phthalonitrile derivative **3** was obtained by the reaction of 2-(benzo[d]thiazol-2-yl)phenol **1** with 4,5-dichlorophthalonitrile **2** in 52% yield (Scheme 1). The nucleophilic substitution reaction was performed in the presence of anhydrous K_2CO_3 in dry DMF at 65 °C [23].

Octa-substituted zinc(II) and cobalt(II) phthalocyanines (**5** and **6**) were synthesized by treatment of phthalonitrile derivatives **3** in the presence of related anhydrous metal salts ($Zn(CH_3COO)_2$ and $CoCl_2$ respectively) as a metal source in dried *n*-pentanol at 160 °C [24]. The yields of the reactions for compounds **5** and **6** were determined as 7% and 25%, respectively. Starting phthalonitrile derivatives **3**, metal-free phthalocyanine compound **4** was synthesized under the same conditions without using metal salt in a 52% yield. The general synthetic procedures of the novel phthalocyanine compounds (**4-6**) were shown in Scheme 1. Purification of the crude products was carried out by column chromatography using the chloroform-methanol solvent system as an eluent.

The structures of novel compounds were characterized by FT-IR, 1H NMR, ^{13}C NMR, UV-vis spectroscopies, and mass spectra.

For compound **3**, the appearance of vibration bands at 2223 $C\equiv N$, 1283 (Ar-O-C) in the FT-IR spectrum showed the formation of **3**. In the 1H NMR spectrum of this phthalonitrile **3**, the proton signal of OH group of 2-(benzo[d]thiazol-2-yl)phenol disappeared as expected. The resonances for the compound **3** in the 1H NMR were observed between 8.57-6.96 ppm integrating for a total of 18 aromatic protons. In the ^{13}C NMR spectrum of **3**, the characteristic signals of nitrile carbon atoms were observed at $\delta = 11.79, 115.62$ ppm. The mass spectrum of phthalonitrile **3** showed a molecular ion peak at $m/z = 578.66 [M]^+$.

For the new phthalocyanine compounds, cyclotetramerization of phthalonitrile **3** was evidenced by the loss of the $-C\equiv N$ signal in the FT-IR spectrum of compounds **4**, **5**, and **6** after the formation of the phthalocyanine rings. Mass spectra of phthalocyanine compounds **4**, **5**, and **6** reasonably supported the expected structures when observing molecular ion peaks at 1550.480 as $[M-6C_7H_4NS+K]^+$ for **4**, 1607.901 as $[M-6C_7H_4NS+K]^+$ for **5** and 1614.725 as $[M-6C_7H_4NS+K]^+$ for **6** (Fig. 1, Fig. 2 and Fig. 3), respectively.

3.2. Electronic absorption spectra

The electronic spectra of phthalocyanines exhibit several bands which are due to $\pi-\pi^*$ and $n-\pi^*$ transitions. In the near UV region, there is the B band or Soret band at

approximately between 300-400 nm and finally, there is the strongest Q band at approximately between 600-700 nm. While the Q bands of the H_2Pc s are observed as split two bands, because of D_{2h} symmetry and the lifting of the degeneracy of the LUMO (eg) level, as Q_x and Q_y bands that of MPc s are observed as a single intense band because of D_{4h} symmetry [10, 25].

Fig. 4 shows the UV-Vis absorption spectra of complexes **4-6** in chloroform. Table 1 contains a summary of the Q band maxima of the complexes (**4-6**). In UV-vis spectra of metal-free (**4**) phthalocyanine gave a split two Q band absorptions at 712 and 675 nm with shoulders 645 and 611 nm, respectively as expected.

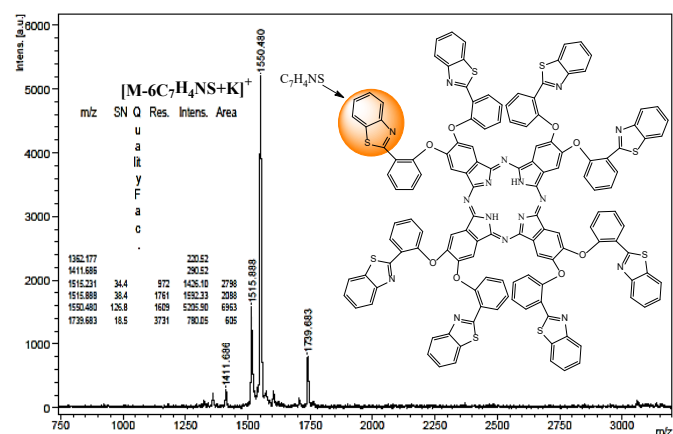


Figure 1. Mass spectrum of phthalocyanine 4

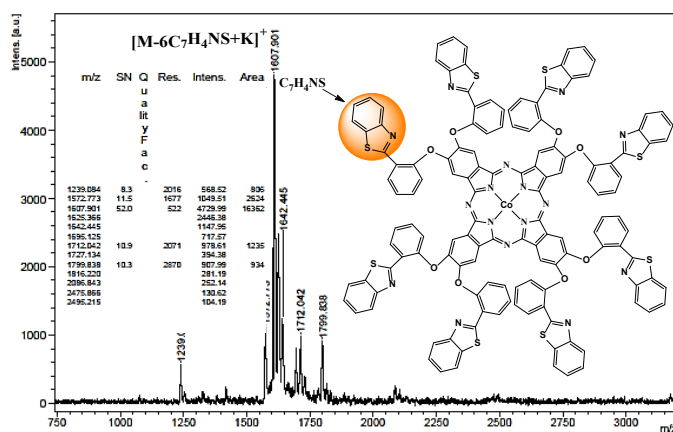


Figure 2. Mass spectrum of phthalocyanine 5

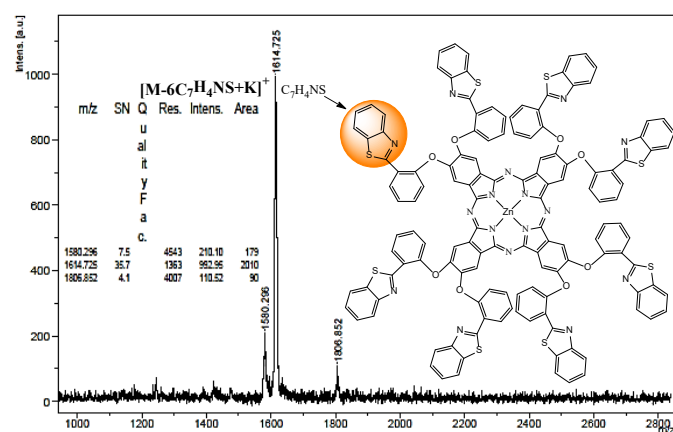


Figure 3. Mass spectrum of phthalocyanine 6

Table 1. Absorption spectral data for 4, 5, and 6 in chloroform

	Solvent	Q band, λ_{\max} (nm)	$\log \epsilon$	B band, λ_{\max} (nm)	$\log \epsilon$
H₂Pc (4)	Chloroform	712	5.40	384	4.92
		675	5.26		
		645	4.79		
		611	4.62		
CoPc (5)	Chloroform	682	5.15	305	5.15
		613	4.48		
ZnPc (6)	Chloroform	691	5.25	358	4.86
		619	4.52		

The cobalt(II) (5) and zinc(II) (6) phthalocyanines gave an intense single Q band absorption of the π - π^* transitions at 682 and 691 nm with shoulders 613 and 619 nm, respectively. The B bands of complexes were observed at 384 nm for 4, 305 nm for 5, and (358, 317) nm for 6, respectively.

3.3. Electrochemical Studies

Electrochemical studies of H₂Pc, ZnPc, CoPc were achieved in DCM using a (DCM)/(TBAP) electrolyte system on a Pt working electrode. The results are shown in Table 2. Fig. 5 shows the CV and the SWV of H₂Pc in DCM. H₂Pc gave two ring-based and quasi-reversible reductions (R₁ = -0.55 V, R₂ = -0.91 V) and one oxidation (O₁ = 1.22 V) process. This data of the H₂Pc is compatible with H₂Pc behavior in literature [26]. Fig. 6 shows the CV and the SWV of ZnPc. Similarly, ZnPc gave two ring-based and quasi-reversible reductions (R₁ = -0.92 V, R₂ = -1.17 V) and one oxidation (O₁ = 0.93 V) process. But, CoPc showed different electrochemical behavior than H₂Pc and ZnPc. Fig. 7 shows the CV and the SWV of CoPc. As shown in Fig. 7, CoPc gave one metal-based and one ring based quasi-reversible reductions (R₁ = -0.20 V, R₂ = -1.24 V), two oxidation (O₁ = 0.92 V, O₂ = 1.29 V) processes.

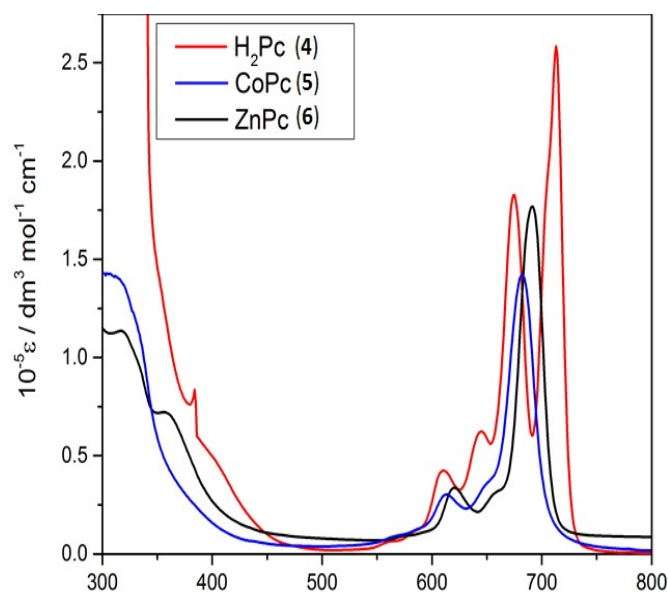


Figure 4. Absorption spectra of novel synthesized octa-substituted phthalocyanines (4-6) in chloroform

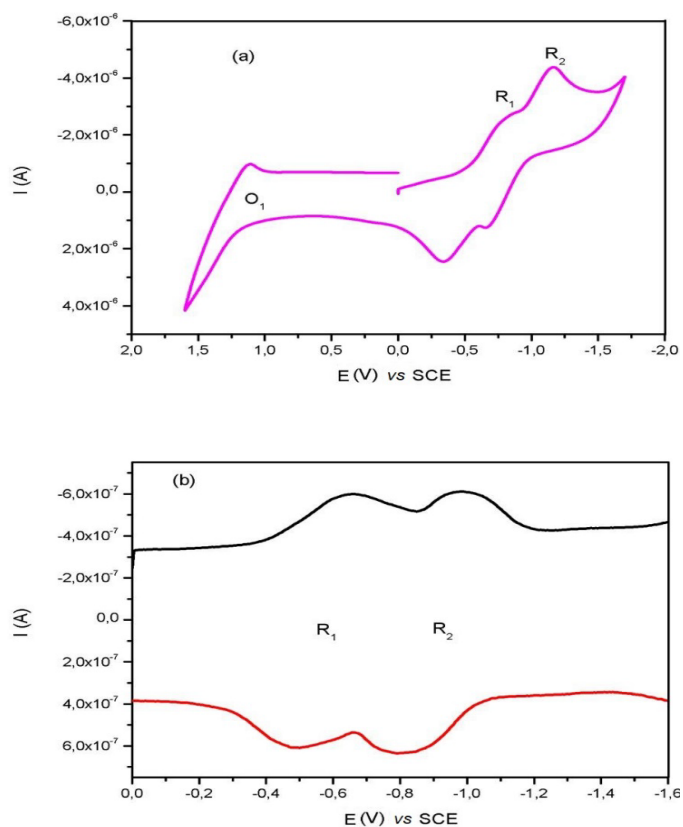


Figure 5. (a) CV of H₂Pc recorded at 0.100 Vs⁻¹ scan rate on a Pt electrode in DCM/TBAP. (b) SWV of H₂Pc recorded at 0.100 Vs⁻¹ scan rate on a Pt electrode in DCM/TBAP

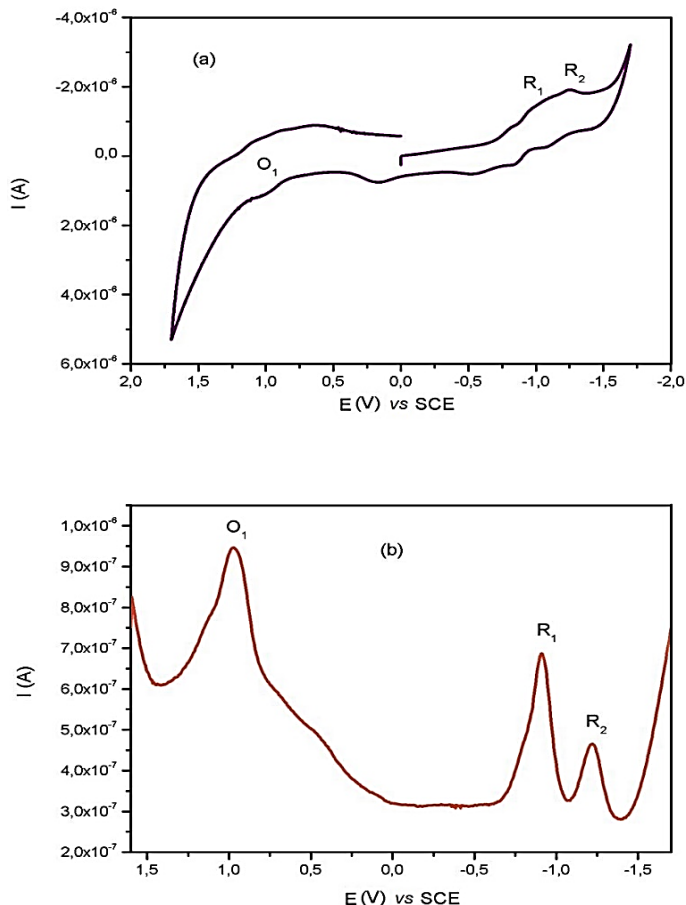


Figure 6. (a) CV of ZnPc recorded at 0.100 Vs⁻¹ scan rate on a Pt electrode in DCM/TBAP. (b) SWV of ZnPc recorded at 0.100 Vs⁻¹ scan rate on a Pt electrode in DCM/TBAP

Table 2. Voltammetric data of the 4-6. The voltammetric data were given versus SCE

Phthalocyanines	Label	^a E _{1/2}	^b ΔE _p (mV)	^c ΔE _{1/2}
H ₂ Pc (4)	R ₁	-0.55	161	1.77
	R ₂	-0.91	156	
	O ₁	1.22	170	
ZnPc (5)	R ₁	-0.92	178	1.85
	R ₂	-1.17	166	
	O ₁	0.93	180	
CoPc (6)	R ₁	-0.20	173	1.12
	R ₂	-1.24	151	
	O ₁	0.92	144	
	O ₂	1.29	163	

^a: E_{1/2} values ((E_{pa}+E_{pc})/2) were given versus SCE at 0.100 Vs⁻¹ scan rate.

^b: ΔE_p= E_{pa}-E_{pc}. ^c: ΔE_{1/2}= E_{1/2} (first oxidation)-E_{1/2} (first reduction)

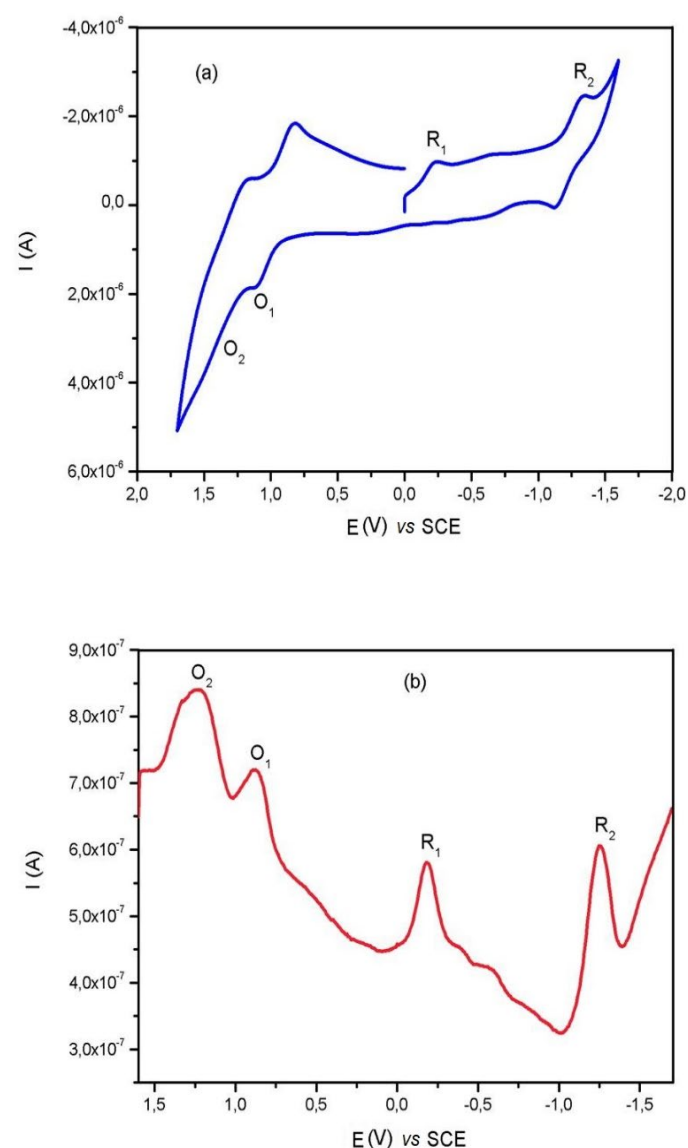


Figure 7. (a) CV of CoPc recorded at 0.100 Vs⁻¹ scan rate on a Pt electrode in DCM/TBAP. (b) SWV of CoPc recorded at 0.100 Vs⁻¹ scan rate on a Pt electrode in DCM/TBAP

4. Conclusions

Octa-benzothiazole substituted H₂Pc, CoPc, and ZnPc phthalocyanines were synthesized in moderate yields and fully characterized by general spectroscopic

techniques such as FT-IR, UV-Vis, ¹H-NMR, and MS. The obtained novel compounds exhibited excellent solubility in most organic solvents such as CHCl₃, CH₂Cl₂, THF, DMSO, and DMF. CV and SWV were used to determine the electrochemical properties of the H₂Pc, the ZnPc, and the CoPc. Electrochemical responses of the H₂Pc, the ZnPc, and the CoPc verified the proposed structure. The H₂Pc and the ZnPc showed only ring-based redox processes. But CoPc exhibited one metal-based and one ring-based redox reactions. These properties increase their possible usage in different electrochemical applications.

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Supplementary Information

1. Materials

All solvents and reagents were dried and purified according to the known methods [1]. 4,5-dichlorophthalonitrile (2) was prepared according to the reported procedure [2]. Reagent grade chemicals and solvents were used obtained from commercial suppliers.

2. Equipment

Infrared and electronic spectra were recorded on a Perkin-Elmer FT-IR spectrometer and Unicam UV2-100 Shimadzu 2101 spectrophotometers using 1 cm path length cuvettes at room temperature, respectively. All of the reactions were carried in a standard Schlenk system under a dry nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer by using CDCl_3 as a solvent, and chemical shifts were reported (δ) relative to TMS as an internal standard. Mass spectra were recorded on a Bruker Microflex LT MALDI-TOF MS spectrometer (Gebze Technical University, Turkey). An electrothermal apparatus was used to determine the melting points. Column chromatography processes was carried out with silica gel 60 (particle size: 0.04-0.063 mm).

Gamry Interface 1000 potentiostat/galvanostat with a three-electrode configuration was employed for all electrochemical measurements at 25 °C. The working electrode was a Pt disc having a surface area of 0.071 cm². A Pt wire was employed as the counter electrode and the saturated calomel electrode (SCE) was used as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was used as the supporting electrolyte at a concentration of 0.10 mol/dm³.

References

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