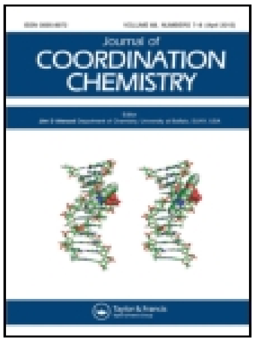

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Synthesis and electrochemistry of new octa-substituted metal-free and metallophthalocyanines

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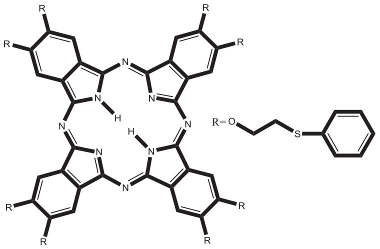

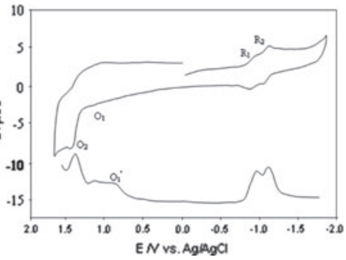

The synthesis and characterization of metal-free (H_2-Pc) and metal-containing (Zn, Co, and Cu) derivatives of a symmetrically octa-substituted phthalocyanine derived from 4,5-bis[2-(phenylthio)ethoxy]phthalonitrile were carried out by microwave irradiation. The electrochemical properties of the metal-free phthalocyanine **4** and metallophthalocyanine complexes **5** and **6** were investigated by cyclic voltammetry and differential pulse voltammetry. We have previously investigated the electrochemical properties of the tetra substituted 2-(phenylthio)ethoxy phthalocyanines. The reduction potential of the octa-substituted metal-free phthalocyanine shifted to more negative potential as a result of the electron donating of the 2-(phenylthio)ethoxy groups on the periphery compared to those of tetra substituted. The H_2Pc and ZnPc demonstrated ligand-based electron transfer processes, while CoPc complex has a metal-based reduction process. Similar aggregation behavior was observed for octa-substituted phthalocyanines. The compounds were characterized using IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and MS spectral data.

Keywords: Metallophthalocyanine; Synthesis; Microwave; Phthalonitrile; Cyclic voltammetry; Differential pulse voltammetry

1. Introduction

Since their discovery, phthalocyanines (Pcs) have received intense research due to their unique properties and applications [1]. They have planar molecular structures with extensive

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π electron delocalization together with chromophoric nature resulting from it, low solubility, high thermal stability and electrochromism [2–5]. Phthalocyanine complexes are utilized in diverse fields of technical and surgical applications such as photodynamic therapy of cancer [6], laser dyes, new red-sensitive photocopying applications [7], optical computer read/write disks [8], and liquid crystals [9] as a result of the synthesis of new compounds [10]. Metallophthalocyanines (MPcs) have electron transfer features based on size of metal core and substituents owing to the conjugated ring π electron system. Investigation of electron transfer of a compound is a fundamental activity for estimation of functional materials [11].

Phthalocyanine complexes have low solubility in most common organic solvents. To increase solubility, many different substituents, for example crown ethers, alkyl, alkoxy, alkilthyio, morpholine, and macrocyclic groups, must be attached to peripheral positions [12–15]. Many axially substituted Pc compounds have been synthesized to improve the solubility of Pcs in protic or non-protic solvents [16–18].

The electrochemistry of phthalocyanine complexes relates to kind of metal center, nature of substituents and solvent. The industrial implementation of Pcs depends on their redox properties. Square-wave voltammetry and cyclic voltammetry (CV) are used to determine electrochemical properties in solution. Electrochemical features of MPcs have been extensively examined [19, 20].

Microwave irradiation has been used for the synthesis of Pcs [21–31]. Microwave irradiation is an alternative to classical thermal method due to controllable interaction directly with components in solvent and solvent-free system. Therefore, microwave irradiation can be used for synthesis of Pcs as an appropriate method, reducing chemical reactions times and also enhancing yield and reproducibility. We have previously synthesized metal-free and MPcs containing tetra-substituted 2-(phenylthio)ethoxy functional group [32]. In this article, the synthesis and characterization of metal-free **4** and MPc complexes **5**, **6**, and **7** by microwave irradiation are described. Also, we have studied electrochemical properties of phthalocyanine complexes by CV and differential pulse voltammetry (DPV) methods.

2. Experimental

2.1. *Materials and methods*

2-(Phenylthio)ethanol **1** [33] and 1,2-dichloro-4,5-dicyanobenzene [34] **2** were prepared according to the literature. All reagents and solvents were of reagent grade quality and obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [35]. The IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. Optical spectra in the UV–vis region were recorded with a PG T80 + spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected.

The CV and DPV measurements were carried out with a BAS E2 Epsilon voltammetric analyzer. A three-electrode system was used: a platinum wire counter electrode, a Ag/AgCl reference electrode, and a 2 mm glassy carbon disk electrode as working electrode. The surface of the working electrode was polished with a H_2O suspension of Al_2O_3 before each run. High purity nitrogen was used for deoxygenating the solution for at least 15 min prior to each run and maintain a nitrogen blanket during the measurements.

2.2. *Synthesis*

2.2.1. Preparation of 4,5-bis[2-(phenylthio)ethoxy]phthalonitrile (3). 2-(Phenylthio) ethanol **1** (2 g, 12.98 mM), 1,2-dichloro-4,5-dicyanobenzene **2** (1.27 g, 6.49 mM), and K_2CO_3 (3.58 g, 25.96 mM) in dry DMF (30 mL) were stirred at 50 °C for 4 days under N_2. Then, the solution was poured into ice-cold water (100 mL). The precipitate formed was filtered off, washed first with water until the filtrate was neutral and then diethyl ether, and dried in vacuo over P_2O_5. The crude product was crystallized from ethanol. Yield: 1.68 g (60%), m.p.: 102–103 °C. Anal. Calcd for $C_{24}H_{20}N_2O_2S_2$: C, 66.64; H, 4.66; N, 6.48; S, 14.83%. Found: C, 66.44; H, 4.86; N, 6.71; S, 15.03. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2927–2851 (C–H), 2233 (C≡N), 1586, 1495, 1376, 1311, 1275, 1133, 1030, 741, 691. ^1H NMR. ($CDCl_3$), (δ:ppm): 7.75 (s, 2H, Ar–H), 7.41 (d, 4H, J = 8.2 Hz, Ar–H), 7.33 (m, 2H, Ar–H), 7.11 (d, 4H, J = 8.4 Hz, Ar–H), 4.22 (t, 4H, J = 6.7 Hz, $–CH_2–O$), 3.36 (t, 4H, J = 6.4 Hz, $–CH_2–S$). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 157.78, 135.09, 130.84, 129.30, 127.61, 119.92, 114.47, 113.32, 68.97, 32.81. MS (ES^+), (*m/z*): 433 $[M + H]^+$.

2.2.2. Preparation of metal-free phthalocyanine (4). Compound **3** (0.4 g, 0.92 mM) was added to 2-(dimethylamino)ethanol (DMAE) (3 mL). The mixture was well stirred and then irradiated by microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture refluxed with ethanol (45 mL) to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, diethyl ether, and dried in vacuo. The green solid product was chromatographed on silica gel with chloroform : methanol (9.5 : 0.5) as eluents. Yield: 0.156 g (39%), m.p.: >300 °C. Anal. Calcd for $C_{96}H_{82}N_8O_8S_8$: C, 66.56; H, 4.77; N, 6.47; S, 14.81%. Found: C, 66.75; H, 4.89; N, 6.57; S, 14.70. IR (KBr tablet) ν_{max}/cm^{-1}: 3280 (N–H), 3049 (Ar–H), 2927–2851 (Aliph. C–H), 1602, 1580, 1473, 1438, 1373, 1259, 1105, 1017, 846, 740, 690. ^1H NMR. ($CDCl_3$), (δ: ppm): 7.80 (s, 8H, Ar–H), 7.51 (m, 16H, Ar–H), 7.36 (m, 8H, Ar–H), 7.21 (d, 16H, J = 8.6 Hz, Ar–H), 4.28 (t, 16H, J = 6.9 Hz, $–CH_2–O$), 3.25 (t, 16H, J = 6.8 Hz, $–CH_2–S$). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 159.24, 136.23, 130.45, 129.22, 128.82, 122.62, 120.45, 118.32, 69.38, 36.32. UV–vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} ε dm^3 M^{-1} cm^{-1})]: 308 (4.54), 332 (4.50), 614 (4.51), 671 (4.44), 707 (4.36). MS (ES^+), (*m/z*): 1732 $[M]^+$.

2.2.3. Preparation of zinc(II) phthalocyanine (5). A mixture of 4,5-bis[2-(phenylthio) ethoxy]phthalonitrile **3** (0.4 g, 0.92 mM), anhydrous metal salts $Zn(CH_3COO)_2$ (42 mg), and 2-(dimethylamino)ethanol (3 mL) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the green suspension was precipitated with ethanol, filtered and washed first with ethanol, then diethyl ether and then dried in vacuo over P_2O_5. The pure green solid product was obtained by column chromatography on silica gel with chloroform as eluents. Yield: 0.182 g (44%), m.p.: >300 °C. Anal. Calcd for $C_{96}H_{80}N_8O_8S_8Zn$: C, 64.21; H, 4.49; N, 6.24; S, 14.29%. Found: C, 64.30; H, 4.59; N, 6.15; S, 14.33. IR (KBr tablet) ν_{max}/cm^{-1}: 3076 (Ar–H), 2917–2856 (Aliph. C–H), 1603, 1478, 1438, 1374, 1261, 1100, 1022, 886, 742, 691. ^{1}H NMR. (CDCl$_3$), (δ:ppm): 7.85 (br, s, 8H, Ar–H), 7.57 (m, 16H, Ar–H), 7.32 (m, 8H, Ar–H), 7.20 (d, 16H, J = 9.0 Hz, Ar–H), 4.29 (t, 16H, J = 7.0 Hz, –CH$_2$–O), 3.28 (t, 16H, J = 6.6 Hz, –CH$_2$–S). ^{13}C NMR. (CDCl$_3$), (δ:ppm): 159.58, 137.13, 130.68, 129.67, 128.32, 122.44, 120.86, 119.22, 70.28, 36.76. UV–vis (CHCl$_3$): λ_{max}/nm: [(10$^{-5}\varepsilon$ dm^3 M^{-1} cm^{-1})]: 315 (4.86), 350 (4.84), 638 (4.34), 686 (4.83). MS (ES$^+$), (m/z): 1795 [M]$^+$.

2.2.4. Preparation of cobalt(II) phthalocyanine (6). **6** was synthesized similarly to **5** from **3** by using anhydrous CoCl$_2$ (30 mg). Yield: 0.190 g (46%), m.p.: >300 °C. Anal. Calcd for $C_{96}H_{80}N_8O_8S_8Co$: C, 64.44; H, 4.51; N, 6.26; S, 14.34%. Found: C, 64.56; H, 4.64; N, 6.39; S, 14.40. IR (KBr tablet) ν_{max}/cm^{-1}: 3065 (Ar–H), 2928–2873 (Aliph. C–H), 1602, 1577, 1439, 1378, 1261, 1089, 1023, 888, 739, 690. UV–vis (CHCl$_3$): λ_{max}/nm: [(10$^{-5}\varepsilon$ dm^3 M^{-1} cm^{-1})]: 310 (4.56), 340 (4.54), 614 (4.56), 677 (4.39). MS (ES$^+$), (m/z): 1789 [M]$^+$.

2.2.5. Preparation of copper(II) phthalocyanine (7). **7** was synthesized similarly to **5** from **3** by using anhydrous CuCl$_2$ (31 mg) Yield: 0.132 g (32%), m.p.: > 300 °C. Anal. Calcd for $C_{96}H_{80}N_8O_8S_8Cu$: C, 64.28; H, 4.50; N, 6.25; S, 14.30%. Found: C, 64.40; H, 4.62; N, 6.20; S, 14.38. IR (KBr tablet) ν_{max}/cm^{-1}: 3058 (Ar–H), 2923–2864 (Aliph. C–H), 1598, 1476, 1439, 1380, 1281, 1182, 1105, 1017, 745, 688. UV–vis (CHCl$_3$): λ_{max}/nm: [(10$^{-5}\varepsilon$ dm^3 M^{-1} cm^{-1})]: 318 (4.55), 346 (4.50), 620 (3.77), 688 (4.56). MS (ES$^+$), (m/z): 1794 [M + H]$^+$.

3. Results and discussion

3.1. *Syntheses and characterization*

The synthesis of substituted Pcs starts generally with the preparation of the corresponding phthalonitrile precursors. The synthesis of the target Pc compounds **4–7** is shown in figure 1. The synthesis of 4,5-disubstituted phthalonitrile is based on the reaction of 2-(phenylthio)ethanol with 1,2-dichloro-4,5-dicyanobenzene. Then, cyclotetramerization of the dinitrile **3** to the octa-substituted Pcs **4–7** occurred in the presence of anhydrous Zn (CH$_3$COO)$_2$, CoCl$_2$, and CuCl$_2$ by microwave irradiation.

Compound **3** was prepared from 2-(phenylthio)ethanol **1** with 1,2-dichloro-4,5-dicyanobenzene **2** in dry DMF with potassium carbonate as the base. Comparison of the IR spectral data clearly confirmed the formation of **3** by the disappearance of the C–Cl band of 1,2-dichloro-4,5-dicyanobenzene at 684 cm^{-1} and the OH band of **1** at 3345 cm^{-1}, and the appearance of a new vibration frequency at 2233 cm^{-1} (C≡N). The spectrum of **3** also indicated the existence of alkyl and CN groups by stretching bands at 2927–2851 (C–H) and 2233 (C≡N) cm^{-1}. ^{1}H NMR spectra of **3** showed a new singlet due to aromatic proton at δ = 7.75 ppm, as expected. The proton-decoupled ^{13}C NMR spectrum indicated the presence of the nitrile carbons in **3** at δ = 113.32 ppm. The mass spectrum of **3**, which showed a peak at m/z = 433 [M + H]$^+$, supported the proposed formula for this compound.

In IR spectra of **4**, signals for the sharp C≡N groups at 2233 cm^{-1} for metal-free phthalocyanine **3** disappeared and a new peak at 3280 cm^{-1} of the N–H group in the

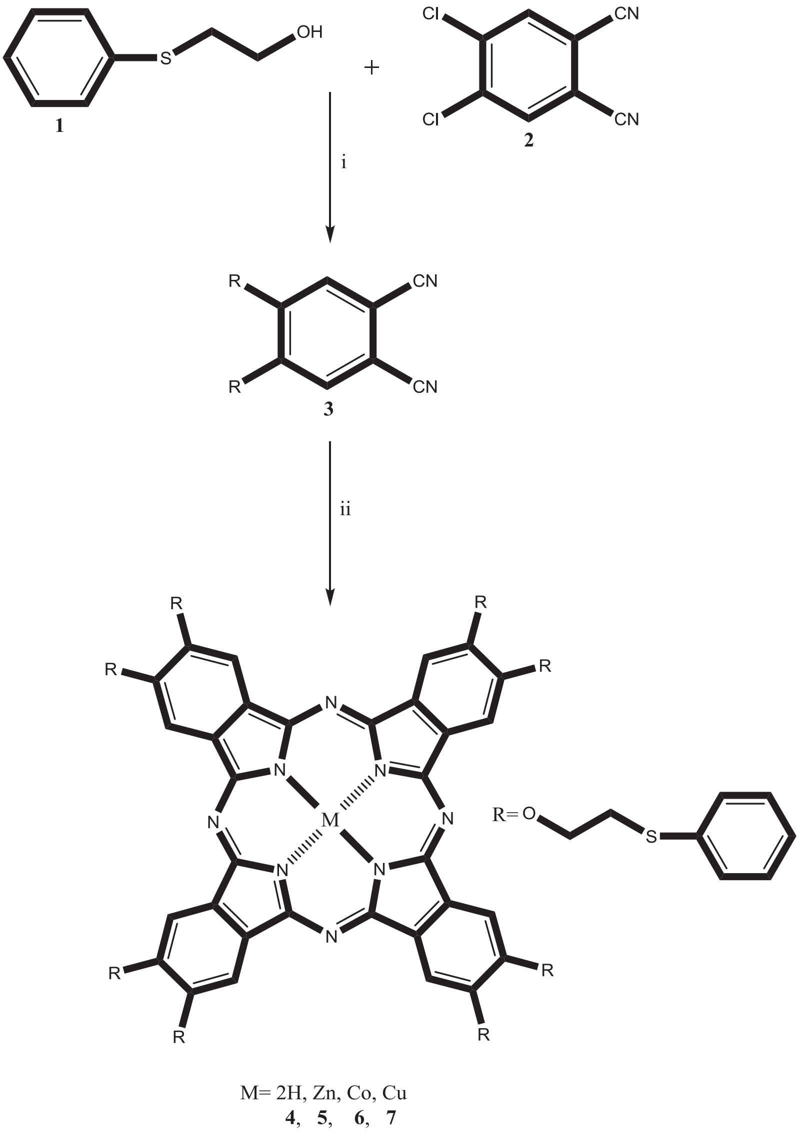

Figure 1. The synthesis of metal-free and MPcs. Reaction conditions: (i) K_2CO_3, N_2, DMF, 50 °C. (ii) Zn $(CH_3COO)_2$, $CoCl_2$, $CuCl_2$, DMAE, 175 °C, 350 W.

phthalocyanine core of **4** appeared. In the ^{1}H NMR spectrum of **4**, the typical shielding of inner core protons could not be observed due to the strong aggregation of the molecules [36]. ^{13}C NMR spectrum of **4** showed signals between 159.24 and 36.32 ppm. Molecular ion peak of **4** was found at $m/z = 1732$ $[M]^+$.

After conversion of the phthalonitrile derivative **3** into Pcs (**5–7**), the sharp C≡N peak at 2233 cm^{-1} disappeared. The IR spectral data of **5**, **6**, and **7** were also very similar to that of the metal-free precursor except for the disappearance of the N–H vibration of the phthalocyanine core. The ^{1}H NMR spectra of all these complexes were nearly equal to those of

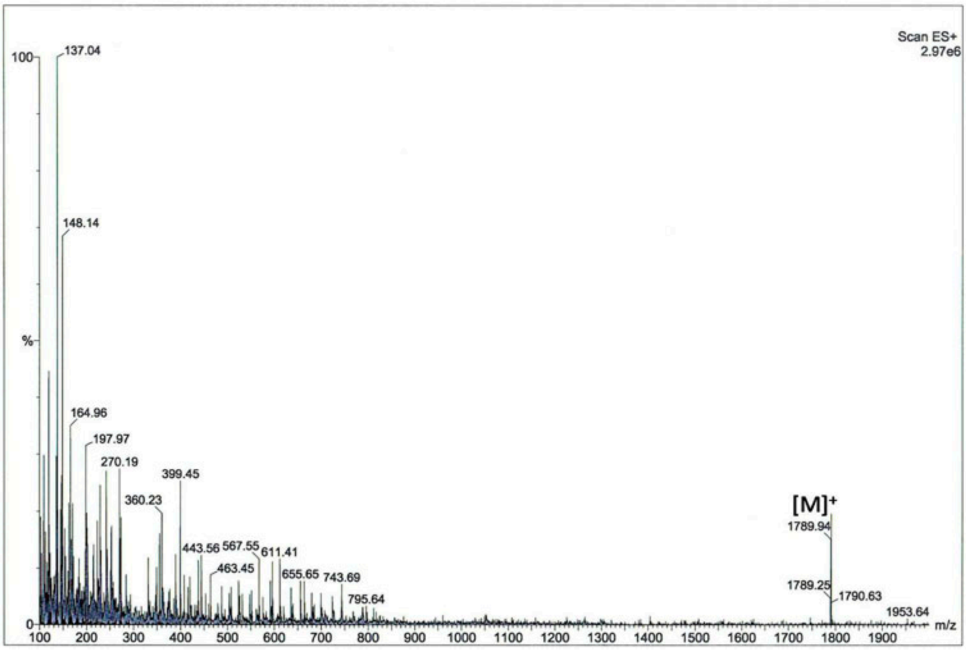

Figure 2. Mass spectrum of **6**.

metal-free complex **4**. ^{1}H NMR spectra of Zn-Pc **5** have broad signals encountered in the case of **5** as a result of the aggregation of phthalocyanine cores at the high concentration used for the NMR measurements [37]. ^{13}C NMR spectrum of **5** showed signals between 159.58 and 36.76 ppm. ^{1}H NMR measurement of the cobalt(II) **6** and copper(II) phthalocyanine **7** were obviated because of their paramagnetic character. In the mass spectra of MPcs complexes **5**, **6**, and **7**, the presence of molecular ion peaks at m/z = 1795 $[M]^+$, 1789 $[M]^+$ (figure 2), and 1794 $[M + H]^+$, respectively, support the proposed formulas for these complexes.

3.2. *Electronic spectra*

The electronic spectra of metal-free and MPcs show two strong absorption regions, one in the UV region at 300–350 nm (B band) and the other one in the visible region at 600–700 nm (Q band) [38]. The split Q bands in **4**, which are characteristic for metal-free Pcs, were observed at λ_{max} = 707 and 671 and B band absorption of **4** was at λ_{max} = 332 nm (in $CHCl_3$). Zn(II) phthalocyanine **5** (in $CHCl_3$) showed an intense single Q band at 686–638 nm and B band at 350–315 nm, respectively. UV–vis spectra of **6** and **7** (in $CHCl_3$) displayed an intense single Q band at 688–614 nm and B band at 346–310 nm, respectively.

The electronic spectra of H_2Pc and MPcs in solution is related to concentration. As the concentration rises, the absorption of the monomer band reduces relative to the bands associated with dimer or higher order aggregates. The UV–vis spectra of metal-free phthalocyanine in $CHCl_3$ shows four absorptions at 614, 628, 664, and 700 nm, which originate from a higher order aggregate, dimer and monomeric phthalocyanine species, respectively (figure 3). The dilution of the solution gradually decreases absorption peaks both at 614

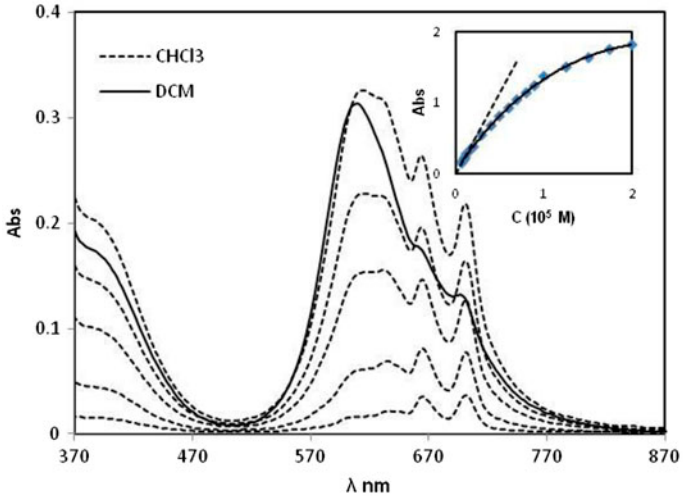

Figure 3. The UV–vis spectra of metal-free phthalocyanine in $CHCl_3$ and DCM (Conc: 1.10×10^{-5} to 1.53×10^{-6} M).

and 628 nm relative to 664 and 700 nm, but the fall in 614 nm was more pronounced. Thus, higher order aggregate was formed in more concentrated solution and decomposed into dimer form (628 nm) with dilution of the solution. Some researchers explain that higher levels of aggregation are probable in Pcs and higher aggregates are accompanied by further blue shifts in the Q band [39]. Figure 3 also shows the UV–vis spectra of the metal-free phthalocyanine in DCM. The bands, located 664 and 700 nm, associated with monomer were seen as a shoulder of the aggregate form and it was found that metal-free phthalocyanine has less as monomer in DCM than in $CHCl_3$.

Co(II) phthalocyanine has similar spectra in DCM (figure 4). When the concentration of the complex decreases as it gets closer to the dilution limit the aggregation decreases. This yields one Q band at 680 nm, characteristic of the MPcs. An unusual situation occurs with the addition of the supporting electrolyte, tetrabutylammonium hexaflourophosphate (TBAHFP). Step-by-step addition of TBAHFP caused a decrease of the dimerization or of higher aggregation in the complex (figure 5). This resulted in a sharp rise in the absorption of the monomer form, whereas there existed no change in absorption spectra of the metal-free phthalocyanine. The reason for this is attributed to coordination of central metal ion with electrolyte anions instead of solvent molecules. The repulsion of the coordinated anions destabilizes the aggregated structures.

3.3. *Electrochemical measurements*

Cyclic and differential pulse voltammograms of metal-free phthalocyanine in DCM containing 0.1 M TBAHFP are shown in figure 6. It gives two reduction processes with one electron, which are labeled as R_1 at −0.897 V, R_2 at −1.068 V and two oxidation processes with one electron, labeled as O_1 at 1.084 V and O_2 at 1.419 V. Based on the well known electrochemical behavior of phthalocyanine compounds, all couples are assigned to the phthalocyanine ring system.

The cyclic voltammogram of zinc(II) phthalocyanine was similar to the voltammogram of the metal-free phthalocyanine. Two reduction and two oxidation processes were seen labeled as R_1, R_2, O_1, and O_2 (figure 7). The separation between the first and second ring reduction was 0.25–0.35 V for zinc(II) phthalocyanine in accord with literature values obtained for complexes which have a redox inactive metal center. The differences in the electrochemical behavior of the zinc(II) and metal-free Pcs are the position of the redox potentials of the couples and the difference between the first oxidation and reduction processes ($\Delta E_{1/2}$) [40].

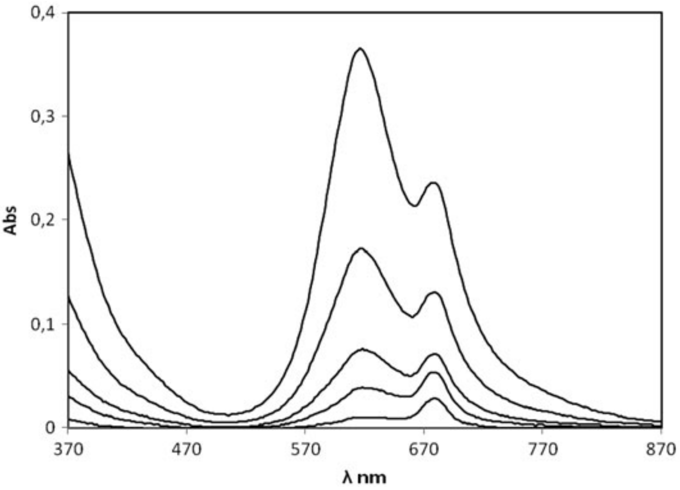

Figure 4. The UV–vis spectra of cobalt(II) phthalocyanine in DCM (Conc: 1.20×10^{-5} to 1.10×10^{-6} M).

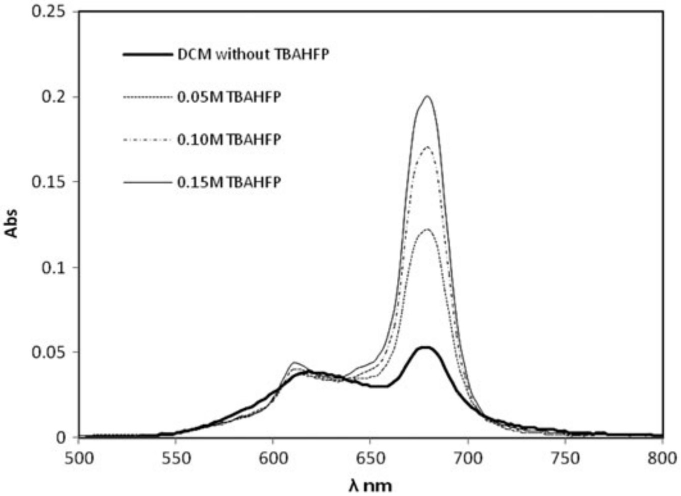

Figure 5. The dilution limit of the UV–vis spectra of cobalt(II) phthalocyanine in DCM and the presence of TBAHFP.

The cyclic voltammogram of the cobalt(II) phthalocyanine showed six redox processes from +1.65 to −1.80 V (figure 8). Scanning the potential to the positive side, two irreversible and one quasi-reversible oxidation processes were seen at 0.778, 0.989, and 1.339 V, and upon scanning cathodically, three reduction peaks were seen at −0.351, −1.075, and −1.361 V.

Both reduction and oxidation behavior of MPc complexes is because of the interplay between the central metal and the phthalocyanine ring [41, 42]. The redox processes in

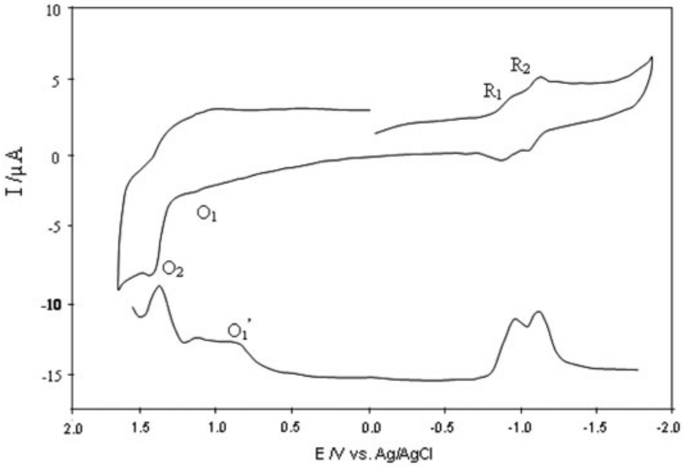

Figure 6. Cyclic and differential pulse voltammograms of metal-free phthalocyanine at 0.100 V s^{-1} scan rate on GCE in DCM/TBAHFP (H_2Pc 1.10^{-3} M dm^{-3}, pulse width = 50 ms, pulse height = 100 mV, step height = 5 mV, step time = 100 ms).

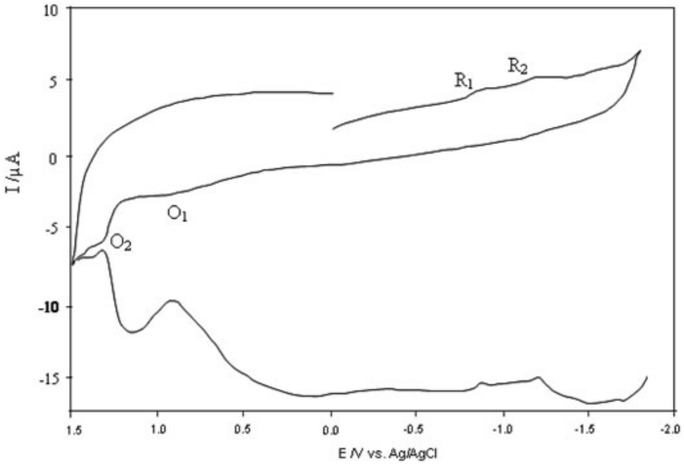

Figure 7. Cyclic and differential pulse voltammograms of zinc(II) phthalocyanine at 0.100 V s^{-1} scan rate on GCE in DCM/TBAHFP (ZnPc 1.10^{-3} M dm^{-3}, pulse width = 50 ms, pulse height = 100 mV, step height = 5 mV, step time = 100 ms).

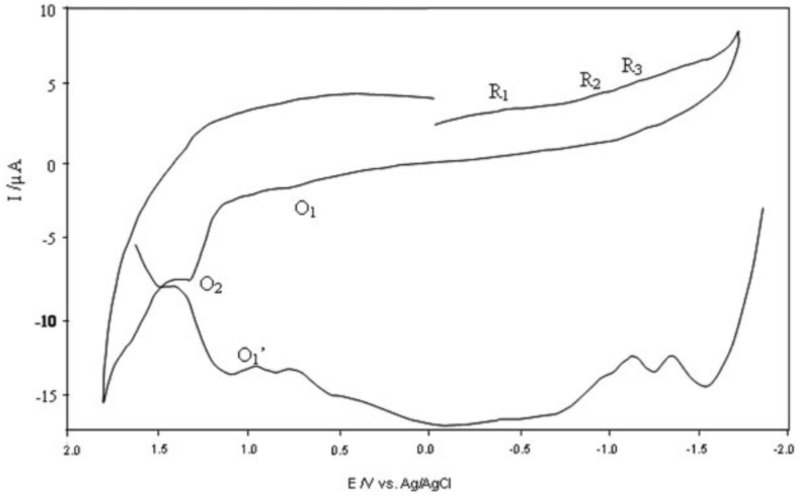

Figure 8. Cyclic and differential pulse voltammograms of cobalt(II) phthalocyanine at 0.100 V s^{-1} scan rate on GCE in DCM/TBAHFP (CoPc 1.10^{-3} Mdm^{-3}, pulse width = 50 ms, pulse height = 100 mV, step height = 5 mV, step time = 100 ms).

MPcs can be located at the ligand or at the metal core. The complexes with a redox inactive metal like Zn undergo successive one-electron reduction and one-electron oxidation to yield cation and anion radicals, respectively. The complexes with redox-active metals like Co, Fe, and Mn possess energy levels lying between the HOMO and lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ligand. This, in general, will exhibit redox processes centered on the metal [43, 44]. Investigations showed for the CoPc complexes, the first oxidation and first reduction processes are on the metal center in polar solvents such as DMF and DMSO; however, the first oxidation processes are on the Pc ring in apolar solvents such as DCM and THF. Our former research points out that the first reduction at

Table 1. Electrochemical data of the Pcs.

Compound	Redox step	E_p (V)	$E_{1/2}$	ΔE_p (mV)	I_{pa}/I_{pc}	$\Delta E_{1/2}$ (V)
H_2Pc	R_1	−0.897 (−0.817)	−0.857	80	1.50	1.846
	R_2	−1.068 (−0.993)	−1.030	75	1.03	
	O_1	1.084 (0.894)	0.989	184	–	
	O_2	1.419 (1356)	1.388	63	0.05	
CoPc	R_1	−0.351 (−0.205)[b]	−0.278	206	0.80	0.980
	R_2	−1.075 (−0.979)[b]	−1.027	96	0.64	
	R_3	−1.361 (−1.303)[b]	−1.332	58	1.12	
	O_1	0.719 (0.586)	0.702	133	0.77	
	O_1[a]	0.989 (0.927)	0.958	62	–	
	O_2	1.339 (1.249)	1.294	90	–	
ZnPc	R_1	−0.895 (−0.807)	−0.851	88	0.93	1.763
	R_2	−1.231 (−1.152)	−1.192	79	0.97	
	O_1	0.980 (0.826)	0.903	154	0.36	
	O_2	1.371 (–)	0.912[a]	–	–	

[a] From DPV.
[b] Can rate 100 mV s^{-1}.

−0.406 V could be designated to the [Co(II)Pc(-2)]/[Co(I)Pc(-2)]$^-$ redox couple and the remaining processes to the phthalocyanine ring [32].

The first and second reduction of the CoPc had a potential difference of 0.700 V, in aggreement with other CoPc complexes. The lower $\Delta E_{1/2}$ gap suggested that the first reduction of CoPc originated from the redox couple [Co(II)Pc(-2)]/[Co(I)Pc(-2)] in DCM [45].

The splitting of the second reduction process (R_2) and first oxidation (O_1) of the cobalt (II) phthalocyanine and of the first oxidation (O_1) of the metal-free phthalocyanine suggested that aggregation occurred in solution [20, 46]. The observation of very flattened peaks also confirmed the existence of aggregation of the Pcs during the electrochemical studies. The aggregation behavior of the phthalocyanine derivatives were clearly shown in electronic spectroscopy studies. In spite of using much more dilute solutions, dimer and higher order aggregated species were apparent in UV–visible spectra (figures 3–5).

The electrochemical data of the Pcs are given in table 1 for redox features of the Pcs investigated with CV and DPV in DCM.

4. Conclusion

We have demonstrated synthetic procedure and characterization of new H_2Pc and MPcs substituted with octakis[2-(phenylthio)ethoxy] groups. We have previously investigated the electrochemical properties of the tetra substituted 2-(phenylthio)ethoxy Pcs [32]. The reduction potential of the octa-substituted metal-free phthalocyanine shifted to more negative potential as a result of the electron donating of the 2-(phenylthio)ethoxy groups on the periphery compared to those of tetra substituted. The direction of the negative potential shift is in accord with predictions from linear free energy relationships. The eight peripheral groups increase the average electron density on the total conjugated system, which results in higher energy levels for the LUMO of the macrocycle. This decreases the electron affinity of the macrocycle from a thermodynamic point of view and thus leads to harder reductions. Solutions of the studied octa-substituted Pcs contain both monomeric and aggregated forms, arising from strong interactions of the peripheral 2-(phenylthio)ethoxy groups, as revealed by spectroscopic studies.

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