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DBU-catalyzed condensation of metal free and metallophthalocyanines containing thiazole and azine moieties: Synthesis, characterization and electrochemical properties

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ABSTRACT

Schiff base that contains carbothioamide moiety, substituted thiazole derivative, novel phthalonitrile compound and its corresponding metal free and metal phthalocyanines (Zn(II), Ni(II), Co(II) and Cu(II)) were synthesized and characterized for the first time. The solubility of these novel phthalocyanines were high in organic solvents and they did not aggregate in chloroform within the concentration range of 1.6×10^{-5}–4×10^{-6} M. Electrochemical properties of the phthalocyanines have been examined by cyclic voltammetry, square wave voltammetry and *in situ* UV–vis spectroelectrochemistry on Pt in dimethylsulfoxide/tetrabutylammonium perchlorate. These measurements suggested that the compounds display subsequent ligand- and/or metal-based one-electron reduction and oxidation processes. Cobalt complex showed both metal-based and ring-based one-electron redox processes, while the other complexes displayed only ring-based one-electron couples. It was observed that the redox processes of metal free, Zn(II), Ni(II) and Cu(II) phthalocyanines are coupled by aggregation phenomenon, whereas those CoPc are not, probably due to the difference in their axial coordinating properties.

1. Introduction

Phthalocyanines (Pcs), blue to green colored pigments, combine four iminoisoindoline units and thus, have 18π-electron heterocyclic aromatic system. This high delocalization makes them usable in many technological applications such as infrared ray absorbents, ink jet inks, data storage, electrophotographic photoreceptors, nonlinear optical devices and photosensitizers in photodynamic therapy [1–3]. Different metallophthalocyanines (MPc) that have metal element at the center can be prepared and different substituents can be placed to the peripheral or non-peripheral positions [4,5].

Heterocyclic compounds such as imidazoles, oxazoles, oxadiazoles, triazoles etc., have been synthesized due to their wide biological activities. Thiazole or 1,3-thiazole is a heterocyclic compound that contains both sulfur and nitrogen and represents an important part of vitamin B1 (thiamine). These type of aromatic heterocyclic compounds containing nitrogen and sulfur have important industrial and pharmaceutical uses such as manufacturing biocides, fungicides, dyes, treatment of inflammation, hypertension, bacterial and HIV infections [6–9].

Both in heterocyclic and in acyclic chemistry term of azine is used. While six-membered rings (pyrazines, pyrimidines) are called as azines in heterocyclic chemistry, in acyclic chemistry, the product of the reaction between one molecule hydrazine hydrate and two molecules of carbonyl compounds are called azine too [10,11]. Azines, biologically active compounds, have antitumor [12], antibacterial [13] and antifungal activity [14].

The redox properties and industrial applications of the Pcs are related to each other. Changing the substituent, central metal ion or axial ligand may notably affect their redox properties [15–20]. The redox properties of Pcs are generally determined by voltammetric methods such as cyclic voltammetry, differential pulse voltammetry and square wave voltammetry. However, the voltammetry may not be enough for distinguishing the type of redox process and in such cases *in situ* spectroelectrochemical measurements which is a combination of spectroscopic and electrochemical techniques may be used [21].

To the best of our knowledge, there are only a few literature about the synthesis of metal free (H_2Pc) and MPcs containing thiazole and

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Schiff moieties on peripheral positions that belongs to our group but there is no any report on their electrochemical properties [22]. Therefore, the strategy of this study has focused on combining thiazole, Schiff base and Pc into a single compound to obtain metal free, Zn(II), Ni(II), Co(II) and Cu(II) Pcs and investigate their electrochemical properties. To this end, firstly the Schiff base moiety bearing active carbothioamide group (**1**) has been prepared. Secondly, thiazole fragment of the target material has been created (**2**), then the new phthalonitrile derivative (**3**) having azine and thiazole groups was synthesized and characterized. At the final stage, Pcs (**4**–**8**) have been prepared and electrochemical properties of these Pcs have been studied via cyclic voltammetry, square wave voltammetry and *in situ* UV–vis spectroelectrochemistry on Pt in dimethylsulfoxide (DMSO)/tetrabutylammonium perchlorate (TBAP).

2. Experimental

2.1. Synthesis and characterization

2.1.1. Materials

All reactions were carried out under N_2 atmosphere by Schlenk techniques. All solvents were desiccated and refined according to Perrin and Armarego's method [23]. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), syringaldehyde and 4-methyl-3-thiosemicarbazide were provided from their commercial suppliers and 4-nitrophthalonitrile were obtained according to the literature procedure [24].

2.1.2. Equipment

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in $CDCl_3$ and DMSO-d_6, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum FT-IR spectrometer using KBr pellets. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer using chloroform–methanol solvent system. All experiments were performed in the positive ion mode. Elemental analyses were performed on a Costech ECS 4010 instrument and the obtained values agreed with the calculated ones. UV–vis spectra were recorded by Unicam UV2-100 using 1 cm pathlength cuvettes at room temperature. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.1.3. Compounds

*2.1.3.1. (E)-2-(4-Hydroxy-3,5-dimethoxybenzylidene)-N-methylhydrazinecarbothioamide (**1**).* In a round-bottomed flask, syringaldehyde (13.65 g, 0.075 mol) and 4-methyl-3-thiosemicarbazide (11.81 g, 0,1125 mol) heated to 140 °C for 3 h and then heated to 160 °C for 1 h under reflux with no solvent. The resulting residue was washed with water, filtrated and crystallized in DMF:ethyl alcohol (1:1) solvent system. Yield: 19.1 g (% 94.4). M.p.: 233–234 °C. Anal. Calc. for $C_{11}H_{15}N_3O_3S$: C 49.06, H 5.61, N 15.60; found: C 49.13, H 5.54, N 15.71. IR [(KBr) ν_{max}/cm^{-1}]: 3331 ν(–OH), 3147 ν(–NH), 3001 ν(Ar–CH), 2937 ν(Aliph. CH), 1583 ν(CH=N), 1553 ν(C=C), 853, 828. ^{1}H NMR (DMSO-d_6), (δ: ppm): 11.32 (s, 1H/NH), 8.79 (bs, 1H/OH), 8.36 (s, 1H/NH(CH_3)), 7.94 (s, 1H/CH=N), 7.04 (s, 2H/Ar–H), 3.81 (s, 6H/O–CH_3), 3.05–3.03 (d, 3H/N–CH_3). ^{13}C NMR (DMSO-d_6), (δ: ppm): 177.24 (C=S), 147.98, 142.46 (CH=N), 137.64, 124.29, 104.87, 56.05 (OCH_3), 30.68 (N–CH_3). MS (ESI), (m/z): calculated: 269.08; found: 269.96 $[M + H]^+$.

*2.1.3.2. (E)-Ethyl-2-((E)-(4-hydroxy-3,5-dimethoxy benzylidene) hydrazono)-3,4-dimethyl-2,3-dihydro-thiazole-5-carboxylate (**2**).* In a two-necked flask, compound **1** (18.45 g, 0.069 mol) was suspended in absolute ethanol. Then the solution of ethyl-2-chloroacetoacetate (11.29 g, 0.069 mol) in ethyl alcohol was dropped into the suspension in 30 min. The reaction mixture was refluxed for 3 days and the cream color of the mixture turned to yellow. The crude product was filtrated, washed with water, ethyl alcohol and diethyl ether and crystallized in DMF:ethyl alcohol (3:1) solvent system. Yield: 24.2 g (% 92.6). M.p.: 228–229 °C. Anal. Calc. for $C_{17}H_{21}N_3O_5S$: C 53.81, H 5.58, N 11.07; found: C 53.78, H 5.67, N 10.98. IR [(KBr) ν_{max}/cm^{-1}]: 3416 ν(–OH), 3122 ν(Ar–CH), 2937 ν(Aliph. CH), 1685 ν(C=O), 1584 ν(CH=N), 1271–1246 ν(C–O–C), 1087 δ(C–O–C), 848 δ(CH). ^{1}H NMR (DMSO-d_6), (δ: ppm): 8.88 (s, 1H/OH), 8.21 (s, 1H/CH=N), 7.02 (s, 2H/Ar–H), 4.16–4.23 (q, 2H/CH_2), 3.81 (s, 6H/O–CH_3), 3.37 (s, 3H/N–CH_3), 2.50 (s, 3H/CH_3), 1.22–1.27 (t, 3H/CH_3CH_2). ^{13}C NMR (DMSO-d_6), (δ: ppm): 165.05 (C=O), 161.36, 153.25 (CH=N), 148.28, 147.95, 137.74, 124.96, 104.68, 100.81, 60.27 (CH_2), 55.86 (OCH_3), 31.36 (N–CH_3), 14.17 (CH_3), 12.54 (CH_3CH_2). MS (ESI), (m/z): calculated: 379.12; found: 380.14 $[M + H]^+$.

*2.1.3.3. (E)-Ethyl 2-((E)-(4-(3,4-dicyanophenoxy)-3,5-dimethoxybenzylidene)hydrazono)-3,4-dimethyl-2,3-dihydrothiazole-5-carboxylate (**3**).* Compound **2** (3.79 g, 0.01 mol) and 4-nitrophthalonitrile (1.73 g, 0.01 mol) were dissolved in dry DMF (50 mL) and the solution was stirred vigorously at 55–60 °C. Then, dry K_2CO_3 (1.38 g, 0.01 mol) was added into this solution in eight equal portions at 15 min intervals. The system was stirred at same temperature for 5 days. Then the solution was poured into ice water (300 mL). The precipitated crude product was filtered and crystallized in ethyl acetate. Yield: 3.64 g, (72%), mp: 171–172 °C. Anal. Calc. for $C_{25}H_{23}N_5O_5S$: C 59.39, H 4.59, N 13.85; found: C 59.36, H 4.63, N 13.88. IR [(KBr) ν_{max}/cm^{-1}]: 3092 ν(Ar–CH), 2921–2874 ν(Aliph. CH), 2227 (C≡N), 1621–1603 ν(C=C), 1568–1553 ν(CH=N), 1278–1250 ν(C–O–C)/(C–N), 1145 δ(C–N), 1092–1013 δ(C–O–C), 985 δ(CH). ^{1}H NMR ($CDCl_3$), (δ: ppm): 8.33 (s, 1H/CH=N), 7.71–7.63 (d, 1H/Ar–H), 7.22–7.18 (d, 2H/Ar–H), 7.08–7.04 (d, 2H/Ar–H), 4.33–4.25 (q, 2H/CH_2), 3.86 (s, 6H/O–CH_3), 3.53 (s, 3H/N–CH_3), 2.61 (s, 3H/CH_3), 1.38–1.27 (t, 3H/CH_3CH_2). ^{13}C NMR ($CDCl_3$), (δ: ppm): 165.11, 163.28, 161.74, 159.78, 152.90, 152.12, 146.82, 135.89, 135.40, 134.43, 133.63, 120.36, 117.56, 115.92, 115.44, 108.63, 106.14, 104.31, 61.23, 56.50, 32.05, 14.68, 13.22. MS (ESI), (m/z): calculated: 505.14; found: 506.23 $[M + H]^+$.

*2.1.3.4. The general procedure for synthesis of metal-free (**4**) metallophthalocyanines (**5**–**8**).* Substituted phthalonitrile (**3**) (0.2 g, 3,96 $\times$ 10^{-4} mol) and for metallophthalocyanines corresponding anhydrous metal salts Zn(Ac)$_2$ (0.018 g, 9.90 $\times$ 10^{-5} mol); Ni(Ac)$_2$ (0.017 g, 9.90 $\times$ 10^{-5} mol); $CoCl_2$ (0.013 g, 9.90 $\times$ 10^{-5} mol); $CuCl_2$ (0.013 g, 9.90 $\times$ 10^{-5} mol) were dissolved in 4 mL of dry *n*-pentanol. After increasing the temperature to 90 °C, DBU (3 drops) was added to the media. Thereafter the temperature was raised to 160 °C and stirred for 24 h under nitrogen atmosphere. After cooling, the solutions were dropped to ethyl alcohol (40 mL) and the solid raw products were filtrated and washed with hot ethanol, methanol, *n*-hexane and diethyl ether. The pure green colored products were isolated through silica gel column. Spectral data of these products are given below.

*2.1.3.4.1. Metal-free phthalocyanine (**4**).* The used solvent system during column chromatography: chloroform. Yield: 0.033 g, (16.5%), mp >300 °C. Anal. Calc. for $C_{100}H_{94}N_{20}O_{20}S_4$: C 59.34, H 4.68, N 13.84; found: C 59.40, H 4.71, N 13.77. IR [(KBr) ν_{max}/cm^{-1}]: 3279 (–NH), 3093 ν(Ar–CH), 2915–2875 ν(Aliph. CH), 1621–1603 ν(C=C), 1565–1544 ν(CH=N), 1279–1262 ν(C–O–C)/(C–N), 1144 δ(C–N), 1091–1012 δ(C–O–C), 980 δ(CH). ^{1}H NMR ($CDCl_3$), (δ: ppm): 8.27 (s, 4H/CH=N), 7.70–7.58 (d, 4H/Ar–H), 7.14–7.02 (bd, 16H/Ar–H) 4.26–4.15 (q, 8H/CH_2), 3.78 (s, 24H/O–CH_3), 3.49 (s, 12H/N–CH_3), 2.60 (s, 12H/CH_3), 1.31–1.20 (t, 12H/CH_3). UV–vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 708 (4.68), 673

(4.67), 644 (4.34), 611 (4.08), 384 (5.00). MS (ESI), (*m*/*z*): calculated: 2023.59; found: 2024.86 $[M + H]^+$.

*2.1.3.4.2. Zn(II) phthalocyanine (**5**).* The used solvent system during column chromatography: chloroform:methanol (100:9). Yield: 0.028 g, (13.5%), mp >300 °C. Anal. Calc. for $C_{100}H_{92}N_{20}O_{20}S_4Zn$: C 57.53, H 4.44, N 13.42; found: C 57.40, H 4.60, N 13.32. IR [(KBr) ν_{max}/cm^{-1}]: 3085 ν(Ar–CH), 2915–2870 ν(Aliph. CH), 1618–1609 ν(C=C), 1560–1547 ν(CH=N), 1270–1263 ν(C–O–C)/(C–N), 1140 δ(C–N), 1090–1015 δ(C–O–C), 981 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 8.32 (s, 4H/CH=N), 7.72–7.59 (d, 4H/Ar–H), 7.12–6.98 (bd, 16H/Ar–H) 4.28–4.18 (q, 8H/CH_2), 3.82 (s, 24H/O–CH_3), 3.55 (s, 12H/N–CH_3), 2.62 (s, 12H/CH_3), 1.30–1.22 (t, 12H/CH_3). UV–vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 684 (5.10), 617 (4.48), 384 (4.98). MS (ESI), (*m*/*z*): calculated: 2085.50; found: 2086.91 $[M + H]^+$.

*2.1.3.4.3. Ni(II) phthalocyanine (**6**).* The used solvent system during column chromatography: chloroform:methanol (100:15). Yield: 0.042 g, (20.4%), mp >300 °C. Anal. Calc. for $C_{100}H_{92}N_{20}O_{20}S_4Ni$: C 57.72, H 4.46, N 13.46; found: C 57.61, H 4.51, N 13.59. IR [(KBr) ν_{max}/cm^{-1}]: 3089 ν(Ar–CH), 2918–2871 ν(Aliph. CH), 1625–1612 ν(C=C), 1565–1549 ν(CH=N), 1271–1265 ν(C–O–C)/(C–N), 1144 δ(C–N), 1095–1017 δ(C–O–C), 983 δ(CH). ^1H NMR ($CDCl_3$), (δ: ppm): 8.30 (bs, 4H/CH=N), 7.70–7.63 (d, 4H/Ar–H), 7.15–7.01 (bd, 16H/Ar–H) 4.35–4.16 (q, 8H/CH_2), 3.80 (s, 24H/O–CH_3), 3.50 (s, 12H/N–CH_3), 2.65 (s, 12H/CH_3), 1.32–1.21 (t, 12H/CH_3). UV–vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 672 (4.86), 607 (4.32), 334 (4.76). MS (ESI), (*m*/*z*): calculated: 2079.51; found: 2102.78 $[M + Na]^+$.

*2.1.3.4.4. Co(II) phthalocyanine (**7**).* The used solvent system during column chromatography: chloroform:methanol (100:17). Yield: 0.046 g, (22.3%), mp >300 °C. Anal. Calc. for $C_{100}H_{92}N_{20}O_{20}S_4Co$: C 57.71, H 4.46, N 13.46; found: C 57.82, H 4.58, N 13.36. IR [(KBr) ν_{max}/cm^{-1}]: 3086 ν(Ar–CH), 2923–2882 ν(Aliph. CH), 1623–1612 ν(C=C), 1562–1546 ν(CH=N), 1273–1260 ν(C–O–C)/(C–N), 1144 δ(C–N), 1091–1015 δ(C–O–C), 980 δ(CH). UV–vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 682 (4.57), 614 (4.08), 388 (4.81). MS (ESI), (*m*/*z*): calculated: 2080.50; found: 2081.44 $[M + H]^+$.

*2.1.3.4.5. Cu(II) phthalocyanine (**8**).* The used solvent system during column chromatography: chloroform:methanol (100:15). Yield: 0.039 g, (18.9%), mp >300 °C. Anal. Calc. for $C_{100}H_{92}N_{20}O_{20}S_4Cu$: C 57.59, H 4.45, N 13.43; found: C 57.66, H 4.52, N 13.28. IR [(KBr) ν_{max}/cm^{-1}]: 3087 ν(Ar–CH), 2916–2872 ν(Aliph. CH), 1628–1611 ν(C=C), 1562–1545 ν(CH=N), 1272–1261 ν(C–O–C)/(C–N), 1143 δ(C–N), 1090–1012 δ(C–O–C), 984 δ(CH). UV–vis ($CHCl_3$): λ_{max}/nm: [(10^{-5} log ε dm^3 mol^{-1} cm^{-1})]: 682 (4.89), 621 (4.51), 368 (4.20). MS (ESI), (*m*/*z*): calculated: 2085.50; found: 2086.77 $[M + H]^+$.

2.2. Electrochemical and in situ spectroelectrochemical measurements

The electrochemical and *in situ* spectroelectrochemical measurements were monitored using a Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. UV–vis absorption spectra were recorded by an Agilent 8453 diode array spectrophotometer equipped with the potentiostat/galvanostat. The electrochemical measurements were carried in extra pure DMSO containing electrochemical grade TBAP as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. For cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements, the working electrode was a Pt plate. A Pt spiral wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. High purity of N_2 was used for deoxygenating the solution at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements. Ferrocene was used as an internal reference, but the potentials were presented as the ones versus SCE. The spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was transparent Pt gauze. Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

3. Results and discussion

3.1. Outlook of the synthesized compounds

The synthesis route of new Schiff base (**1**) derived from the reaction between syringaldehyde and 4-methyl-3-thiosemicarbazide, thiazole containing Schiff base (**2**), substituted phthalonitrile (**3**) and target metal-free (**4**) and MPcs (**5**, **6**, **7** and **8**) is shown in Fig. 1. The structures of novel compounds have been characterized by a combination of ^1H and ^{13}C NMR, IR, UV–vis spectroscopy, elemental analysis and mass spectral data.

3.1.1. Synthesis of compounds 1, 2 and 3

1,3-Thiazoles derivatives can be prepared from the reactions between substituted hydrazinecarbothioamides and ethyl 2-chloroacetoacetate [22]. Therefore at the first stage we have prepared the Schiff base containing active hydrazinecarbothioamide moiety (**1**) from the reaction between syringaldehyde and 4-methyl-3-thiosemicarbazide. From the IR data of the compound **1**, the absence of the vibration of carbonyl group of syringaldehyde and vibration of $-NH_2$ group of 4-methyl-3-thiosemicarbazide and presence of new absorption at 1583 cm^{-1} belonging to (CH=N) supported that the Schiff base (**1**) has been successfully prepared. The structure of the compound **1** has been identified by the help of NMR spectroscopy, too. In the ^1H NMR data of **1**, the signals of the aldehyde proton of syringaldehyde and NH_2 proton of 4-methyl-3-thiosemicarbazide disappeared and a new signal at 7.94 ppm belongs to proton of CH=N group appeared. Furthermore, in its ^{13}C NMR data, the signal of the carbon of the carbonyl group of syringaldehyde disappeared and a new signal at 142.46 ppm that belongs to the iminic carbon appeared. On the other hand, in the mass spectrum of compound **1**, molecular ion peak at *m*/*z*: 269.96 $[M + H]^+$ and elemental analysis data also supported the structure of the product.

At the second step, the thiazole moiety of the target material was obtained from the condensation of compound **1** and ethyl-2-chloro-acetoacetate at 1:1 ratio in absolute ethanol in high yield. The absence of the absorptions of –NH groups of compound **1** in the IR spectra of compound **2**, confirmed the realization of the reaction. Furthermore, the absence of the –NH signals and the presence of the new methyl and ethoxy group signals at 2.50, 4.16–4.23 (for OCH_2) and 1.22–1.27 ppm (for CH_3 of ethoxy group), respectively, in the ^1H NMR spectra of compound **2** also supported the proposed structure. ^{13}C NMR spectrum of **2** also provided satisfactory data for its characterization. The signal of the thione group (C=S) of the compound **1** disappeared and new signals at 60.27 (OCH_2), 14.17 (CH_3), 12.54 (CH_3CH_2O) appeared. On the other hand, the molecular ion peak at *m*/*z*: 380.14 $[M + H]^+$ in the mass spectrum of **2** and the elemental analysis data also proved the reaction.

The preparation of the phthalonitrile derivative (**3**) was achieved by the nucleophilic aromatic substitution of the nitro group of 4-nitrophthalonitrile by compound **2** in the presence of anhydrous

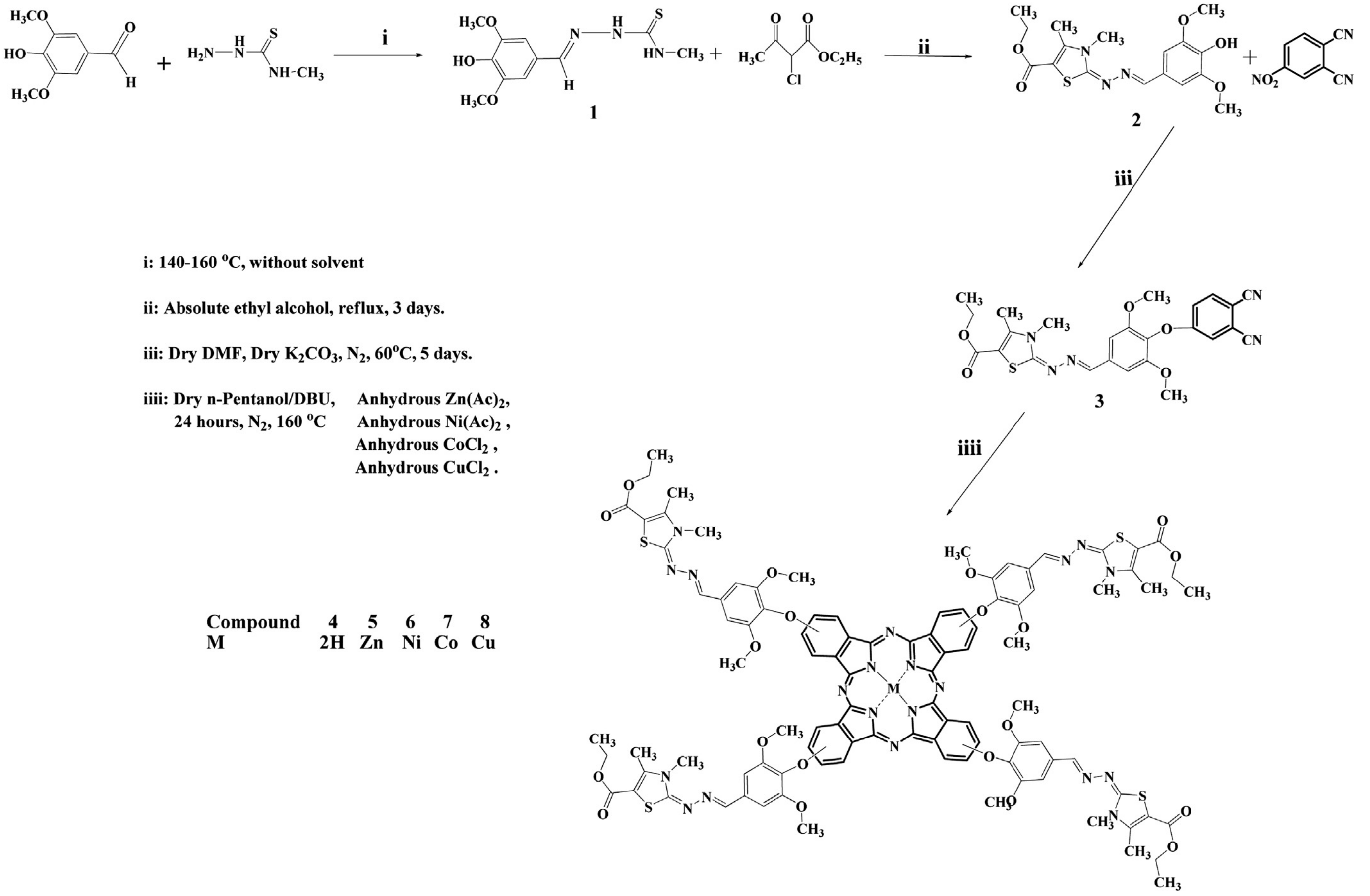

Fig. 1. Synthetic scheme of the novel compounds.

K_2CO_3 in DMF [25–27]. The structure of the compound was confirmed by spectral investigation. In the IR spectrum, the formation of compound **3** was clearly defined by the disappearance of –OH absorption of compound **2**, NO_2 stretching of the 4-nitrophthalonitrile and the appearance of C≡N absorption band at 2227 cm^{-1}. Its ^1H NMR spectrum was also in good agreement with the structure of the synthesized compound. Phenolic –OH signal disappeared after condensation. The integral ratios of aromatic and aliphatic proton signals are obtained as expected. In proton-decoupled ^{13}C NMR spectrum, the signals at 115.92 and 115.44 ppm indicated the presence of nitrile carbons for compound **3**. Additionally, the mass spectrum of **3** showed molecular ion peak at $m/z = 506.23$ $[M + H]^+$, supporting the proposed formula for this compound. Furthermore the results of the elemental analysis report were satisfactory.

*3.1.2. Syntheses of metal free (**4**) and metallophthalocyanines (**5–8**)*

The preparation of the metal-free Pc (**4**) was achieved by cyclotetramerization of compound **3** in n-pentanol by the catalyst of DBU at 160 °C for 24 h. Similarly, as a result of the cyclotetramerization of compound **3** in the presence of the corresponding metal salts and at the same conditions as mentioned above for metal free Pc (**4**) the tetra-substituted metallophthalocyanines (**5–8**) were obtained.

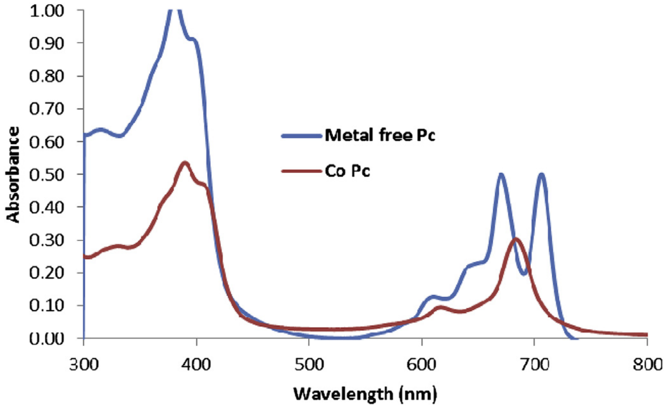

Fig. 2. Absorption spectra of compounds **4** and **7** in $CHCl_3$ at 1×10^{-5} M.

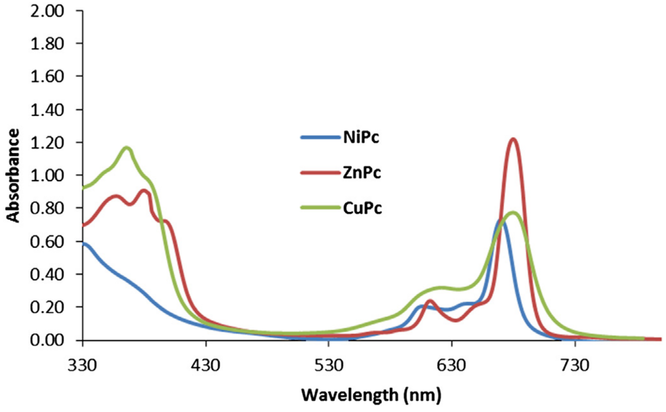

Fig. 3. Absorption spectra of compounds **5**, **6** and **8** in $CHCl_3$ at 1×10^{-5} M.

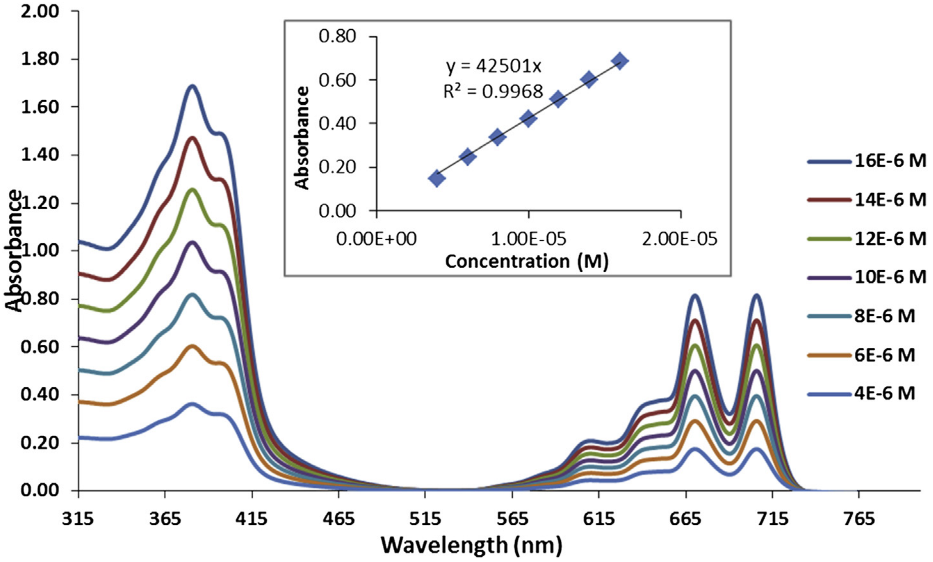

Fig. 4. Absorption spectra of metal free Pc (**4**) in chloroform at different concentrations.

The characterization of the structure of the Pcs were accomplished by ^{1}H NMR, IR, UV/vis and mass spectral investigations. Cyclotetramerization of compound **3** to metal-free Pc (**4**) was confirmed by the disappearance of the C≡N vibration at 2227 cm^{-1} in its IR spectrum. Furthermore, in the IR spectrum of the metal-free Pc (**4**) general inner core –NH absorption was observed at 3279 cm^{-1}, that is characteristic for metal-free Pcs. The rest of the spectrum of **4** was similar to that of substituted phthalonitrile (**3**). In the ^{1}H NMR spectrum of compound **4**, shielded inner core –NH protons could not be observed, probably due to the aggregation [27]. The signals corresponding to aromatic and aliphatic protons of **4** represent the significant absorbance characteristics of the proposed structure. Furthermore, the ESI mass spectrum of compound **4** showed a molecular ion peak at m/z = 2024.86 $[M + H]^+$. In addition, elemental analysis values were also satisfactory.

The disappearance of the C≡N vibration of compound **3** at 2227 cm^{-1} in the IR spectra of MPcs (**5**–**8**) proves the formation of these Pcs. The ^{1}H NMR spectra of Co(II)Pc and Cu(II)Pc (**7** and **8**) could not be determined because of the presence of paramagnetic cobalt and copper atoms in the Pc core [28]. The ^{1}H NMR spectra of the Zn(II)Pc and Ni(II)Pc (**5** and **6**) were similar to those of the metal-free Pc (**4**). In the mass spectra of compounds **5**–**8**, the parent molecular ion peaks were observed at m/z = 2086.91 $[M + H]^+$ for **5**, 2102.78 $[M + Na]^+$ for **6**, 2081.44 $[M + H]^+$ for **7** and 2086.77 $[M + H]^+$ for **8**, and confirmed the proposed structures.

The metal-free Pc (**4**) and MPcs (**5**–**8**) show two strong absorption regions in their electronic spectra. The first one – called as “B” or Soret band – is observed at around 300 nm because of the transitions from deeper π-HOMO to n^*-LUMO energy levels and the second one is – called as “Q” band – observed at around 600–750 nm due to transitions from π-HOMO to π*-LUMO energy levels [29]. One of the best indicators of the formation of Pcs is their UV–vis spectra in dilute ($\sim 1 \times 10^{-5}$ M) solution. The Q band of the metal-free Pc (**4**) was observed as splitted two bands due to D_{2h} symmetry, as Q_x and Q_y bands [30]. The electronic absorption spectrum of the metal free Pc (**4**) in chloroform at 1×10^{-5} M concentration at room temperature is shown in Fig. 2. The splitting Q band was observed at λ_{max} 708 and 673 nm, indicating the structure with non-degenerate D_{2h} symmetry.

Differently from metal free Pc (**4**), the Q bands of the MPcs (**5**–**8**) are observed as singlet due to their D_{4h} symmetry (Figs. 2 and 3). The UV–vis absorption spectra of MPcs in chloroform show intense Q absorption bands between 684 and 672 nm with shoulders at around 615 nm and B bands at ca. 360 nm. The sharpness of the observed bands in Figs. 2 and 3 are evidence of the presence of non-aggregated species at 1×10^{-5} M concentration in chloroform. For further investigation of aggregation behaviors of all novel phthalocyanines, absorption spectral changes were investigated in chloroform at 1.6×10^{-5}–4×10^{-6} M concentration range. At these concentrations, all phthalocyanines showed monomeric behavior (Fig. 4 as an example for metal free Pc (**4**)).

Table 1
Voltammetric data for the Pc compounds **4**–**8**.

Complex		Ring oxidations		M^{II}/M^{III}	M^{II}/M^{I}	Ring reductions			$\Delta E_{1/2}$[c]
4 (H_2Pc) in DMSO/TBAP)	$E_{1/2}$ (V)[a]		0.68			−0.64	−1.04		1.32
	ΔE_p (V)[b]		–			0.080	0.060	–	
5 (ZnPc) in DMSO/TBAP)	$E_{1/2}$ (V)[a]	0.68	0.45			−0.57	−0.84	−1.32	1.02
	ΔE_p (mV)[b]	0.060	0.060			–	0.060	–	
6 (NiPc) in DMSO/TBAP)	$E_{1/2}$ (V)[a]		0.62			−0.54	−0.90	−1.21	1.16
	ΔE_p (mV)[b]		–			–	0.14	0.100	
8 (CuPc) in DMSO/TBAP)	$E_{1/2}$ (V)[a]		0.65			−0.87	−1.17	−1.45	1.52
	ΔE_p (mV)[b]		–			0.160	0.060		
7 (CoPc) in DMSO/TBAP)	$E_{1/2}$ (V)[a]			0.42	−0.42	−1.39			0.84
	ΔE_p (mV)[b]			0.06	0.080	0.060			

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.050 V s^{-1}.
[b] $\Delta E_p = E_{pa} + E_{pc}$ at 0.050 V s^{-1}.
[c] $\Delta E_{1/2} = E_{1/2}$ (first oxidation) – $E_{1/2}$ (first reduction).

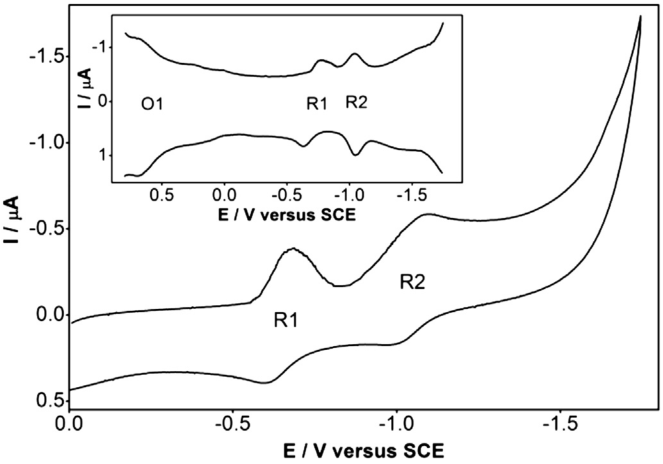

Fig. 5. Cyclic and square wave (inset) voltammograms of **4** at 0.050 V s^{-1} scan rate in DMSO/TBAP.

3.2. Electrochemistry and in situ spectroelectrochemistry

Redox properties of the Pc compounds (**4**–**8**) were studied by cyclic voltammetry and square wave voltammetry on platinum working electrode in DMSO/TBAP. Table 1 lists the half-peak potentials ($E_{1/2}$), the peak to peak potential separations (ΔE_p), and the difference between the first oxidation and reduction processes ($\Delta E_{1/2}$). Pc compounds undergo one-electron reduction and one-electron oxidation to yield the anion and cation radicals.

Fig. 5 shows cyclic and square wave (inset) voltammograms of metal-free Pc **4**. The cyclic voltammogram involves only two one-electron reduction processes. However, the square wave voltammetry enabled us to record also the one-electron oxidation process of the compound. All redox processes in Fig. 5 are ring-based since compound **4** is a metal-free Pc. The broad cyclic voltammetry signals point out that compound **4** may form aggregated species in DMSO/TBAP.

Voltammetric measurements suggested that the general voltammetric behavior of **5** (ZnPc), **6** (NiPc) and **8** (CuPc) is similar to each other and that of **4** (H_2Pc), in terms of the positions of voltammetric signals on the voltage scale (Table 1). The similarity in general redox behavior between metal-free and metal Pcs probably suggests that Zn(II), Ni(II) and Cu(II) behave as redox-inactive metal centers [31,32]. On the other hand, the differences between the $E_{1/2}$ values and the number and shapes of the voltammetric signals can be attributed to the different polarizing powers of central atoms and different aggregation effects. While compound **4** displayed broad cyclic voltammetry signals, the splitting into two waves was observed for the first reduction process of **5**, **6** and **8**, and also for the first oxidation couple of **5**. Fig. 6A shows cyclic and square wave (inset) voltammograms of **5** as example. The redox processes in the MPcs are located at the ring and at the metal center, [21,33–39]. Moreover, it appears that a general trend for some Pc compounds in this study is their aggregation character implied by splitting or broadening of the redox waves. In most cases, it was not possible to identify the nature of redox processes and also to understand possible aggregation effects on these processes with great detail on the basis of electrochemical measurements alone. For this reason, *in situ* spectroelectrochemical measurements during the controlled-potential electrolysis of the

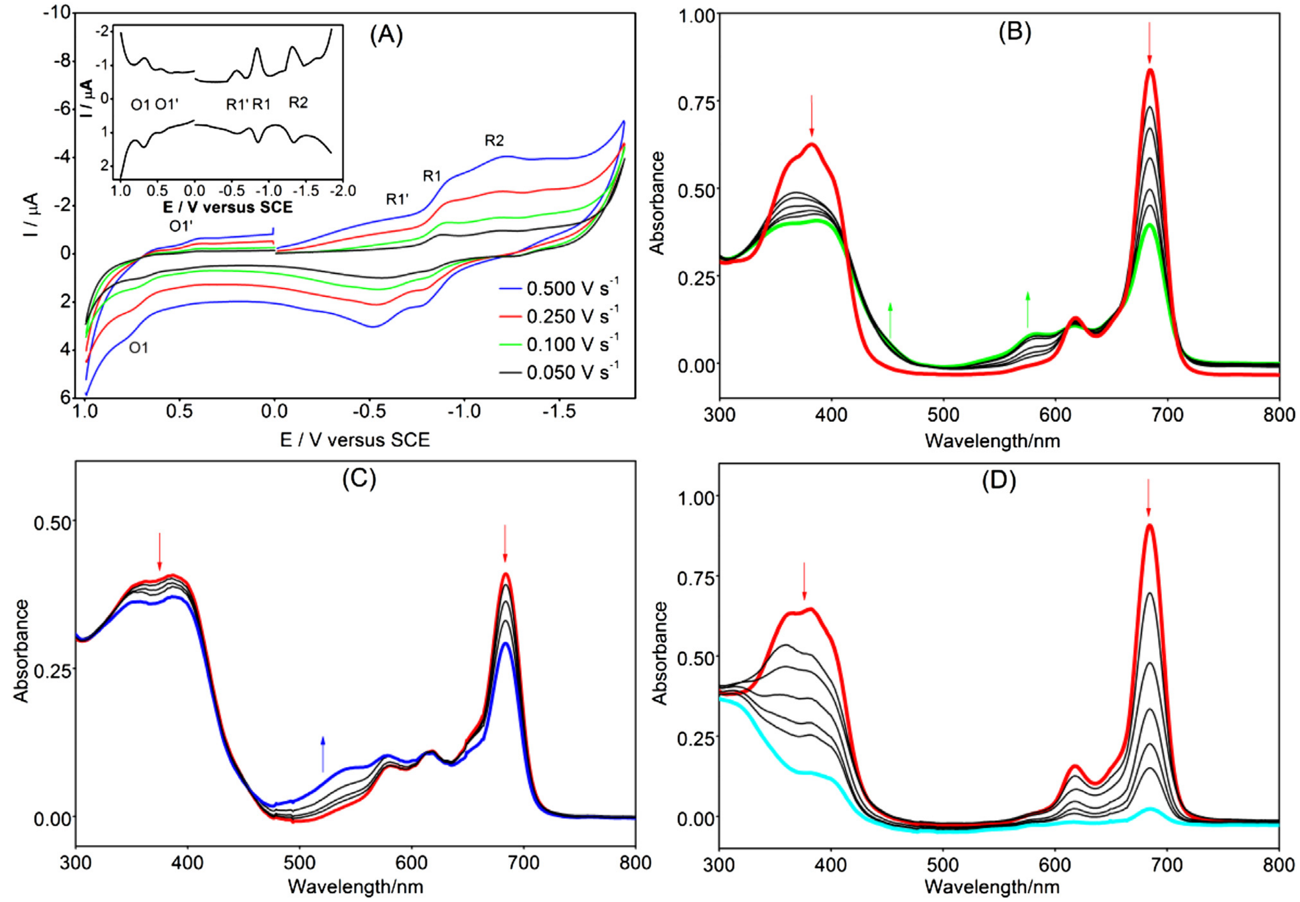

Fig. 6. Cyclic and square wave (inset) voltammograms of 5.0 × 10^{-4} M **5** in DMSO/TBAP (A) and *in situ* UV–vis spectral changes monitored during the controlled-potential electrolysis of **5** in DMSO/TBAP at (B) −0.95 V, (C) −1.25 V and (D) 0.85 V *vs.* SCE.

complexes at suitable potentials were also carried out to provide additional support for the assignment of redox processes and the identification of possible aggregation effects.

Although the shape of the voltammetric peaks of **5** in Fig. 6A appears as if the redox processes are associated with the aggregation phenomenon, our observations during *in situ* spectroelectrochemical measurements did not indicate the coupling of the redox processes by aggregation–deaggregation transformations (Fig. 6B–D). This can be attributed to the fact that *in situ* UV–vis spectroelectrochemical measurements was carried out relatively dilute solutions, in comparison with the voltammetric measurements. The spectral changes observed when the working electrode was polarized at −0.95 V *vs*. SCE are shown in Fig. 6B. The sharp Q-band absorption at 684 nm in the spectrum monitored at the beginning of the electrolysis at the constant potential is indicative of the absence of aggregated species. During the first reduction process, the Q band absorption at 684 nm, and the broad B band absorption at about 375 nm decreases while a new absorption band appears at 580 nm. These spectral changes, accompanied by the formation of well-defined isosbestic points can be attributed to the ring-based reduction of disaggregated species of **5** [40–43]. Therefore, the R1′ and R1 couples of **5** in Fig. 6A can be attributed to the Pc ligand-based reduction processes. During the second reduction with −1.25 V potential application, the absorption of the main Q band continues to decrease without shift, while a new band around 542 nm appears (Fig. 6C). These spectral changes, accompanied by the formation of well-defined isosbestic points, correspond to the second ring reduction with the formation of [Zn(II)Pc(−4)]$^{2-}$ dianion species. During the oxidation at 0.85 V *vs*. SCE, the absorption of all bands decreases without formation of a new band which is attributed to the decomposition of the complex immediately after the ring oxidation (Fig. 6D). This is an expected observation due to the high positive oxidation potential.

Fig. 7A shows the cyclic voltammogram of CoPc (**7**). The complex gives two one-electron reductions and a one-electron oxidation. The ΔE_p parameter of the redox couples takes the values within the range of 0.060–0.080 V at 0.050 V s^{-1} scan rate, indicating reversible or quasi-reversible character of electron transfer processes. The unity of the peak current ratios (I_{pa}/I_{pc} for reductions and I_{pc}/I_{pa} for oxidation) with the scan rate and linear changes of peak currents with the square root of scan rate for the redox couples indicated purely diffusion-controlled electron transfer mechanism for these processes. Metal center in **7** probably prefers six-coordination and thus binds donor DMSO molecules. It is known that six coordinate MPc species generally do not aggregate since they are kept apart by the axially bound ligands [31]. Redox potentials of **7** are considerably different as compared with those of the other Pc compounds (Table 1). $\Delta E_{1/2}$ value of **7**, 0.84 V, is low in comparison with those of **4**, **5**, **6**, and **8**. Thus, it is reduced and oxidized more easily than the others. This distinctive behavior of **7**

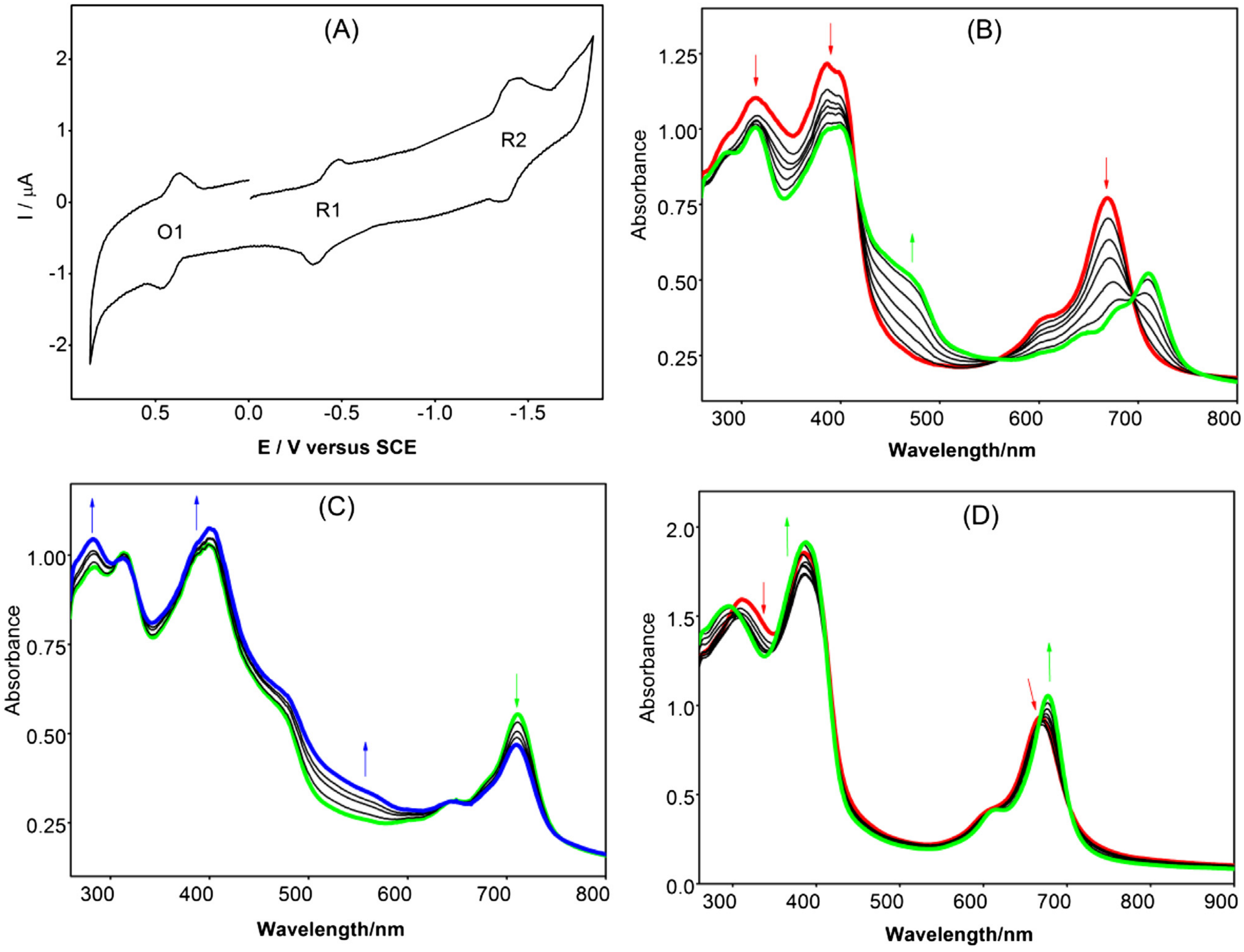

Fig. 7. Cyclic and square wave (inset) voltammograms of 5.0 × 10^{-4} M **7** in DMSO/TBAP (A) and *in situ* UV–vis spectral changes monitored during the controlled-potential electrolysis of **7** in DMSO/TBAP at (B) −0.53 V, (C) −1.50 V and (D) 0.50 V *vs*. SCE.

can be attributed to the fact that Co(II) center has accessible d orbital levels lying between the HOMO and LUMO gap of the Pc species, then metal center can be oxidized and reduced before the ring-based redox processes. However, this type of Pc complexes can vary their electrochemical behavior according to their environment, depending on whether there are any available coordinating species that would stabilize the Co(II) center. The main difference lies in whether the metal or the ring is oxidized first. Donor solvents strongly favor Co(III)Pc(−2) by coordinating along the axis to form six coordinate species. If such donor solvents are absent, then oxidation to Co(III) is inhibited and ring oxidation occurs first. Thus, the first oxidation and the first reduction processes of **7** are probably metal-based and correspond to Co(II)Pc(−2)/[Co(III)Pc(−2)]$^{+}$ and Co(II)Pc(−2)/[Co(I)Pc(−2)]$^{-}$ redox couples, respectively, since the voltammetric measurements were carried out in DMSO/TBAP. On the other hand, it is also well known from the literature that the other reduction processes and the second oxidation process are ring-based [31,32]. Spectroelectrochemical measurements were also carried out to assign especially the first reduction and the first oxidation processes of **7** certainly. Fig. 7B represents *in situ* UV–vis spectral changes during the first reduction of **7** at −0.53 V *vs*. SCE, corresponding to the redox process labeled R1 in Fig. 7A. The Q band at 669 nm shifts to 710 nm, while new band at 476 nm appears. The spectral changes have well-defined isosbestic points at 415, 561 and 695 nm. The band at 476 nm and the shifting of the Q band indicate the formation of [Co(I)Pc(−2)]$^{-}$ species, confirming the CV assignment of the couple R1 to Co(II)Pc(−2)/[Co(I)Pc(−2)]$^{-}$ process [33–36,42–45]. During the second reduction at −1.50 V *vs*. SCE, the Q band at 710 nm decreases without shift and the absorption between 500 and 600 nm increases (Fig. 7C). These spectral changes at the potential of the couple R2 are characteristics for a ring-based reduction in Co(II)Pc complex and confirm the voltammetric assignment of this process to [Co(I)Pc(−2)]$^{-}$/[Co(I)Pc(−3)]$^{2-}$. Fig. 7D displays *in situ* UV–vis spectral changes during the first oxidation process. The Q band at 669 nm increases in intensity with red shift to 676 nm. The increase of the Q band with red shift is typical of a metal-based oxidation in CoPc complexes and thus, confirms the CV assignment of Co(II)Pc(−2)/[Co(III)Pc(−2)]$^{+}$ for couple O1 of **7** in Fig. 7A [33–36,42–45].

4. Conclusion

In the presented paper, the syntheses of new substituted metal free, zinc(II), nickel(II), Co(II) and Cu(II) phthalocyanines containing azine and thiazole moieties on peripheral positions were described and these new compounds were characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR, electronic spectroscopy and mass spectra. The yields of the reactions were moderate and the solubilities of the phthalocyanines were good in non-aqueous media. All these Pcs showed monomeric behavior in chloroform between 1.6×10^{-5}–4×10^{-6} M concentration range. The voltammetric measurements showed that the Pc compounds indicate subsequent one-electron reduction and oxidation processes. *In situ* spectroelectrochemical measurements enabled us to identify ligand- and metal-based redox processes. Furthermore, the measurements suggested that the redox processes of H_2Pc **4**, ZnPc **5**, NiPc **6** and CuPc **8** are coupled by aggregation phenomenon, while those of CoPc **7** are not. Metal center in **7** probably prefer six-coordination and bind donor DMSO molecules. Thus, they are kept apart by the axially bound solvent molecules. This prevents it from aggregating.

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