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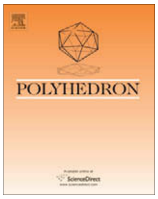

Synthesis, electrochemical, in situ spectroelectrochemical and in situ electrocolorimetric characterization of new metal-free and metallophthalocyanines substituted with 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy} groups

Irfan Acar [a], Zekeriya Bıyıklıoğlu [b], Atıf Koca [c], Halit Kantekin [a,*]

[a] Department of Chemistry, Faculty of Arts & Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
[b] Macka Vocational School, Karadeniz Technical University, 61750 Macka, Trabzon, Turkey
[c] Department of Chemical Engineering, Faculty of Engineering, Marmara University, Göztepe 34722, İstanbul, Turkey

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ABSTRACT

The synthesis of novel metal-free and metallophthalocyanines [Ni(II), Zn(II), Co(II), Cu(II)] were prepared by cyclotetramerization of a novel 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile and the corresponding metal salts ($NiCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$). The structures of the target compounds were confirmed using elemental analysis, IR, ^1H NMR, ^{13}C NMR, UV–Vis and MS spectral data. Voltammetric and in situ spectroelectrochemical measurements show that while cobalt phthalocyanine complex gives both metal-based and ring-based redox processes, metal-free, and zinc phthalocyanines show only ring-based reduction and oxidation processes. All complexes decomposed and coated on the electrode as non-conductive film at positive potential window of the electrolyte. An in situ electrocolorimetric method has been applied to investigate color of the electro-generated anionic and cationic forms of the complexes.

1. Introduction

Phthalocyanine (Pc) and its derivatives have been under systematic study more than 70 years; however, researchers are still interested in this class of compounds [1]. Owing to their fascinating properties, Pc-based materials find applications in nonlinear optics [2], optical data storage [3], photodynamic cancer therapy [4], sensors [5], catalysis [6], and solar energy conversion [7]. Due to intermolecular interactions between the macrocycles, peripherally unsubstituted phthalocyanines are insoluble in common organic solvents and aqueous media, in this way minimizing their applications [8]. Adding functional groups on the periphery that increase the distance between the 18-π electron-conjugated systems of phthalocyanines enhances the solubility of these compounds [9–11]. The solubility can also be increased by introducing alkyl or alkoxy groups in the peripheral position of phthalocyanines framework [12]. The major advantage of phthalocyanines over porphyrins is that their Q-bands are at longer wavelengths and have much higher intensity than the Q-bands of porphyrins. Some complexes of phthalocyanines show photobiological activity against tumors [13].

Condensed multicyclic aromatic compounds (e.g., naphthalene derivatives) are functional groups effective in photoemission studies [14]. As bulky electron rich units, the presence of naphthalenyl groups on the periphery phthalocyanines is also expected to change the ordering of molecules in the solid state. However, in the case of naphthalocyanines, the physical and chemical identity of naphthalene units is no longer distinct [15].

Microwaves have been previously used for the synthesis of phthalocyanines and include a wider range of references on the topic [16–19]. In this paper, we describe the synthesis and characterization of metal-free **4** and metallophthalocyanines **5, 6, 7** and **8** substituted with 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy} groups by microwave irradiation. Also, we have investigated the voltammetric, in situ spectroelectrochemical and in situ electrocolorimetric responses of the metallophthalocyanines in solution to open a way to their possible electrochromic application depending on the spectroelectrochemical and chromaticity data. It is well known that many phthalocyanine complexes show excellent electrochromic properties [20,21] both in solution and as films. Therefore, we report here in situ electrocolorimetric analysis of the phthalocyanines to determine possible electrochromic application of the complexes. Because electrocolorimetry technique provides a more precise way to define color of the electro-generated species [22].

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[*] Corresponding author. Tel.: +90 462 377 2589; fax: +90 462 325 3196.
E-mail address: halit@ktu.edu.tr (H. Kantekin).

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2. Experimental

2.1. Materials

2-[2-(1-Naphthyloxy)ethoxy]ethanol (**1**) [23] and 4-nitrophthalonitrile (**2**) [24] were prepared according to the literature. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [25].

2.2. Equipment

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. Melting points were measured on an electrothermal apparatus and are uncorrected.

The electrochemical and spectroelectrochemical measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. For CV, and SWV measurements, the working electrode was a Pt disc with a surface area of 0.071 cm^2. The surface of the working electrode was polished with a diamond suspension before each run. A Pt 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. Ferrocene was used as an internal reference. TBAP in DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. High purity N_2 was used to remove dissolved O_2 at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements. IR compensation was applied to the CV and SWV scans to minimize the potential control error. UV/Vis absorption spectra and chromaticity diagrams were measured by an OceanOptics QE65000 diode array spectrophotometer. In situ

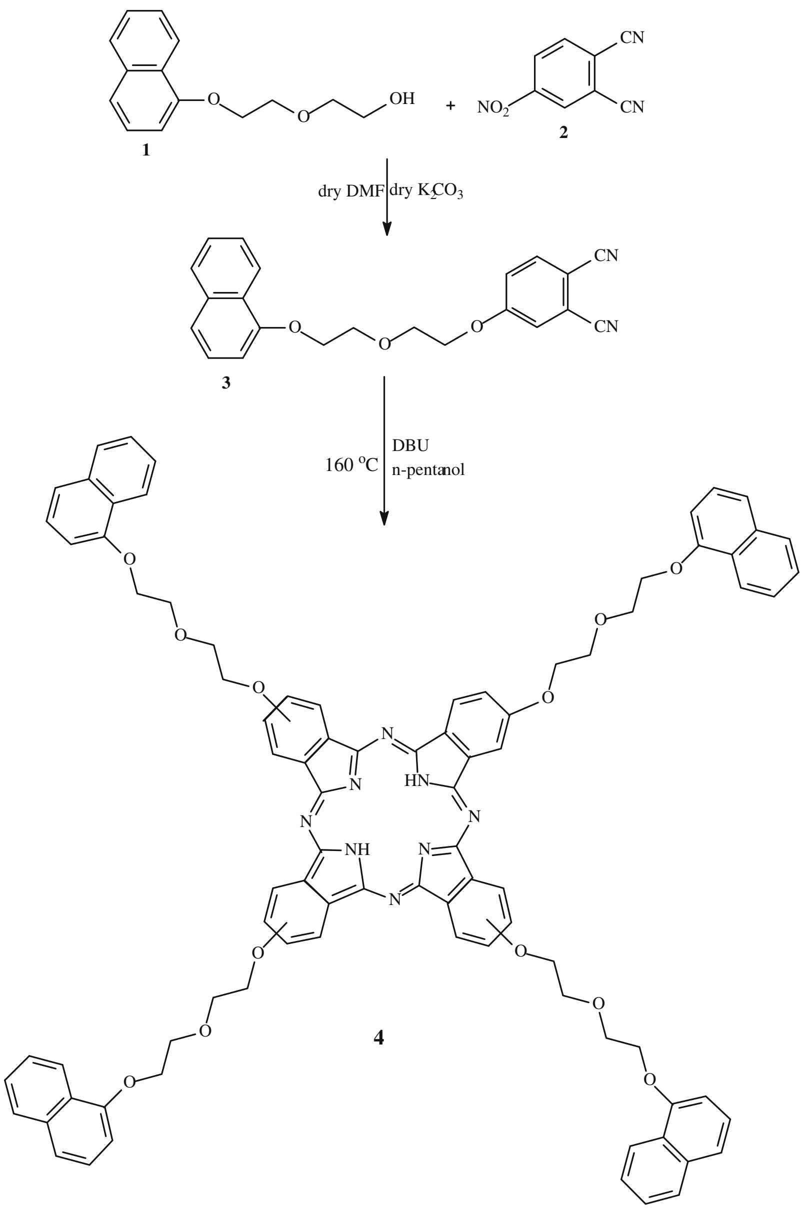
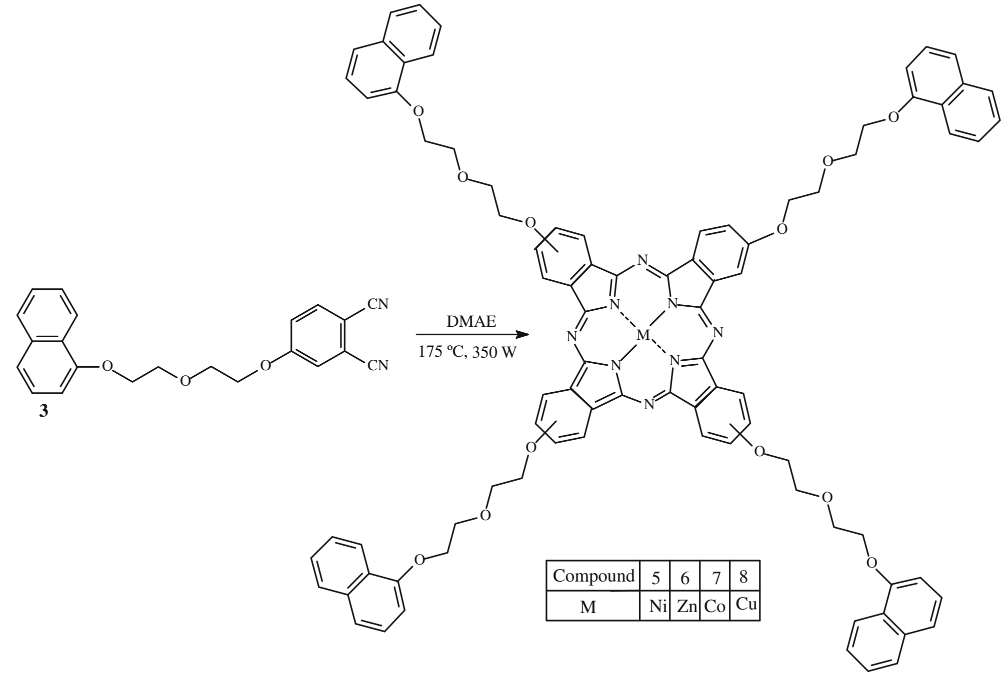


Fig. 1. The synthesis of the metal-free phthalocyanine.

spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was Pt tulle. 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.



Compound	5	6	7	8
M	Ni	Zn	Co	Cu

Fig. 2. The synthesis of the metallophthalocyanines.

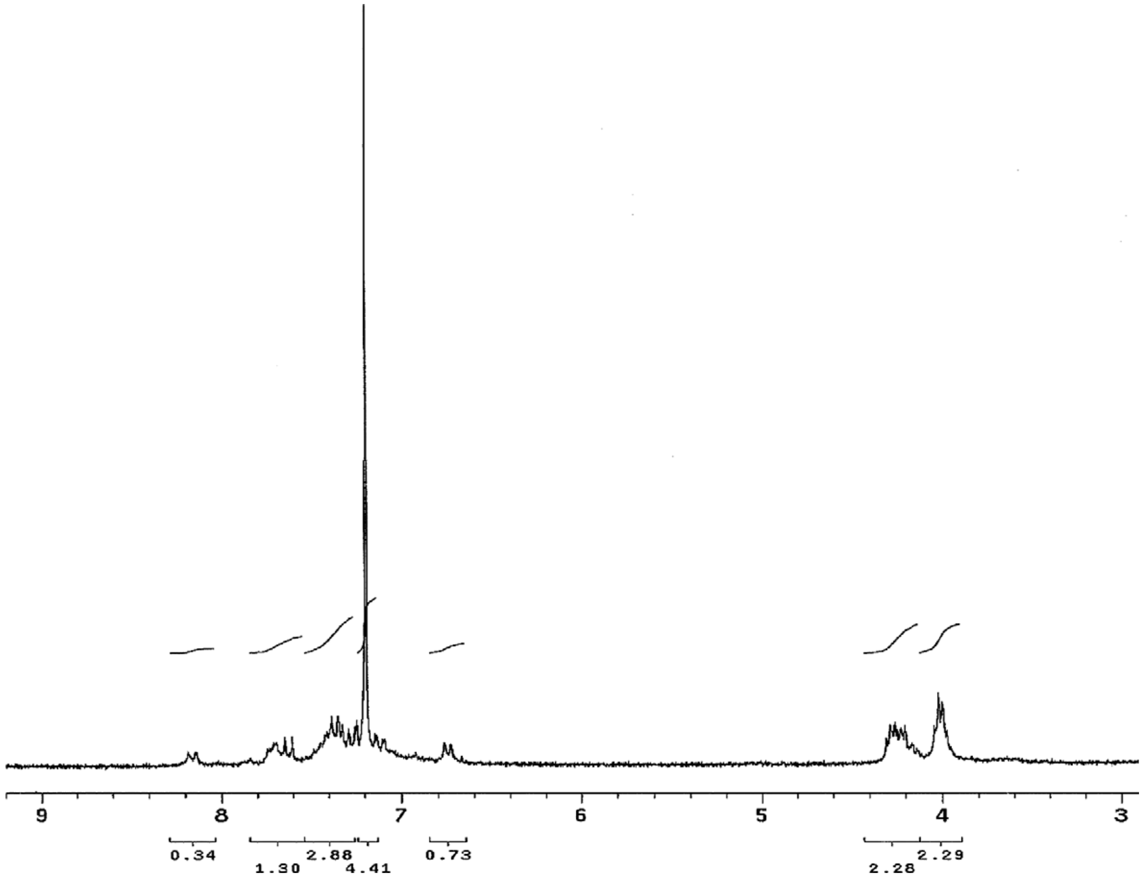


Fig. 3. ^{1}H NMR spectra of complex **6** in $CDCl_3$.

In situ electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The standard illuminant A with 2 degree observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (*x*,*y*, and *z* values) were taken at open-circuit, using the electrolyte solution without MPc under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and final of each redox processes were reported.

2.3. Synthesis

*2.3.1. Synthesis of 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile (**3**)*

2-[2-(1-Naphthyloxy)ethoxy] ethanol **1** (2 g, 8.62 mmol) was dissolved in dry DMF (20 ml) under N_2 atmosphere and 4-nitrophthalonitrile **2** (1.5 g, 8.62 mmol) was added to the solution. After stirring 10 min, finely ground anhydrous K_2CO_3 (3.6 g, 25.86 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50 °C for four days. Then the solution was poured into ice-water (100 g). 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: 1.64 g (53%), mp: 184–186 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3053 (Ar–H), 2925–2868 (Aliph. C–H), 2230 (C≡N), 1598, 1580, 1563, 1489, 1462, 1397, 1321, 1269, 1255, 1137, 1101, 1050, 967, 837, 794, 773. ^1H NMR. ($CDCl_3$), (δ:ppm): 8.22 (d, 1H, Ar–H), 7.82 (d, 1H, Ar–H), 7.57-7.36 (m, 5H, Ar–H), 7.19–7.09 (m, 2H, Ar–H), 6.82 (d, 1H, Ar–H), 4.35 (t, 2H, CH_2–O), 4.24 (t, 2H, CH_2–O), 4.05 (t, 4H, CH_2–O). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 161.75, 154.24, 134.95, 134.40, 127.49, 126.45, 125.77, 125.42, 125.13, 121.79, 120.56, 119.70, 119.23, 117.02, 115.68, 115.23, 107.08, 104.78, 70.02, 69.42, 68.57, 67.76. MS (ES^+), (*m*/*z*): 358 $[M]^+$. *Anal* Calc. for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.76; H, 5.04; N, 7.97%.

*2.3.2. Synthesis of metal-free phthalocyanine (**4**)*

Compound **3** (0.3 g, 0.84 mmol), 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drop) and dry *n*-pentanol (4 ml) was added in a Schlenk tube and then was heated and stirred at 160 °C for 24 h under N_2. After cooling to room temperature the reaction mixture refluxed with ethanol (50 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 preparative silicagel plate with chloroform:methanol (100:3) as eluents. Yield: 0.105 g (35%), mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3291 (N–H), 3049 (Ar–H), 2925–2854 (Aliph. C–H), 1613, 1577, 1463, 1393, 1378, 1270, 1240, 1122, 1073, 952, 771, 744. ^1H NMR. ($CDCl_3$), (δ:ppm): 8.27 (bs, 8H, Ar–H), 7.76 (m, 8H, Ar–H), 7.45–7.28 (m, 16H, Ar–H), 7.16 (m, 4H, Ar–H), 6.82 (m, 4H, Ar–H), 4.33 (m, 16H, CH_2–O), 4.08 (m, 16H, CH_2–O). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 161.62, 154.34, 136.92, 134.41,

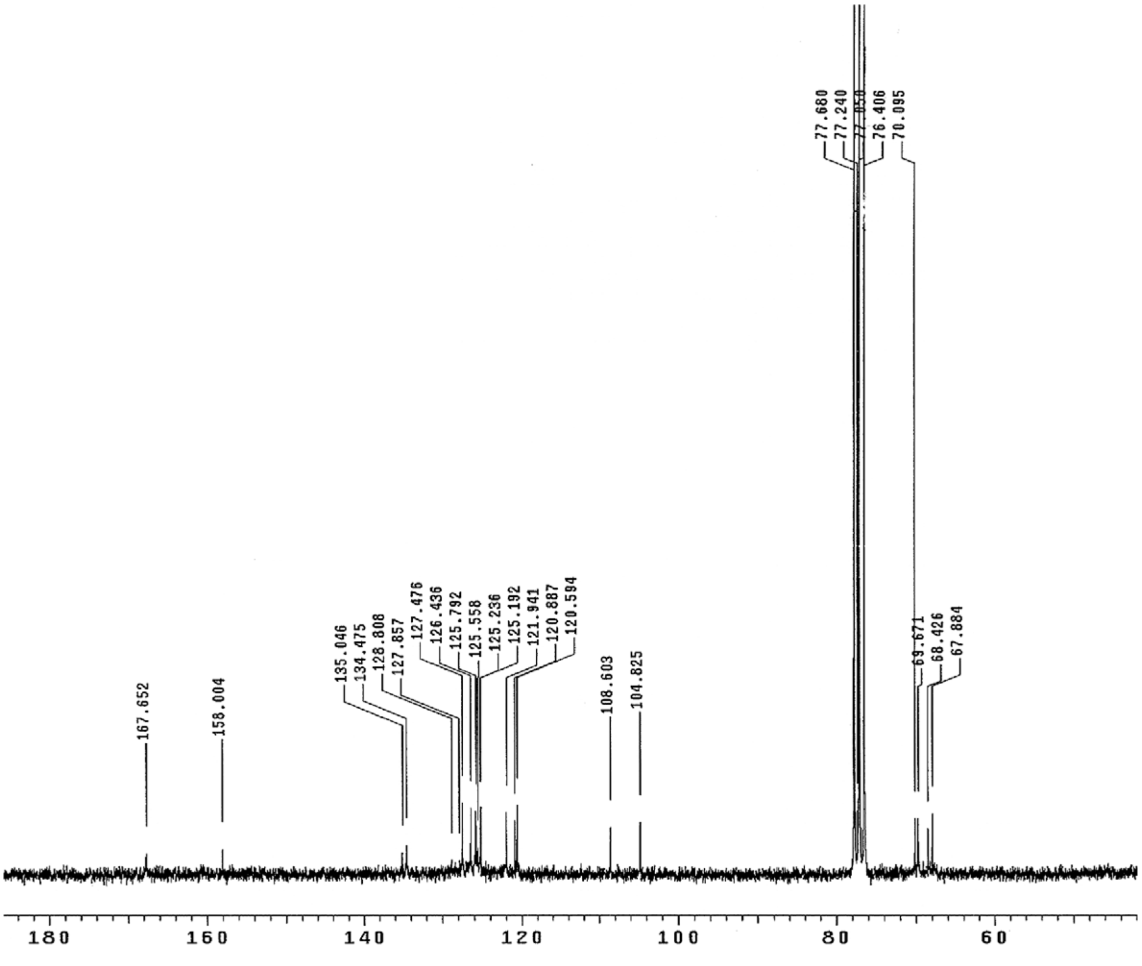


Fig. 4. ^{13}C NMR spectra of complex **6** in $CDCl_3$.

127.40, 126.39, 125.76, 125.54, 125.19, 125.10, 121.92, 120.50, 120.43, 118.82, 117.16, 116.14, 104.84, 103.91, 70.03, 69.62, 68.20, 67.82. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 287 (5.17), 611 (4.71), 645 (4.86), 669 (5.08), 707 (5.12). MS (ES$^+$), (*m*/*z*): 1436 [M + H]$^+$. *Anal* Calc. for $C_{88}H_{74}N_8O_{12}$: C, 73.63; H, 5.20; N, 7.81. Found: C, 73.56; H, 5.33; N, 7.77%.

2.3.3. Synthesis of nickel(II) phthalocyanine (**5**)

Compound **3** (0.3 g, 0.84 mmol) and anhydrous $NiCl_2$ (27 mg, 0.21 mmol) were added in 2-(dimethylamino)ethanol (DMAE) (3 ml). Then the mixture was irradiated by microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol (40 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 preparative silicagel plate with chloroform:methanol (100:3) as eluents. Yield: 0.175 g (56%), mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2925–2855 (Alif. C–H), 1610, 1580, 1463, 1394, 1270, 1241, 1123, 1098, 1072, 963, 790, 771. ^{1}H NMR. ($CDCl_3$), (δ:ppm): 8.15 (d, 4H, Ar–H), 7.69–7.61 (m, 8H, Ar–H), 7.33–7.28 (m, 24H, Ar–H), 6.76 (d, 4H, Ar–H), 4.28 (m, 16H, CH_2–O), 4.04 (m, 16H, CH_2–O). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 172.76, 154.49, 135.04, 134.47, 127.47, 126.50, 125.79, 125.57, 125.20, 122.26, 121.81, 120.88, 120.71, 120.44, 119.76, 119.33, 108.61, 104.85, 70.11, 69.55, 68.44, 67.85. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 295 (5.17), 625 (4.89), 677 (5.17). MS (ES$^+$), (*m*/*z*): 1491 [M–H]$^+$. *Anal* Calc. for $C_{88}H_{72}N_8O_{12}Ni$: C, 70.83; H, 4.86; N, 7.51. Found: C,70.66; H, 4.93; N, 7.45%.

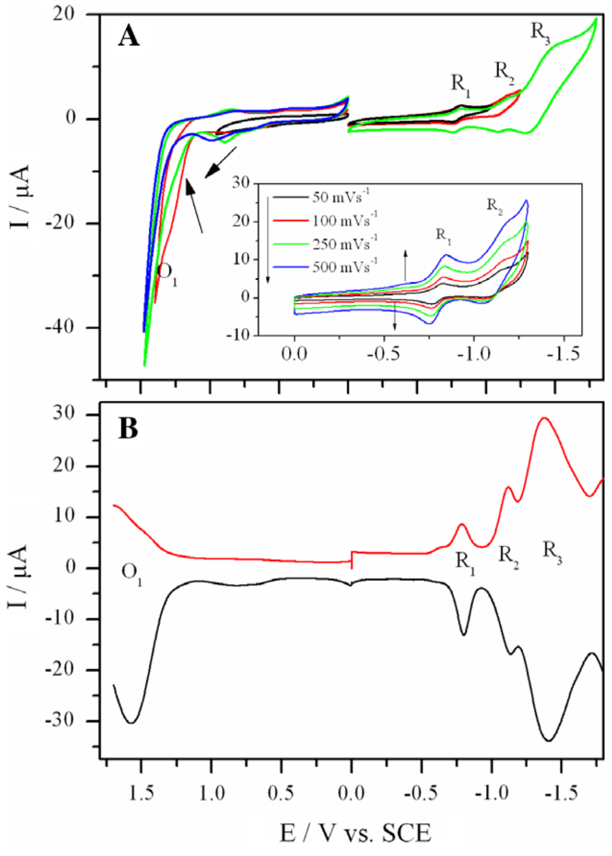


Fig. 5. (A) CVs of $\mathbf{H_2Pc}$ recorded with different switching potentials at 0.100 mV s^{-1} scan rate on Pt in DCM/TBAP. (CVs of $\mathbf{H_2Pc}$ recorded at different scan rates) (B) SWVs of $\mathbf{H_2Pc}$. SWV parameters: pulse size = 100 mV; frequency:25 Hz).

2.3.4. Synthesis of zinc (II) phthalocyanine (**6**)

Compound **3** (0.3 g, 0.84 mmol) and anhydrous $Zn(CH_3COO)_2$ (39 mg, 0.21 mmol) were added in 2-(dimethylamino)ethanol (DMAE) (3 ml). Then the mixture was irradiated by microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol (40 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 preparative silica gel plate with chloroform:methanol (100:4) as eluents. Yield: 0.208 g (66%), mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2925–2854 (Aliph. C–H), 1596, 1580, 1463, 1395, 1359, 1269, 1240, 1100, 1056, 953, 771, 774. ^{1}H NMR. ($CDCl_3$), (δ:ppm): 8.18 (d, 4H, Ar–H), 7.71–7.60 (m, 8H, Ar–H), 7.41–7.32 (m, 20H, Ar–H), 7.25 (m, 4H, Ar–H), 6.76 (d, 4H, Ar–H), 4.24 (m, 16H, CH_2–O), 4.04 (m, 16H, CH_2–O). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 167.65, 158.00, 135.04, 134.47, 128.80, 127.85, 127.47, 126.43, 125.79, 125.62, 125.55, 125.23, 125.19, 121.94, 120.88, 120.59, 108.60, 104.82, 70.09, 69.67, 68.42, 67.88. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 289 (5.19), 357 (5.00), 619 (4.65), 687 (5.24). MS (ES$^+$), (*m*/*z*): 1499 [M + H]$^+$. *Anal* Calc. for $C_{88}H_{72}N_8O_{12}Zn$: C, 70.51; H, 4.84; N, 7.48. Found: C, 70.24; H, 4.89; N, 7.43%.

2.3.5. Synthesis of cobalt (II) phthalocyanine (**7**)

Compound **3** (0.3 g, 0.84 mmol) and anhydrous $CoCl_2$ (27 mg, 0.21 mmol) were added in 2-(dimethylamino)ethanol (DMAE)

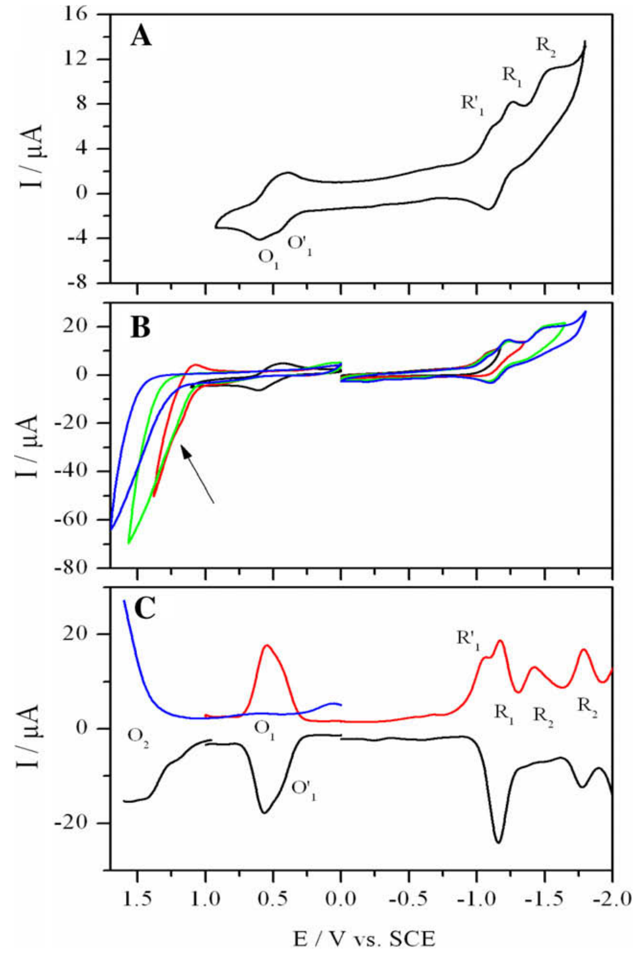


Fig. 6. (A) CVs of **ZnPc** recorded at at 0.100 mV s^{-1} scan rate on Pt in DCM/TBAP. (B) CVs of **ZnPc** recorded with different switching potentials at 0.100 mV s^{-1} scan rate. (C) SWVs of **ZnPc**. SWV parameters: pulse size = 100 mV; frequency:25 Hz).

(3 ml). Then the mixture was irradiated by microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol (40 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 preparative silicagel plate with chloroform:methanol (100:5) as eluents. Yield: 0.195 g (62%), mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 (Ar–H), 2927–2862 (Aliph. C–H), 1596, 1572, 1506, 1463, 1397, 1269, 1240, 1122, 1099, 1067, 962, 752. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 295 (5.09), 613 (4.74), 679 (5.06). MS (ES$^+$), (*m*/*z*): 1492 [M]$^+$. *Anal* Calc. for $C_{88}H_{72}N_8O_{12}Co$: C, 70.82; H, 4.86; N, 7.51. Found: C, 70.65; H, 4.66; N, 7.43%.

*2.3.6. Synthesis of copper (II) phthalocyanine (**8**)*

Compound **3** (0.3 g, 0.84 mmol) and anhydrous $CuCl_2$ (28 mg, 0.21 mmol) were added in 2-(dimethylamino)ethanol (DMAE) (3 ml). Then the mixture was irradiated by microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture refluxed with ethanol (40 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 preparative silicagel plate with chloroform:methanol (100:4) as eluents. Yield: 0.154 g (49%), mp > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1}: 3054 (Ar–H), 2927–2868 (Aliph. C–H), 1646, 1595, 1577, 1508, 1452, 1396, 1269, 1240, 1132, 1100, 953, 793, 749. UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} ε dm^3 mol^{-1} cm^{-1})]: 283 (5.06), 621 (4.66), 685 (5.01). MS (ES$^+$), (*m*/*z*): 1498 [M + H]$^+$. *Anal* Calc. for $C_{88}H_{72}N_8O_{12}Cu$: C, 70.60; H, 4.85; N, 7.48. Found: C, 70.52; H, 4.91; N, 7.46%.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of substituted phthalocyanines starts generally with the preparation of the corresponding phthalonitrile precursors. The synthesis of the target metal-free **4** and metallophthalocyanines **5–8** undertaken in this work are shown in Figs. 1 and 2. 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy}phthalonitrile **3** was prepared from 2-[2-(1-naphthyloxy)ethoxy]ethanol **1** with 4-nitrophthalonitrile **2** in dry dimethylformamide containing potassium carbonate as the base. The reaction was carried out in dry dimethylformamide at 50 °C and gave moderate yields (53%). Comparison of the IR spectral data clearly indicated the formation of compound **3** by the disappearance of the OH band of compound **1** at 3449 cm^{-1}, and the appearance of a new vibration at 2230 cm^{-1} (C≡N). The spectrum of **3** also indicates the presence of alkyl and CN groups by the intense stretching bands at 2925–2868 (C–H) and 2230 (C≡N) cm^{-1}. ^{1}H NMR spectrum of **3**, OH group of compound **1** disappeared as expected. ^{1}H NMR spectrum of **3** exihibited signals at δ = 8.22 (d, 1H, Ar–H), 7.82 (d, 1H, Ar–H), 7.57–7.36 (m, 5H, Ar–H), 7.19–7.09 (m, 2H, Ar–H), 6.82 (d, 1H, Ar–H) belonging to aromatic protons. The proton-decoupled ^{13}C NMR spectrum indicated the presence of the nitrile carbon atoms in **3** at δ = 115.68 ppm. The MS mass spectrum of compound **3**, which shows a peak at *m*/*z* = 358 [M]$^+$, support the proposed formula for this compound.

According to the IR spectrum of compound **4**, the signals for the C≡N groups at 2230 cm^{-1} for compound **3** disappeared and new peaks appeared at 3291 and 1613 cm^{-1} that are dedicated to the N–H group in the phthalocyanine core of **4**. In the ^{1}H NMR spectrum of **4**, the typical shielding of inner core protons could not be observed due to the probable strong aggregation of the molecules [26]. The mass spectrum of compound **4** was measured as *m*/*z* = 1436 [M + H]$^+$ and is in good accord with the suggested structure.

In the IR spectra of the metallophthalocyanines (**5–8**) cyclotetramerization of **3** was confirmed by the disappearance of the sharp C≡N stretching vibration at 2230 cm^{-1}. The IR spectra of NiPc, ZnPc, CoPc and CuPc are also very similar to that of the precursor H_2Pc except for the disappearance of the N–H vibration of the phthalocyanine core. The ^{1}H NMR spectra of these compound were almost identical to those of H_2Pc **4**. ^{1}H NMR spectra of compounds **5, 6** were the broad signals encountered in the case of compound **5, 6** as a result of the aggregation of phthlocyanine cores at the considerable high concentration used for the NMR measurements [27]. In the ^{1}H NMR spectrum of **6** exhibited signals at δ = 8.18 (d, 4H, Ar–H), 7.71–7.60 (m, 8H, Ar–H), 7.41–7.32 (m, 20H, Ar–H), 7.25 (m, 4H, Ar–H), 6.76 (d, 4H, Ar–H), 4.24 (m, 16H, CH_2–O), 4.04 (m, 16H, CH_2–O) belonging to aromatic and aliphatic protons (Fig. 3). In the ^{13}C NMR spectrum of **6** indicated carbon atoms at δ = 167.65, 158.00, 135.04, 134.47, 128.80, 127.85, 127.47, 126.43, 125.79, 125.62, 125.55, 125.23, 125.19, 121.94, 120.88, 120.59, 108.60, 104.82, 70.09, 69.67, 68.42, 67.88 (Fig. 4). ^{1}H NMR measurements of the cobalt(II) and copper(II) phthalocyanine **7**, **8** were precluded due to its paramagnetic nature. In the mass spectrum of compounds **5**, **6, 7** and **8** the presence of molecular ion peaks at *m*/*z* = 1491 [M–H]$^+$, 1499 [M + H]$^+$, 1492 [M]$^+$ and 1498 [M + H]$^+$, respectively, confirmed the proposed structures.

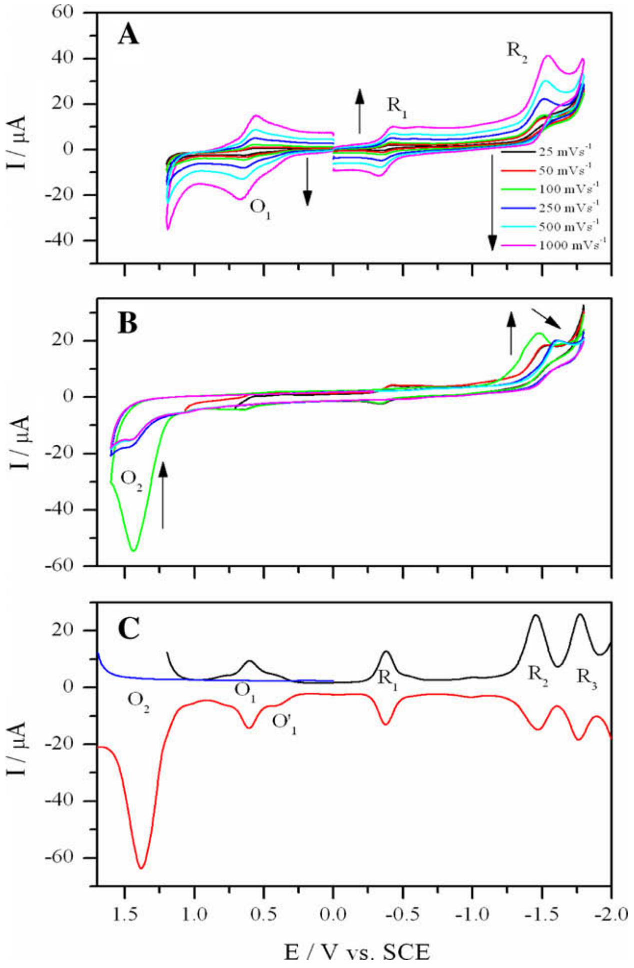


Fig. 7. (A) CVs of **CoPc** recorded with different switching potentials at 0.100 mV s^{-1} scan rate on Pt in DCM/TBAP. (B) CVs of **CoPc** recorded at different scan rates. (C) SWVs of **CoPc**. SWV parameters: pulse size = 100 mV; frequency:25 Hz).

3.2. Electrochemical measurements

Fig. 5 shows CV and SWV responses of metal-free phthalocyanine **4** recorded with different switching potentials and at various scan rates. Upon cathodic potential scans, metal-free phthalocyanine **4** gives two reversible reduction couples at −0.79 and −1.12 V versus SCE, when the potential is switched before −1.30 V (Fig. 5A inset), which are agreement with the reported metal-free phthalocyanine **4** studies in the literature [28–31]. However, when the potential is switched from more negative potentials, a very intense couple (R_3) at −1.39 V is recorded (Fig. 5A). After R_3 couple, reverse waves of R_1 and R_2 couples decrease in current intensity. These voltammetric behaviors may due to the decomposition of the complex at more negative potentials which product reduces at −1.39 V. Decomposition of metal-free phthalocyanine **4** is also recorded during positive potential scans. Metal-free phthalocyanine **4** give a very intense wave at 1.55 V which shifts to positive potentials during repetitive scans. During repetitive scans, a new wave is recorded at 0.85 V assigned to the product of decomposition reaction. During repetitive scans, all couples of metal-free phthalocyanine **4** disappear, which indicates the formation of a nonconductive film of the decomposition product on the electrode surface.

Zinc(II) phthalocyanine **6** give very similar voltammetric responses with metal-free phthalocyanine **4** (Fig. 6). It gives three reduction and an oxidation couples at −1.17, −1.42, −1.79 and 0.56 V respectively, when the potential is scans from 1.0 to −2.0 V. Differently, first reduction and oxidation couples of the complex split into two waves due to aggregation of the complexes. Diluting the solution decreased the peak current of the waves assigned to the aggregated species (R'_1 and O'_1) more than that of the monomeric ones (R_1 and O_1) that supports the existence of the aggregation–disaggregation equilibrium. When the potential is switched from more positive potentials, an intense peak at 1.55′V is recorded, which shifts to positive potentials during repetitive scans. During repetitive scans, all couples of zinc(II) phthalocyanine **6** disappear, which indicates the formation of a nonconductive film of the decomposition product on the electrode surface.

Fig. 7 shows the CV and SWV of cobalt(II) phthalocyanine **7**. Within the electrochemical window of TBAP/DCM in CV measurements, cobalt(II) phthalocyanine **7** undergoes one reversible one electron oxidation and three reversible one electron reduction processes at −0.37, −1.45, −1.77 and 0.59 V respectively. CV and SWV analysis show that cobalt(II) phthalocyanine **7** also has aggregation–disaggregation equilibria in solution during positive potential scans thus the oxidation couple splits into two wave due to electron transfer of aggregated (O'_1 at 0.39 V) and monomeric species (O_1 at 0.59 V). Assignments of the redox couple are confirmed by spectroelectrochemical measurements which are given below. As the cases in metal-free phthalocyanine **4** and zinc(II) phthalocyanine **6**, cobalt(II) phthalocyanine **7** also decomposes at more positive potentials (the wave at 1.38 V).

3.3. Spectroelectrochemical studies

Spectroelectrochemical studies were employed to confirm the assignments in the CVs of the complexes. UV–Vis spectral changes of metal-free phthalocyanine **4** are given in Fig. 8. For mononuclear metal-free phthalocyanine (H_2Pc), the symmetry is D_{2h} and there are two Q-bands at 667 and 698 nm, accompanied by a vibrational

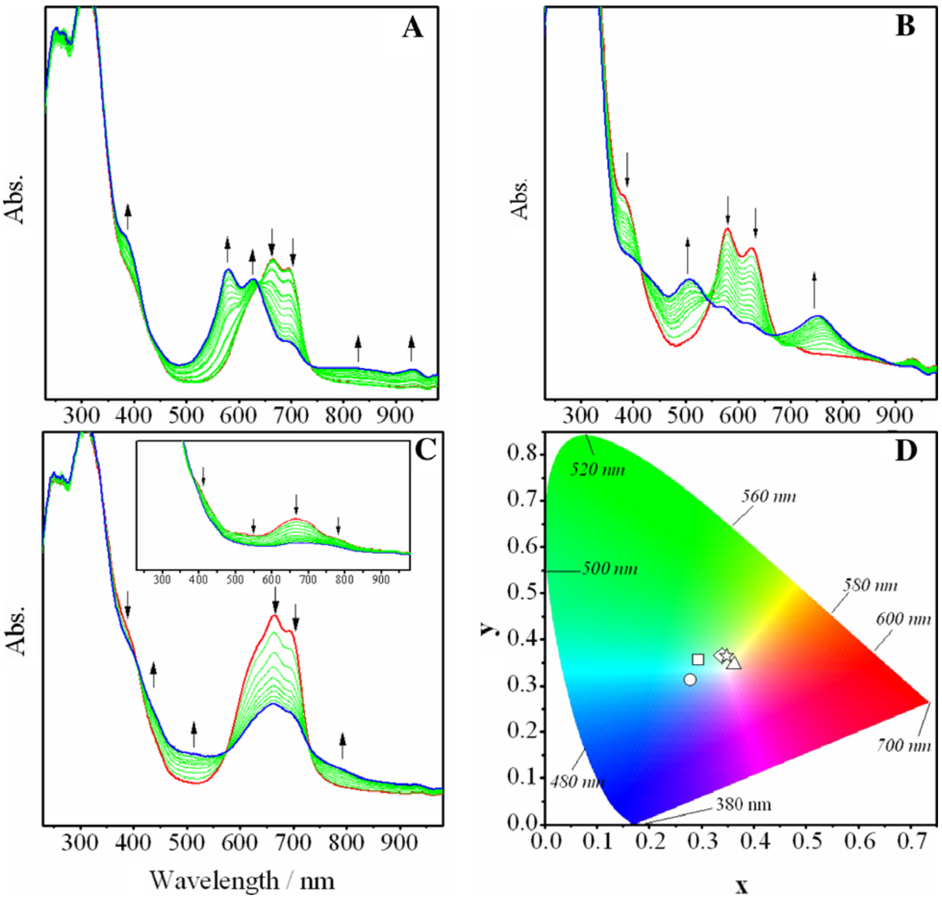


Fig. 8. In situ UV–Vis spectral changes of $\mathbf{H_2Pc}$. (A) E_{app} = −1.00 V. (B) E_{app} = −1.35 V. (C) E_{app} = 1.00 V (inset: E_{app} = 1.60 V). (D) Chromaticity diagram of $\mathbf{H_2Pc}$ (each symbol represents the color of electro-generated species; □: neutral $\mathbf{H_2Pc}$, H_2Pc^{-2}, ○: H_2Pc^{-3}, △: H_2Pc^{-4}, ☆: H_2Pc^{-}).

component to higher energy of the main absorption at 614 nm, resulted from the aggregation of the monomers. When the working electrode is polarized at −1.00 V, $H_2Pc(-2)$ is one electron reduced to form the $[H_2Pc(-3)]^-$ anion (Fig. 8A). When $[H_2Pc(-2)]$ is reduced, the bands at 667 and 669 nm decrease and new bands at 580 and 620 nm are recorded. Two new bands at 830 and 931 nm at NIR region are observed. During electrochemical reduction at −1.00 V, well-defined isosbestic points are observed at 636 and 740 nm, which demonstrates that the reduction proceeds cleanly in deoxygenated DCM to give a single, reduced species. During the second reduction of H_2Pc at −1.35 V, intensities of the bands at 580 and 620 nm decreases without shift, while new bands at 502, and 750 nm are recorded (Fig. 8B). At the same time, the band at 385 nm decreases in intensity. During the reduction of $[H_2Pc(-3)]^-$ anion, well-defined isosbestic points are observed at 415, 548, 666, and 900 nm, which demonstrates that the reduction proceeds cleanly to give a single, reduced $[H_2Pc(-4)]^{-2}$ species. During the oxidation of H_2Pc at 1.0 V (Fig. 8C), absorption of the Q-bands decreases in intensity without shift, while the absorption of the region between 450 and 550 nm and at around 790 nm increase in intensity. Clear isosbestic points are recorded at 405, 573, and 771 nm in the spectra. These changes are typical of the oxidation of $[H_2Pc(-2)]$ to $[H_2Pc(-1)]^+$ [26–28]. Under potential application at 1.60 V, decreasing of all bands in intensity indicate the decomposition of $[H_2Pc(-1)]^+$ monocations.

The color change of the complexes during the redox processes were recorded using in situ colorimetric measurements. Fig. 8D gives the chromaticity diagrams of the complex H_2Pc recorded simultaneously during the spectroelectrochemical measurements. Without any potential application, solution of H_2Pc is bluish green ($x = 0.294$ and $y = 0.356$). As potential is stepped from 0 to −1.00 V color of the neutral H_2Pc starts to changes and light blue color ($x = 0.2789$ and $y = 0.3128$) of monoanionic form of $[H_2Pc^{-3}]^{-1}$ was obtained at the end of the first reduction. Similarly color of the dianionic species, $[H_2Pc^{-4}]^{-2}$ was recorded as light orange ($x = 0.3624$ and $y = 0.3458$). Monocationic species, $[H_2Pc^{-1}]^+$ has light green color ($x = 0.3392$ and $y = 0.3659$). Decomposition of $[H_2Pc^{-1}]^+$ do not change the color of the solution significantly (point ☆: $x = 0.3481$ and $y = 0.3642$). Measurement of the *xyz* coordinates allows quantification of each color of the redox species that is very important to decide their possible electrochromic application.

Zinc(II) phthalocyanine **6** has redox inactive metal centers, thus indicate ring-based characters for all redox couples during in situ spectroelectrochemical measurements (Fig. 9). During the potential application at −1.20 V, First of all, two bands at 500 and 760 nm and the Q-band at 680 nm increase first and decrease again in intensity while intensity of the Q-band shoulder at 635 nm decreases due to the reduction of aggregated species. Then the Q-band at 680 nm decreases in intensity without shift, while new bands in the MLCT region at 443, 580, 872, and 956 nm are observed. These characteristic changes indicate a ring-based redox process and assign the couple R_1 to $[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-1}$ process (Fig. 9A). At the −1.60 V potential application, while the Q-band at 680 nm and the band at 580 nm decrease in intensity without shift, new bands are recorded at 510, 793 and 876 nm (Fig. 9B). These

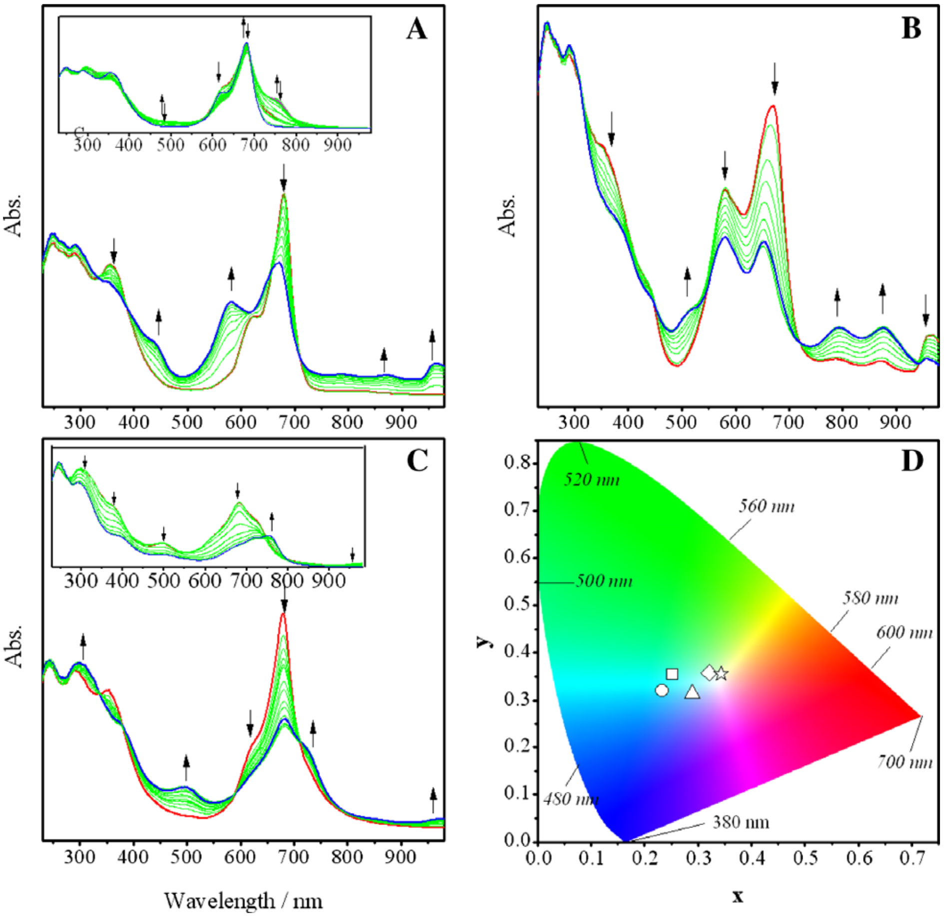


Fig. 9. In situ UV–Vis spectral changes of **ZnPc**. (A) final part of the spectral changes (inset: initial part of the spectral changes) at $E_{app} = -1.20$ V. (B) $E_{app} = -1.60$ V. (C) $E_{app} = 0.80$ V. (inset: $E_{app} = 1.60$ V). (D) Chromaticity diagram of **6** (each symbol represents the color of electro-generated species; □: neutral **6**, $Zn^{II}Pc^{-2}$, ○: $Zn^{II}Pc^{-3}$, △: $Zn^{II}Pc^{-4}$, ☆: $Zn^{II}Pc^{-}$).

spectroscopic changes are easily assigned to the reduction of the monoanionic species, $[Zn^{II}Pc^{-3}]^{-1}$ to $[Zn^{II}Pc^{-4}]^{-2}$ dianionic species. Spectroscopic changes given in Fig. 9C are characteristic for the oxidation of $[Zn^{II}Pc^{-2}]$ to monocationic $[Zn^{II}Pc^{-1}]^{+1}$ species [32]. While the Q-band decreases in intensity, new bands at 500 and 730 nm are recorded during the oxidation process. Well-defined isosbestic points are observed during each redox processes, which demonstrates that the redox reactions proceed cleanly to give a single, reduced/oxidized species. During the potential application at 1.60 V, spectroscopic changes indicate the decomposition of the monocationic species. The color changes of the solution during the redox processes were recorded using in situ colorimetric measurements (Fig. 9D). Without any potential application, the solution of zinc(II) phthalocyanine is bluish green (point: □; $x = 0.2522$ and $y = 0.3539$). As the potential is stepped from 0 to −1.70 V, the color of the neutral $[Zn^{II}Pc^{-2}]$ start to changes and greenish blue color (point: ○; $x = 0.2332$ and $y = 0.3195$) was obtained for the monoanionic form of $[Zn^{II}Pc^{-3}]^{-1}$ at the end of the first reduction. Similarly the color of the dianionic species, $[Zn^{II}Pc^{-4}]^{-2}$ was recorded as bluish purple (point: △; $x = 0.2898$ and $y = 0.314$). During the oxidation process, the color of the solution is changed from bluish green to light yellow (point:☆; $x = 0.3434$ and $y = 0.356$).

Fig. 10 represents in situ UV–Vis spectral changes and in situ recorded chromaticity diagram of cobalt(II) phthalocyanine **7** in DCM/TBAP during potential application at potentials of the redox processes. Before potential application, observation of the band at 625 nm as a sholder of the Q-band at 668 nm indicates the existence of the aggregated species. Shifting of the Q-band from 668 to 704 nm and observation of new bands at 462 nm indicate metal center reduction of cobalt(II) phthalocyanine at −0.50 V potential application (Fig. 10A). This process resulted in clear isobestic points at 347, 552, 678, and 756 nm in the spectra. Color change blue (point □: $x = 0.2632$ and $y = 0.3137$) to light green (point ○: $x = 0.3552$ and $y = 0.406$) was recorded as shown in the chromaticity diagram (Fig. 10D). These spectroscopic data assign the first reduction couple to $[Co^{II}Pc^{-2}]/[Co^{I}Pc^{-2}]^{1-}$. Further reduction of $[Co^{I}Pc^{-2}]^{1-}$ at −1.60 V indicate a ligand-based redox process. Because the Q-band at 704 nm decreases without shift while a new broad band is recorded at 536 nm. (Fig. 10B). Clear isosbestic points were observed at 404, 474, 600, and 754 nm in the spectra. Color changes from green to yellow (point △: $x = 0.3747$and $y = 0.3674$) was recorded (Fig. 10D). These changes assign the second reduction couple to $[Co^{I}Pc^{-2}]^{1-}/[Co^{I}Pc^{-3}]^{2-}$. Fig. 10C (inset) represents initial part of the spectral changes during the oxidation process at 0.80 V. Decreasing of the shoulder of the Q-band and increasing the intensity of the Q-band indicate the oxidation of the aggregated CoPc species. Then the Q-band at 668 nm decreases without shift and two new bands are recorded at 527 and 727 nm. These spectroscopic changes indicate ligand-based process and assigned to $[Co^{II}Pc^{-2}]/[Co^{II}Pc^{-1}]^{1+}$ [33–37]. Greenish blue color of the solution changes to first bluish green (point ◇: $x = 0.281$ and $y = 0.3473$) and then to light green (point ☆: $x = 0.281$ and $y = 0.3473$) at the end of the oxidation process.

4. Conclusion

In this work, we describe the synthetic procedure and characterization of new metal-free and metallophthalocyanines substi-

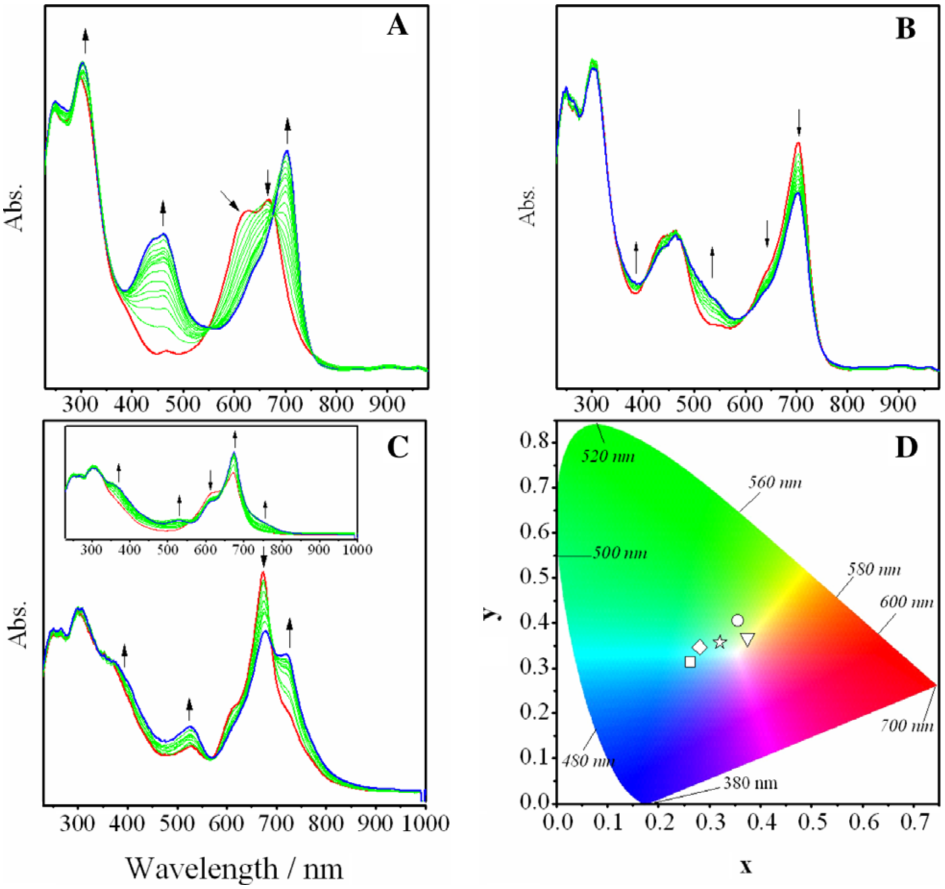


Fig. 10. In situ UV–Vis spectral changes of **7**. (A) $E_{app} = -0.50$ V. (B) $E_{app} = -1.60$ V. (C) $E_{app} = 0.75$ V. (D) Chromaticity diagram of **7** (each symbol represents the color of electro-generated species; □: neutral **7**, $Co^{II}Pc^{-2}$, ○: $Co^{I}Pc^{-2}$, △: $Co^{I}Pc^{-3}$, ☆: $Co^{II}Pc^{-}$).

tuted with 4-{2-[2-(1-naphthyloxy)ethoxy]ethoxy} groups. The target symmetrical phthalocyanines were separated by preparative thin-layer chromatograph and characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, elemental analysis and MS spectral data. Voltammetric and spectroelectrochemical studies show that while metal-free and zinc phthalocyanine complexes give ligand-based, redox processes, cobalt phthalocyanine complex give both metal and ligand-based redox processes. All of the complexes decomposed at more positive potentials than 1.30 V versus SCE. Definite determination of the colors of the electro-generated anionic and cationic form of the complexes is important to decide possible electrochromic application of the complexes. Electrochromic applications of the complexes are under investigation.

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