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Water soluble novel phthalocyanines containing dodeca-amino groups

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ABSTRACT

Water soluble metal phthalocyanines (where the metal is Co, Cu or Pd) as well as a cationic Pd phthalocyanine, each bearing 12 dimethylamino groups to enhance solubility, were prepared. A phthalonitrile derivative was synthesized by the reaction of 4-nitrophthalonitrile with 2,4,6-tris(*N*,*N*-dimethylaminomethyl)phenol. Solution studies indicated that phthalocyanines containing tertiary amine substituents were monomeric only in acidic medium ($\text{pH} < 6$) whereas the quaternized dye was monomeric at all pH values. The electrochemical behavior of the phthalocyanines was investigated by cyclic voltammetry and differential pulse voltammetry. Spectroelectrochemical measurements were carried out to confirm assignments made to the metallophthalocyanines. All compounds were characterized by UV–vis, FT-IR, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis.

1. Introduction

The physical and chemical properties of phthalocyanines (Pc) have long attracted attention due to their interesting electrical, optical, catalytic and photochemical properties [1]. A particularly attractive feature of phthalocyanines is the possibility of tuning these properties through slight changes on the nature of the peripheral substituents or using different central metal ions in the phthalocyanine core [1,2]. In order to overcome the insolubility of unsubstituted phthalocyanine parent molecule, peripheral groups have been extensively used to enhance solubility and, at the same time, processibility and mesophase formation. In this sense, long alkyl, alkyloxy, alkylsulfanyl or bulky apolar groups lead to soluble products in common organic solvents while anionic or cationic substituents (e.g. sulfo groups, carboxylic acids, ammonium groups) result with products soluble in aqueous media [3–5].

During the last decade, our group has been heavily engaged with the synthesis of phthalocyanines and porphyrazines with substituents such as esters, fluorinated aromatic groups, quaternized amino groups, crown ethers or multicyclic aromatic rings [6–14].

Water soluble phthalocyanines have appeared as attractive photosensitizers for photodynamic therapy [15–18] and Boron Neutron Capture Therapy [19]. One limitation of these photosensitizers is their high tendency to form aggregated species in aqueous solution. An efficient strategy for number of practical uses might be to add some groups to inhibit aggregation.

In this paper we report the synthesis and characterization of several phthalocyanines bearing 12 tertiary amino groups which enable the molecules to dissolve in number of organic solvents as well as water. The solution properties have been especially investigated in water and in buffer solutions in order to follow the aggregation property of these compounds. Electrochemical properties of the novel phthalocyanines have been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

2. Experimental

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrophotometer using TMS as internal reference. Mass spectra were performed on Ultima Fourier Transform and Varian 711 mass spectrometer. All reagents, solvents and 2,4,6-tris(*N*,*N*-dimethylaminomethyl)phenol (**2**) were of reagent grade quality obtained from commercial suppliers. 4-Nitrophthalonitrile (**1**) was prepared according to a reported procedure [20].

The cyclic voltammetry (CV), differential pulse voltammetry (DPV), and double potential step coulometry (CPC) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. The surface of the working electrode

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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. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure tetrahydrofuran (THF) 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 also applied to the CV scans to further minimize the potential control error.

The spectroelectrochemical measurements were carried out with an Ocean-optics QE65000 diode array spectrophotometer equipped with the potentiostat/galvanostat 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 an SCE reference electrode separated from the bulk of the solution by a double bridge were used.

*2.1. 2,4,6-Tris(N,N-dimethylaminomethyl)phenoxy-4,5-dicyanobenzene (**3**)*

2,4,6-Tris(*N,N*-dimethylaminomethyl)phenol (**2**) (530.8 mg, 2 mmol) was reacted with anhydrous K_2CO_3 (828 mg, 6 mmol) in dry DMF (5 cm^3) for 1 h at room temperature. Then 4-nitrophthalonitrile (**1**) (173 mg, 1 mmol) was dissolved in dry DMF (10 cm^3) and added dropwise to the mixture at a period of 15 min. The reaction was stirred overnight. Then the mixture was poured onto cold water (20 cm^3), filtered and the filtrate was evaporated to dryness. The residue was treated with benzene (20 cm^3) for 1 h at room temperature and the insoluble inorganic by-products were filtered. The filtrate was evaporated to dryness. Oily yellow residue was dried *in vacuo*. Yield: 187 mg (47.8%). ^{1}H NMR (chloroform-*d*) δ: 7.66–7.62 (d, 1H, Hb), 7.36 (s, 1H, Ha), 7.06–7.04 (d, 1H, Hc), 6.91 (s, 2H, Hd), 3.49 (s, 4H, *o*-N–CH$_2$), 3.16 (s, 2H, *p*-N–CH$_2$), 2.18 (s, 12H, *o*-N–CH$_3$), 2.12 (s, 6H, *p*-N–CH$_3$). IR, ν (cm^{-1}): 2941–2767, 2230, 1593, 1455, 1356, 1263, 1129, 1076, 870, 800, 744. Found (%): C, 70.45; H, 7.66; N, 17.48. Calc. (%) for $C_{23}H_{29}N_5O$: C, 70.59; H, 7.42; N, 17.90.

*2.2. General procedure for 2,9,16,23-tetrakis[2,4,6-tris(N,N-dimethylaminomethyl)phenoxy]phthalocyaninates (**4** and **5**)*

Compound **3** (278 mg, 0.71 mmol) was reacted with anhydrous metal salt {45.55 mg (0.35 mmol) $CoCl_2$ or 47.07 mg (0.35 mmol) $CuCl_2$} in *n*-pentanol (5 cm^3) with two drops of DBU under N_2 at 130 °C for 8 h. The reaction mixture was extracted with distilled water (20 cm^3) to remove impurities until the water was colorless. After the evaporation of pentanol, the crude product is stirred with 35 cm^3 of THF for 1 h at room temperature. The mixture was filtered and then the filtrate was evaporated to dryness. The crude product was treated with 30 cm^3 of acetone for 2 h at room temperature. The mixture was filtered and the filtrate was evaporated to dryness. Finally, the crude product was stirred in 30 cm^3 of diethyl ether for 2 h at room temperature. Then the filtrate was evaporated to dryness. The product was dissolved in (20 cm^3) CH_2Cl_2 and treated with HCl(g) for 15 min. The mixture was filtered. The precipitate was dissolved in water and then neutralized by adding excess amount of NaOH solution. The precipitate was filtered and dried *in vacuo*.

*CuPc (**4**)*. Yield: 30 mg (10.36%). IR, ν (cm^{-1}): 2935–2768 (alkyl CH), 1605 (aryl CH), 1462, 1405, 1353, 1223, 1091, 748. MS (ES) *m/e*: 1628.89 [M]$^+$, 1631.19 [M + 2]$^+$. UV–vis λ_{max} (nm) (log ε) in CH_2Cl_2: 341 (4.72), 616 (4.45), 685 (5.14). Found (%): C, 67.82; H, 7.49; N, 17.32. Calc. (%) for $C_{92}H_{116}N_{20}O_4Cu$: C, 67.74; H, 7.12; N, 17.18.

*CoPc (**5**)*. Yield: 35 mg (12.11%). IR, ν (cm^{-1}): 2936–2767, 1613, 1463, 1405, 1355, 1223, 1096, 753. MS (ES) *m/e*: 1623.72 [M]$^+$, 1626.30, 1627.43. UV–vis λ_{max} (nm) (log ε) in MeOH: 327 (4.39), 663 (4.36). Found (%): C, 68.15; H, 7.36; N, 17.08. Calc. (%) for $C_{92}H_{116}N_{20}O_4Co$: C, 67.93; H, 7.14; N, 17.23.

*2.3. 2,9,16,23-Tetrakis[2,4,6-tris(N,N-dimethylaminomethyl)phenoxy]phthalocyaninato palladium(II) (**6**)*

Compound **3** (242 mg, 0.61 mmol) was reacted with 53.4 mg (0.30 mmol) of anhydrous $PdCl_2$ in *n*-pentanol with one drop of DBU under N_2 at 130 °C for 24 h. The reaction mixture was extracted with distilled water to remove impurities until the water was colorless. After the evaporation of pentanol, the crude product is stirred with 35 cm^3 of THF for 1 h at room temperature. The mixture was filtered and then the filtrate was evaporated to dryness. The crude product was dissolved in acetone (10 cm^3) and poured into cold diethyl ether (35 cm^3) and it was left overnight at 5 °C in order to precipitate the impurities completely. After filtration, the filtrate was evaporated to dryness. The crude product was dissolved in DMF (10 cm^3) and extracted by cyclohexane. Cyclohexane phase was evaporated and dried *in vacuo*. Yield: 40 mg (13.84%). ^{1}H NMR (acetone-*d*$_6$) δ: 8.11–6.95 (m, 20H, Ar–H), 3.45 (s, 16H, *o*-N–CH$_2$), 2.44 (s, 8H, *p*-N–CH$_2$), 2.20 (s, 48H, *o*-N–CH$_3$), 2.06 (s, 24H, *p*-N–CH$_3$). IR, ν (cm^{-1}): 2938–2767, 1618, 1453, 1401, 1355, 1266, 1040, 839, 748. UV–vis λ_{max} (nm) (log ε) in CH_2Cl_2: 329 (4.76), 601 (4.49), 669 (5.15). Found (%): C, 66.32; H, 7.11; N, 16.54. Calc. (%) for $C_{92}H_{116}N_{20}O_4Pd$: C, 66.01; H, 6.93; N, 16.74.

*2.4. 2,9,16,23-Tetrakis[2,4,6-tris(N,N,N-trimethylammoniummethyl)phenoxy]phthalocyaninato palladium(II) dodecaiodide (**7**)*

Compound **6** (100 mg, 0.059 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and stirred with 203.82 mg (1.44 mmol) of CH_3I at room temperature for 4 h. Then the mixture was filtered and the precipitate washed with CH_2Cl_2. The precipitate was dried *in vacuo*. Yield: 38 mg (34.29%). IR, ν (cm^{-1}): 3420, 3008, 2958, 2760, 1608, 1405, 1325, 1230, 1159, 1106, 972, 909, 881, 749. UV–vis λ_{max} (nm) (log ε) in water: 328 (4.47), 599 (4.65), 665 (5.18). Found (%): C, 67.12; H, 8.48; N, 14.85. Calc. (%) for $C_{104}H_{152}N_{20}O_4Pd$: C, 67.35; H, 8.20; N, 15.11.

3. Results and discussion

The synthetic procedure as outlined in Fig. 1 started with the synthesis of namely 2,4,6-tris(*N,N*-dimethylaminomethyl)phenoxy-4,5-dicyanobenzene (**3**) by the reaction of 4-nitrophthalonitrile (**1**) with 2,4,6-tris(*N,N*-dimethylaminomethyl)phenol (**2**). Metallophthalocyanines (Fig. 2) and quaternized palladium phthalocyanine (Fig. 3) (M = Co, Cu, Pd) were synthesized directly by cyclotetramerization of the phthalonitrile derivative (**3**) in the presence of anhydrous metal salt and an N-donor base DBU in a high-boiling solvent such as *n*-pentanol. One important point which should be always taken into account during this synthesis is that temperatures higher than 130 °C lead to decomposition of the precursor and totally diminish the yield of the reaction.

In the IR spectrum of compound **3**, alkyl C–H vibrations around 2941–2767 cm^{-1} were observed. The characteristic CN vibration at 2230 cm^{-1} in the spectrum of **3** disappeared after Pc formation in those of **4**–**6**.

The ES mass spectral results on newly synthesized phthalocyanines exhibited molecular ion species for **4** and **5**. Molecular ion peaks for both showed good agreement with the calculated values; for CuPc (*m/z* 1629.58), CoPc (*m/z* 1624.57). Since a monosubstituted phthalonitrile (**3**) was the precursor for the synthesis of

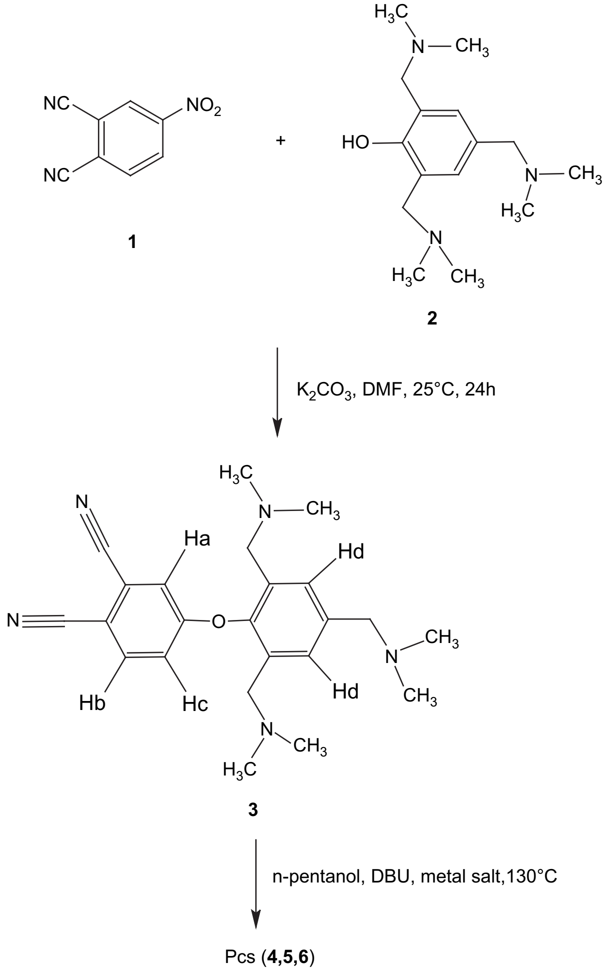
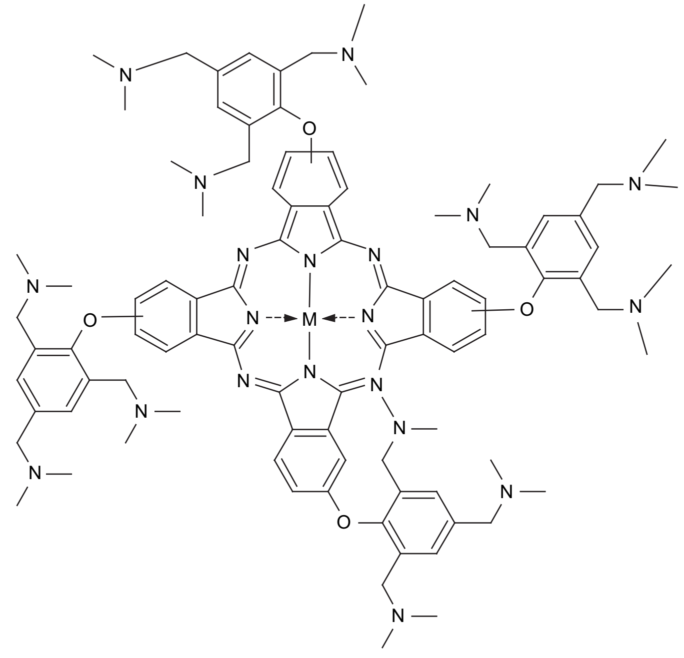


Fig. 1. Synthesis of **3** and related phthalocyanines.

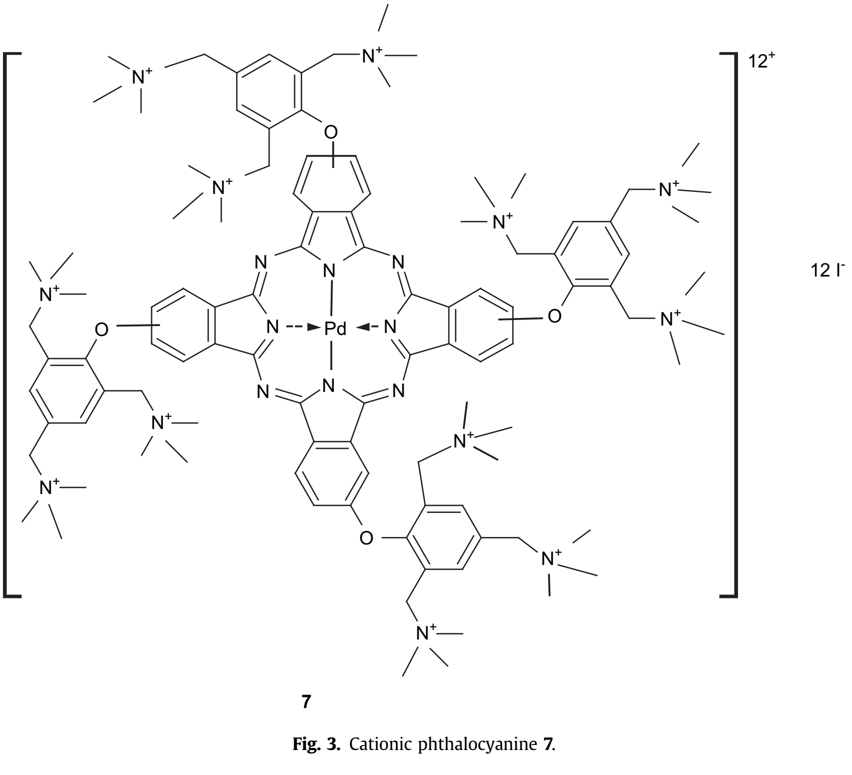


4 **5** **6**

M = Cu^{+2}, Co^{+2}, Pd^{+2}

Fig. 2. Tetrakis[2,4,6-tris(*N*,*N*-dimethylaminomethyl)phenoxy]phthalocyaninates (**4–6**).

phthalocyanines in the present work, all products were obtained as isomer mixtures. Strong adsorption of the molecules with tertiary amino groups on both alumina and silica hindered the possibility of using column chromatography in purification and also isomer isolation of phthalocyanines (**4–6**). ^1H NMR spectrum of **3** showed two different singlets for $N–CH_2$ protons at 3.49 and at 3.16 ppm corresponding to *ortho*- and *para*-



7

Fig. 3. Cationic phthalocyanine **7**.

substitutions. Similarly, N–CH_3 protons were observed also as two singlets at 2.18 and 2.12 ppm indicating the *ortho*- and *para*-position of the substituents. Between 7.66 and 6.91 ppm aromatic protons were observed.

The Co^{II}, Cu^{II} and Pd^{II} phthalocyanines show similar spectra in water solution with two maxima of comparable intensity appearing in the Q (at ca. 660–685 nm) and B (at 325–345 nm) band regions. A common feature of these compounds is the solubility of these dyes both in number of organic solvents (e.g. chloroform, dichloromethane, methanol, THF, DMF, DMSO, etc.) and water. The high number of polar and bulky dimethylaminomethyl substituents should be responsible for this interesting feature. When the solutions of phthalocyanines in organic solvents are investigated as a function of decreasing concentration from 10^{-5} to 10^{-7} M, almost no change occurred in the Q band region. This spectral behavior indicates that phthalocyanine molecules are present in monomeric state in all these solutions due to bulky tris(dimethylaminomethyl)phenyloxy substituents without any appreciable tendency to form aggregates [21,22].

The spectra of metallophthalocyanines with dimethylamino substituents in water are quite sensitive to changes in pH of the solution. It should be noted here that these molecules are present almost only as monomers in strongly acidic aqueous solutions due to the repulsion of amino groups converted into cationic form under these conditions. In order to visualize the changes in absorption spectra of the phthalocyanines with respect to changes in pH, buffer solutions (pH = 6–7.8) were prepared by mixing 0.067 M KH_2PO_4 with 0.067 M Na_2HPO_4 in different amounts. After that, **4** and **5** were dissolved in these buffer solutions and changes occurring in the Q band region were observed from pH = 6–7.8 (Fig. 4). The monomeric form of **4** gave a sharp and intense Q band absorption at 680 nm at pH = 6.2; the absorption for aggregated species appeared only as a shoulder around 645 nm. By increasing the pH, intermolecular interaction led to an increase in the higher energy band around 645 nm corresponding to aggregated species together with a sharp decrease in the band arising from monomeric ones as shown in Fig. 4. This indicates that neutralization of 12+ charges located externally at the peripheral dimethylamino substituents in **4** or **5** precludes contact between adjacent phthalocyanine central sites and leads to higher aggregation in aqueous medium. The electronic spectrum of quaternized palladium phthalocyanine (**7**) with positive charges on the periphery again gives the typical spectrum corresponding to monomeric species in aqueous solution (Fig. 5).

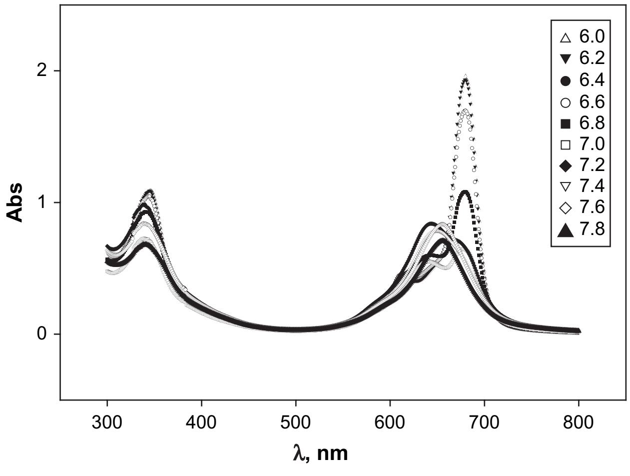


Fig. 4. Changes in the electronic spectra of **4** with respect to pH in aqueous solutions.

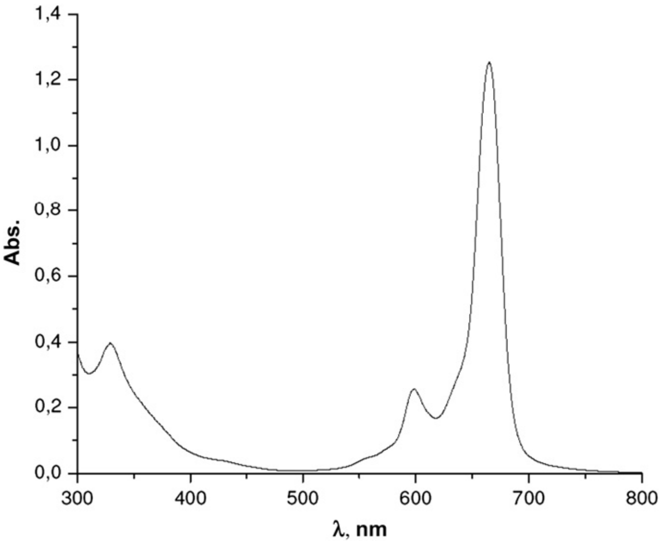


Fig. 5. Electronic spectra of **7** in water.

3.1. Electrochemical measurements

The electrochemical behavior of the phthalocyanines was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) on a platinum working electrode in DMSO. Within the electrochemical window of TBAP/DMSO, CuPc undergoes a quasi-reversible one-electron oxidation at 0.20 V and three quasi-reversible one-electron reduction processes at −0.73, −1.08 and −1.63 V vs. SCE at 0.100 V s^{-1} scan rate. DPV of the complex confirms the recorded redox processes clearly. Reversibility is illustrated by the similarity in the forward and reverse DPV scans [23,24]. CV and DPV show the adsorption character of the oxidation process recorded at 0.20 V continuous scan after the negative potential scans in solution. As shown in Fig. 6A, this process could not be recorded when just the positive potentials are scanned. Because of the electro-inactive copper center of the complex, all of these processes are attributed to successive removal of electrons from, or addition of electrons to the macrocycle orbitals [25].

Spectroelectrochemistry was used to confirm some of the assignments in the CV of CuPc (Fig. 7). During the controlled potential reduction of CuPc at −0.75 V vs. SCE, while the absorption of Q band at 683 nm, its shoulder at 645 nm and B band at 345 nm decrease in intensity, the bands at 580 and 822 nm (MLCT) increase in intensity. The spectral changes in Fig. 7A, decreasing of Q band without shifting and observation of new bands at 580 and 822 nm (MLCT), are characteristic of ligand-based processes [25–29]. As shown in Fig. 7A, the process occurred with clear isosbestic points at 312, 385, 598, and 721 nm in the spectra. During the controlled potential reduction of CuPc (Fig. 7B) at −1.15 V vs. SCE, while the absorption of Q band at 683 nm and B band completely disappears, a new band appears in the MLCT region at 722 nm with the bands at 580 and 822 nm (MLCT), increasing in intensity. These spectral changes are typical for the formation of dianionic species due to further reduction of $[Cu^{II}Pc^{3-}]^{1-}$ species to $[Cu^{II}Pc^{4-}]^{2-}$. This process occurred with clear isosbestic points at 406, 443, 593, and 717 nm in the spectra. The lack of any spectral change during the potential application at 0.30 V supports the adsorption character of the process recorded at 0.20 V (assigned by the CV measurements). Further evidences are provided by the spectral changes such as increasing of Q band without shift and decreasing of B band in intensity during the potential application at 1.00 V. These changes are typical of ring-based oxidation of MPc complexes (Fig. 7C) [25–29].

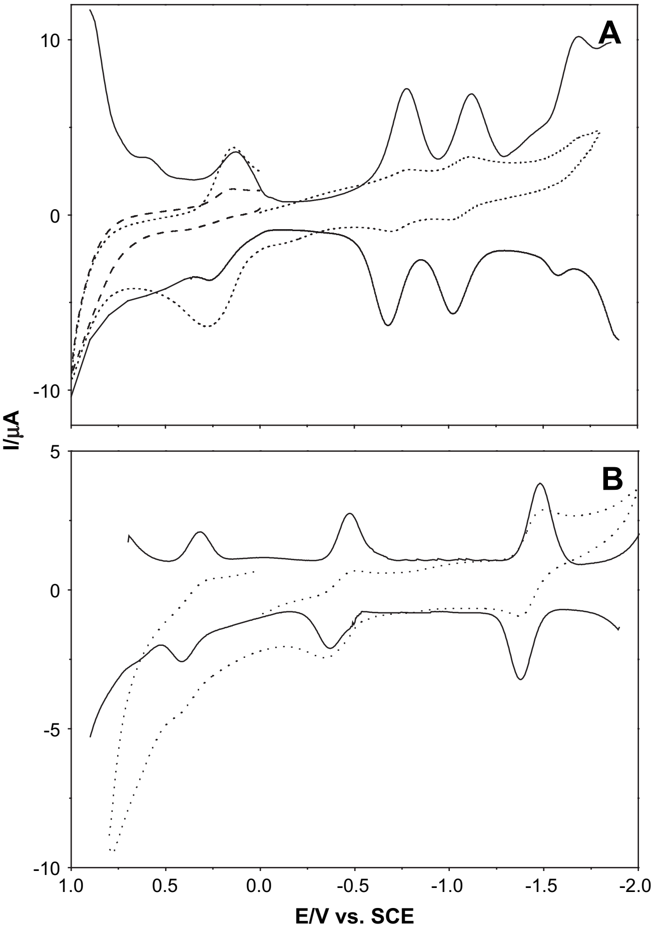


Fig. 6. (A) CVs (⋯ graph represents full scale; - - - - graph represents only positive scan) and DPVs (—) of CuPc at 0.100 mV s^{-1} scan rate on Pt in DMSO/TBAP. (B) CVs and DPVs of CoPc at 0.100 mV s^{-1} scan rate on Pt in DMSO/TBAP.

Fig. 6B shows the CV and DPV of the complex CoPc. Within the electrochemical window of TBAP/DMSO, CoPc undergoes one quasi-reversible one-electron oxidation process at 0.35 V and two reversible one-electron reductions at −0.43 and −1.44 V vs. SCE at 0.100 V s^{-1} scan rate. First-row transition metals Pc differ from those of the main-group metals Pc due to the fact that metal “d” orbitals may be positioned between HOMO and LUMO of the phthalocyanine (Pc^{2-}) ligand. The first oxidation and first reduction processes occur on the metal center in the metal Pc only for Mn, Fe and Co derivatives in polar solvent such as DMF and DMSO. For Ni, Cu and Zn phthalocyanines, redox processes take place on the Pc ring [25]. In this work, the first reduction and first oxidation processes of CoPc recorded at 0.35 and −0.43 could be assigned easily to the Co^{II}/Co^{III} and Co^{II}/Co^{I} redox couple, respectively, and the remaining processes to the phthalocyanine ring. All predicted redox processes are given in Eq. (1). Furthermore, the separation between the metal center reduction and oxidation processes (∼0.79 V) is comparable with the CoPc papers [25,29–31].

$$\left[\mathrm{Co^{III}Pc^{-2}}\right]^{+} \underset{0.35\,\mathrm{V}}{\overset{-e^{-}}{\Leftrightarrow}} \left[\mathrm{Co^{II}Pc^{-2}}\right] \underset{-0.43\,\mathrm{V}}{\overset{+e^{-}}{\Leftrightarrow}} \left[\mathrm{Co^{I}Pc^{-2}}\right]^{1-} \underset{-1.44\,\mathrm{V}}{\overset{+e^{-}}{\Leftrightarrow}} \left[\mathrm{Co^{I}Pc^{-3}}\right]^{2-} \tag{1}$$

For the reduction couples of CoPc, to cathodic peak separations (ΔE_p) changed from 65 to 130 mV with the scan rates from 10 to 500 mV s^{-1} (ΔE_ps, 60–110 mV, were obtained for ferrocene reference) support reversible electron transfer. Reversibility is illustrated by the similarity in the forward and reverse DPV scans [23,24]. The values of $I_{p,a}/I_{p,c}$ for all couples of the complex CoPc are close to unity and the peak currents increased linearly with the square root of scan rates, for scan rates ranging from 10 to 500 mV s^{-1}, indicating that the electrode reactions are purely diffusion-controlled for the couples.

To confirm the assignment for CoPc, spectroelectrochemical measurements were carried out. Fig. 8A shows the UV–vis spectral changes during a controlled potential reduction of CoPc at −0.50 V vs. SCE. The Q band at 667 nm and its shoulder at 605 nm shift to 710 and 643 nm, respectively, while a new band at 472 nm forms as the reduction process continued. The B2 band at 333 nm shift to 316 nm, while the intensity of B1 band at 322 nm increases in intensity. The band at 472 nm and shifting of Q band indicate the formation of the $[Co^{I}Pc^{2-}]^{1-}$ species, confirming the CV assignment of the couple to $[Co^{II}Pc^{2-}]/[Co^{I}Pc^{2-}]^{1-}$ couple. This process resulted with clear isosbestic points at 328, 370, 335, 562, 696 and 766 nm in the spectra. The spectral changes in Fig. 8B are typical of ring-based reduction in phthalocyanine complexes [25–28,32–34]. There is a decrease in the intensity of the band at 472 nm and the Q band without shift upon further reduction of the $[Co^{I}Pc^{2-}]^{1-}$ species at the potential of couple at −1.50 V. The B band decreases in intensity without shift while new bands at 348, 605 and 675 nm appear during this process. This process resulted with clear isosbestic points at 330, 380, 585 and 695 nm in the spectra. This confirms our earlier assignment of the process recorded at −1.10 V to $[Co^{I}Pc^{2-}]^{1-}/[Co^{I}Pc^{3-}]^{2-}$. Fig. 8C shows the spectral changes observed when the potential corresponding to oxidation process at 0.40 V was applied to the solution of $[Co^{II}Pc^{2-}]$. The Q band at 675 nm increases in intensity with red shift to 680 nm while B2 band decreases with red shift from 338 to 345 nm. Red shifting of Q band with increasing is typical of a metal-based oxidation in cobalt

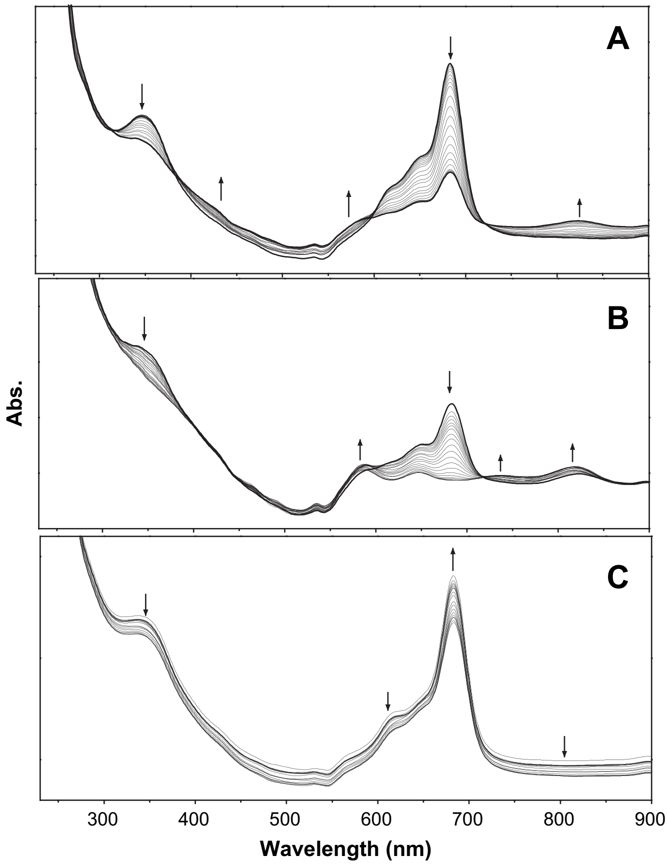


Fig. 7. In situ UV–vis spectral changes of CuPc. (A) $E_{app} = -0.75$ V; (B) $E_{app} = -1.15$ V; (C) $E_{app} = 1.00$ V.

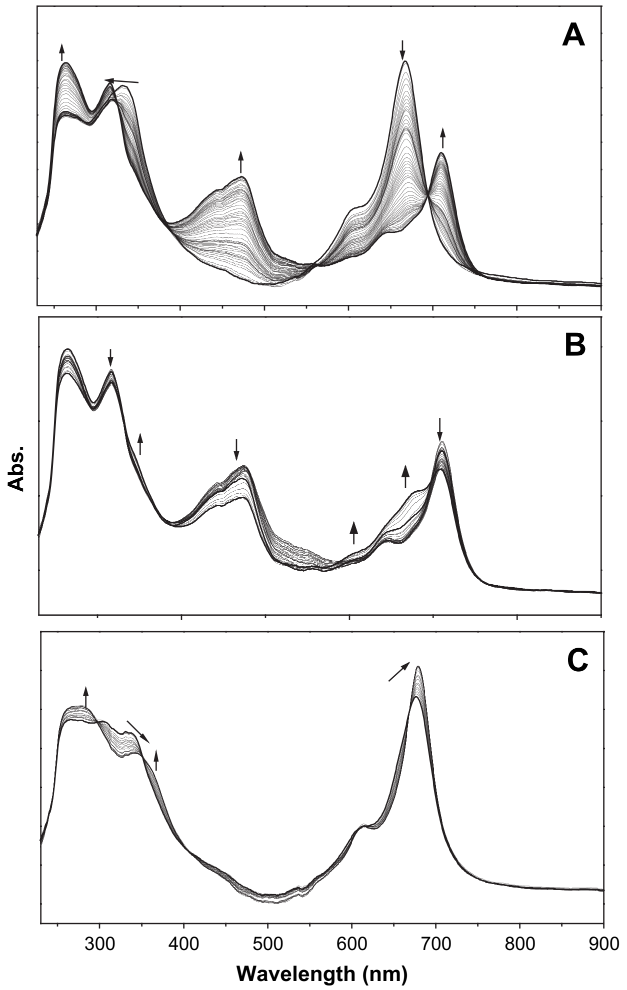


Fig. 8. In situ UV–vis spectral changes of CoPc. (A) $E_{app} = -0.50$ V; (B) $E_{app} = -1.50$ V; (C) $E_{app} = 0.40$ V.

Pc complexes [25–28,32–35]. The final spectrum in Fig. 8C is therefore assigned to $[Co^{III}Pc^{2-}]^+$, confirming CV assignments. This process resulted with clear isosbestic points at 295, 350, 404, 611 and 668 nm in the spectra.

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References

[1] Leznoff CC, Lever ABP. Phthalocyanines: properties and applications, vols. 1–4. New York: VCH; 1989–1996.
[2] Mack J, Kobayashi N, Stillman MJ. Magnetic circular dichroism spectroscopy and TD-DFT calculations of metal phthalocyanine anion and cation radical species. Journal of Porphyrins and Phthalocyanines 2006;10(9–10):1219–37.
[3] Sakamoto K, Kato T, Ohno-Okumura E, Watanabe M, Cook MJ. Synthesis of novel cationic amphiphilic phthalocyanine derivatives for next generation photosensitizer using photodynamic therapy of cancer. Dyes and Pigments 2005;64(1):63–71.
[4] Arvand M, Pourhabib A, Shemshadi R. The potentiometric behavior of polymer-supported metallophthalocyanines used as anion-selective electrodes. Analytical and Bioanalytical Chemistry 2007;387(3):1033–9.
[5] Chen JC, Chen NS, Huang JF. Derivatizable phthalocyanine with single carboxyl group: synthesis and purification. Inorganic Chemistry Communications 2006;9(3):313–5.
[6] Dinçer HA, Gül A, Koçak MB. A novel route to 4-chloro-5-alkyl-phthalonitrile and phthalocyanines derived from it. Journal of Porphyrins and Phthalocyanines 2004;8:1204–8.
[7] Dinçer HA, Gül A, Koçak MB. Tuning of phthalocyanine absorption ranges by additional substituents. Dyes and Pigments 2007;74(3):545–50.
[8] Selçukoğlu M, Hamuryudan E. Novel phthalocyanines with pentafluorobenzyloxy substituents. Dyes and Pigments 2007;74(3):17–20.
[9] Bayır ZA. Synthesis and characterization of novel soluble octa-cationic phthalocyanines. Dyes and Pigments 2005;65(3):235–42.
[10] Kocak M, Cihan A, Okur AI, Gül A. Novel crown ether-substituted phthalocyanines. Dyes and Pigments 2000;45(1):9–14.
[11] Özçesmeci I, Okur AI, Gül A. New phthalocyanines bearing tetra(hydroxyethylthio) functionalities. Dyes and Pigments 2007;75(3):761–5.
[12] Sesalan BŞ, Koca A, Gül A. Synthesis and electrochemical properties of porphyrazines with annulated 1,4-dithiaheterocycles. Polyhedron 2003;22(23):3083–90.
[13] Sesalan ŞB, Gül A. Synthesis and characterization of a phthalocyanine–porphyrazine hybrid and its palladium complex. Monatshefte für Chemie 2000;131(11):1191–5.
[14] Sesalan BŞ, Gül A. Synthesis of novel maleonitrile derivatives. Phosphorus, Sulfur, and Silicon and the Related Elements 2003;178(9):2081–6.
[15] Chiti G, Dei D, Fanfetti L, Roncucci G. In vitro photosensitizing efficacy of cationic phthalocyanine derivatives against *C. albicans*: effect of serum albumins. Journal of Porphyrins and Phthalocyanines 2005;9(7):463–9.
[16] Segalla A, Borsarelli CD, Braslavsky SE, Spikes JD, Roncucci G, Dei D, et al. Photophysical, photochemical and antibacterial photosensitizing properties of a novel octacationic Zn(II)-phthalocyanine. Photochemical & Photobiological Sciences 2002;1(9):641–8.
[17] Minnock A, Vernon DI, Schofield J, Griffiths J, Parish JH, Brown SB. Photoinactivation of bacteria. Use of a cationic water-soluble zinc phthalocyanine to photoinactivate both gram-negative and gram-positive bacteria. Journal of Photochemistry and Photobiology B: Biology 1996;32(3):159.
[18] Giuntini F, Raoul Y, Dei D, Municchi M, Chiti G, Fabris C, et al. Synthesis of tetrasubstituted Zn(II)-phthalocyanines carrying four carboranyl units as potential BNCT and PDT agents. Tetrahedron Letters 2005;46(17):2979–82.
[19] Bregadze VI, Sivaev IB, Gabel D, Wöhrle D. Polyhedral boron derivatives of porphyrins and phthalocyanines. Journal of Porphyrins and Phthalocyanines 2001;5(11):767–81.
[20] Young JG, Onyebuagu W. Synthesis and characterization of di-substituted phthalocyanines. Journal of Organic Chemistry 1990;55(7):2155–9.
[21] Bergami C, Donzello MP, Monacelli F, Ercolani C, Kadish KM. Tetra-2,3-pyrazinoporphyrazines with externally appended pyridine rings. 4. UV–visible spectral and electrochemical evidence of the remarkable electron-deficient properties of the new tetrakis-2,3-[5,6-di{2-(*N*-methyl)pyridiniumyl}pyrazino] porphyrazinatometal octacations, [(2-Mepy)(8)TPyzPzM](8+) (M = Mg-II(H_2O), Co-II, Cu-II, Zn-II). Inorganic Chemistry 2005;44(26):9862–73.
[22] Bergami C, Donzello MP, Monacelli F, Ercolani C, Kadish KM, Rizzoli C. Tetra-2,3-pyrazinoporphyrazines with externally appended pyridine rings. 3. A new highly electron-deficient octacationic macrocycle: tetrakis-2,3-[5,6-di{2-(*N*-methyl)pyridiniumyl}pyrazino] porphyrazine, [(2-Mepy)(8)TPyzPzH(2)] (8+). Inorganic Chemistry 2005;44(26):9852–61.
[23] Kissinger PT, Heineman WR. Laboratory techniques in electroanalytical chemistry. 2nd ed. New York: Marcel Dekker; 1996.
[24] Bard AJ, Faulkner LR. Electrochemical methods: fundamentals and applications. New York: Wiley; 2001.
[25] Lever ABP, Milaeva ER, Speier G. In: Leznoff CC, editor. The redox chemistry of metallophthalocyanines in solution in phthalocyanines: properties and applications, vol. 3. New York: VCH; 1993.
[26] Tau P, Nyokong T. Electrocatalytic activity of arylthio tetra-substituted oxotitanium(IV) phthalocyanines towards the oxidation of nitrite. Electrochimica Acta 2007;52(13):4547–53.
[27] Koca A, Özkaya AR, Arslanoğlu Y, Hamuryudan E. Electrochemistry, spectroelectrochemistry and electrochemical polymerization of titanylphthalocyanines. Electrochimica Acta 2007;52(9):3216–21.
[28] Koca A, Dinçer HA, Koçak MB, Gül A. Electrochemical characterization of Co(II) and Pd(II) phthalocyanines carrying diethoxymalonyl and carboxymethyl substituents. Russian Journal of Electrochemistry 2006;41(1):31–7.
[29] Silver J, Lukes P, Hey P, Ahmet MT. Electrochromism in titanyl and vanadyl phthalocyanine thin films. Journal of Materials Chemistry 1991;1(5):881–8.
[30] Koca A, Sener MK, Koçak MB, Gül A. Electrochemical characterization of phthalocyanine derivatives carrying a bulky triester unit on each benzo group. Transition Metal Chemistry 2005;30(4):399–403.
[31] Obirai J, Nyokong T. Synthesis, spectral and electrochemical characterization of mercaptopyrimidine-substituted cobalt, manganese and Zn(II) phthalocyanine complexes. Electrochimica Acta 2005;50(16–17):3296–304.
[32] Kandaz M, Yaraşır MNU, Koca A, Bekaroğlu Ö. Synthesis, characterization and electrochemistry of novel differently octasubstituted phthalocyanines. Polyhedron 2002;21(3):255–63.
[33] Matlaba P, Nyokong T. Synthesis, electrochemical and photochemical properties of unsymmetrically substituted zinc phthalocyanine complexes. Polyhedron 2002;21(24):2463–72.
[34] Obirai J, Nyokong T. Synthesis, electrochemical and electrocatalytic behaviour of thiophene-appended cobalt, manganese and zinc phthalocyanine complexes. Electrochimica Acta 2005;50(27):5427–34.
[35] Agboola B, Ozoemena KI, Nyokong T. Electrochemical properties of benzylmercapto and dodecylmercapto tetra substituted nickel phthalocyanine complexes: electrocatalytic oxidation of nitrite. Electrochimica Acta 2006;51(28):6470–8.