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The synthesis, characterization, electrochemical and spectroelectrochemical properties of a novel, cationic, water-soluble Zn phthalocyanine with extended conjugation

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ABSTRACT

A novel Zn phthalocyanine substituted with four dimethylaminocinnamaldiminophenyloxy substituents at peripheral positions was obtained by the condensation of various 4′-aminophenoxy substituted phthalocyanines and 4-(dimethylamino)cinnamaldehyde. Quaternization of the dimethylamino functionality produced cationic Zn phthalocyanines which were soluble in both water and other polar solvents such as methanol and DMSO. The novel compounds were characterized using elemental analysis, IR, ^{1}H NMR, UV–Vis and MALDI-TOF MS spectral data. Electrochemical, *in situ* spectroelectrochemical, and *in situ* electrocolorimetric measurements revealed that the complexes undergo electron transfer reactions via the nitro and amine groups in addition to common Pc ring-based processes.

1. Introduction

Phtalocyanines and metallo phthalocyanines (MPcs) enjoy many applications in fields such as non-linear optics [1–3], chemical sensors [4], semiconductors [5], liquid crystals [6–8] and catalysis [9]. Moreover, phthalocyanine derivatives are also used in photodynamic therapy (PDT) [10] owing to their strong absorption of visible radiation between 600 and 850 nm, which offers high penetration of tissue [11] and which is capable of photo-sensitization of singlet oxygen [12]. The PDT properties of the phthalocyanine dyes are strongly influenced by the presence and nature of the central metal ion. Complexation of phthalocyanine with transition metals results in dyes of short triplet lifetimes; closed shell, diamagnetic ions, such as Zn^{2+}, Al^{3+} and Ga^{3+}, provide phthalocyanine complexes with both high triplet quantum yield and long triplet lifetime [13].

The periphery of such macrocycles can be diversified by substitution with various groups which enable enhanced solubility in common organic solvents and which impart changes to the electronic properties of the Pc ring [14]. The presence of various positional isomers in tetra-substituted derivatives has been shown to account for their higher solubility versus their octa-substituted counterparts [15].

Improving the solubility of phthalocyanines is an important aspect of their chemistry, as the insolubility of unsubstituted phthalocyanine molecules in common organic solvents causes difficulties for many applications. For this reason, one of the important aims of research on the chemistry of phthalocyanines is to enhance their solubility in various solvents. Whereas peripheral substitution with bulky or long-chain hydrophobic moieties leads to pc derivatives that are soluble in apolar solvents [16–26], in contrast, amino, sulfo or carboxyl groups result in water-soluble products, at least within certain pH ranges [23–29].

An efficient way of shifting the low energy absorption of the phthalocyanines to longer wavelengths is the addition of unsaturated groups to aromatic core structure. Fusion of further aromatic rings to phthalocyanine core results with products such as naphtocyanines, phenantrocyanines, *etc.* which show Q band absorption in IR range rather than visible radiation. However, an immediate disadvantage encountered in these materials has been lower solubility even lower than phthalocyanine analogs.

This paper concerns a group of phthalocyanines in which multi-unsaturated groups were attached to the periphery together with

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an additional group to enhance solubility in the aqueous phase. In this part of the paper, the synthesis of dimethylaminocinnamaldiiminophenoxy-substitued zinc phthalocyanine from suitable precursors is described. Moreover, the electrochemical properties of this compound together with that of other precursors were studied in detail using cyclic voltammetry and spectroelectrochemistry. Such voltammetric, *in situ* spectroelectrochemical, and *in situ* electrocolorimetric characterization is essential to determine the compounds' technological potential especially in the case of electrochemical applications.

2. Experimental

All reagents and solvents were of reagent grade quality, obtained from commercial suppliers. The solvents were stored over molecular sieves (4A°). 4-Nitrophthalonitrile (**1**), 4-(4-nitrophenoxy)phthalonitrile (**3**) and [2,9,16,23-tetra-(4-[4-nitrophenoxy])-phthtalocyaninato-zinc(II)] (**4**) were synthesized as given in the literature [30–32]. 4-Nitrophenol was used as supplied commercially. The progress of the reactions was monitored by TLC (SiO_2). IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer, electronic spectra in the UV–Vis region were recorded with an Agilent 8453 UV/Vis spectrophotometer. ^{1}H NMR spectra were recorded in *d*-tetrahydrofuran on a Varian UNITY INOVA 500 MHz spectrophotometer using TMS as internal reference. Mass spectra were performed on a Bruker microflex LT MALDI-TOF MS. Melting points were determined on an Electrothermal Gallenkamp apparatus. Elemental analyses were performed on a Thermo Flash EA 1112.

2.1. Synthesis

2.1.1. 4-(4-nitrophenoxy)phthalonitrile (*3*)

4-Nitrophenol (1.500 g, 11.00 mmol) and 4-nitrophthalonitrile (1.900 g, 11.00 mmol) were added successively with stirring to dry DMF (50 mL). After dissolution, anhydrous K_2CO_3 (4.550 g, 33.00 mmol) was added and the reaction mixture was stirred at 60 °C for 24 h under argon. The progress of the reaction was monitored by TLC. The reaction mixture was poured into 250 mL of cold water and stirred for 15 min. The precipitate was filtered, washed several times with cold water until the filtrate became neutral. It was dried *in vacuo* at 50 °C. Yield: 1.70 g (59%); m.p. 160 °C. FTIR $\upsilon_{max}/\mathrm{cm}^{-1}$: 3076, 3041 (CH arom.), 2233 (−C≡N), 1582, 1345 ($-NO_2$), 1569, 1481 (Ar C=C), 1248 (Ar–O–Ar), 1214, 1166, 1084, 948, 850, 760, 694; ^{1}H NMR ($CDCl_3$) δ, ppm: 7.28–7.30 (d, 1H, H_a), 6.84 (d, 1H, H_b), 7.15–7.19 (d, 1H, H_c) 7.09–7.10 (d, 1H, H_d), 8.27–8.29 (d, 1H, H_e); *Anal.* Calc. for $C_{14}H_7N_3O_3$ (265.224 g/mol): C, 63.40; H, 2.66; N, 15.84. Found: C, 63.45; H, 2.65; N, 15.80%. MS m/z (100%) 265[M]$^+$.

2.1.2. [2,9,16,23-Tetra-(4-[4-nitrophenoxy])-phthtalocyaninatozinc(II)] (*4*)

A mixture of compound **3** (300 mg, 1.131 mmol), anhydrous Zn $(CH_3COO)_2$ (17.3 mg, 0.094 mmol) and a catalytic amount of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in dry DMF (1 mL) was heated at 178 °C with stirring under argon for 24 h. After cooling to room temperature, the reaction mixture was precipitated by adding methanol. The product was separated by filtration as a green solid which was washed several times with methanol and ethanol to remove any unreacted precursor and by products and dried *in vacuo*. This compound is soluble in THF, DMF and DMSO. Yield: 0.25 g (79%); m.p. >200 °C. FTIR $\upsilon_{max}/\mathrm{cm}^{-1}$ 3068 (CH, arom.), 1586, 1392 ($-NO_2$), 1505, 1468 (Ar C=C), 1220 (Ar–O–Ar), 1083, 1042, 941, 826, 745; ^{1}H NMR ($CDCl_3$) δ, ppm: 7.25–8.65 (28H, m, Ar–H); UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L. mol^{-1} cm^{-1}): 672 (4.96), 607 (4.30), 348 (4.57); Anal. Calc. for $C_{56}H_{28}N_{12}O_{12}Zn$ (1126.306 g/mol): C, 59.72; H, 2.51; N, 14.92. Found: C, 60.01; H, 2.48; N 14.90%; MS (MALDI-TOF): m/z (100%) 1127 [M + H]$^+$.

2.1.3. [2,9,16,23-Tetra-(4-[4-aminophenoxy])-phthtalocyaninatozinc(II)] (*5*)

A mixture of **4** (0.2 g, 0.177 mmol), hydrazine hydrate (24 mL, in excess), and a catalytic amount of 10% Pd/C was refluxed in dry dioxane (30 mL) under argon for 72 h. The cooled reaction mixture was quickly filtered and the residue was discarded, whilst the filtrate was evaporated to dryness gently under vacuum in a rotary evaporator and then washed successively with cold ethanol and methanol. After being dried in vacuum, the crude dark green product was isolated with column chromatography over silica gel using $CHCl_3$:THF as eluent system changing from10/0.1 to 10/1.5 (v/v). Compound **5** is fairly soluble in THF, acetone, DMF and DMSO and slightly soluble in chloroform. Yield: 0.076 g (43%). FTIR $\upsilon_{max}/\mathrm{cm}^{-1}$ 3050 (Ar–H), 3339, 3214, 1607 ($-NH_2$), 1506, 1484, (Ar C=C), 1227 (Ar–O–Ar), 1091, 1043, 944, 827, 746. ^{1}H NMR ($CDCl_3$) δ, ppm: 6.52–8.42 (28H, m, Ar–H), 5.2 (8H, s, $-NH_2$); UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L. mol^{-1} cm^{-1}): 679 (5.06), 613 (4.34), 349 (4.66); Anal. Calc. for $C_{56}H_{36}N_{12}O_4Zn$ (1006.372 g/mol): C, 66.83; H, 3.61; N, 16.70; O, 6.36; Zn, 6.50 Found: C, 67.01; H, 3.89; N, 16.73. MS (MALDI-TOF): m/z (100%) 1006 [M]$^+$.

2.1.4. [2,9,16,23-Tetra-(4-[4-({(1Z,2E)-3-[4-(dimethylamino)phenyl]prop-2-en-1-ylideneimino)phenoxy])-phthtalocyaninatozinc(II)] (*7*)

A solution of **5** (70 mg, 0.07 mmol) in 15 mL dry THF was added dropwise to a solution of 4-(dimethylamino)cinnamaldehyde (4.87 mg, 0.028 mmol) in 10 mL dry THF and the mixture was refluxed under argon for 15 h. The solvent was evaporated to 1/10 of the initial volume and the reaction mixture was precipitated by adding methanol at room temperature. The crude product was separated by filtration as a green solid which was dissolved in chloroform (5 mL) and **7** was precipitated by the dropwise addition of methanol. The precipitate was filtered, washed several times successively with cold water, methanol and ethanol and dried *in vacuo*. Yield: 80 mg (37%); m.p.>200 °C. FTIR $\upsilon_{max}/\mathrm{cm}^{-1}$ 3050 (Ar–H, w.), 2923–2853 ($-CH_3$, m), 1599 (−HC=N, s), 1229 (Ar–O–Ar). ^{1}H NMR ($CDCl_3$) δ, ppm: 6.83–8.32 (m, 28H, Ar–H), 3.11 (s, 24H, $-NCH_3$), 6.76–8.19 (m,12H, =CH–); UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L. mol^{-1} cm^{-1}): 678 (4.97), 612 (4.23), 383 (4.93); Anal. Calc. for $C_{100}H_{80}N_{16}O_4Zn$ (1635.219 g/mol): C, 73.45; H, 4.93; N, 13.71; Found: C, 73.55; H, 5.02; N, 16.70. MS (MALDI-TOF): m/z (100%) 1636 [M + H]$^+$.

2.1.5. Tetrakis-([4-(trimethylamino)phenyl]prop-2-en-1-ylideneimino)phenoxy])-phthtalocyaninatozinc(II)) tetraiodide(*8*)

Coumpound **7** (40 mg, 0.018 mmol) was dissolved in $CHCl_3$ (4.5 mL) and CH_3I (14.1 mg, 0.099 mmol) was added to this solution. The mixture was refluxed for 6 h and then was filtered and the precipitate washed with $CHCl_3$ and was dried *in vacuo*. Yield: 26 mg (48%); m.p.>200 ^{0}C. FTIR $\upsilon_{max}/\mathrm{cm}^{-1}$ 3022 (Ar–H, w.), 2945–2853 ($-CH_3$, m), 1598 (−HC=N, s), 1225 (Ar–O–Ar); ^{1}H NMR ($CDCl_3$) δ, ppm: 6.83–8.32 (m, 28H, Ar–H), 4.10 (s, 36H, $-NCH_3$), 6.76–8.22 (m, 12H, =CH–); UV–Vis (THF): λ_{max}/nm (10^{-5} log ε, L. mol^{-1} cm^{-1}): 679 (5.02), 613 (4.50), 349 (4.75); Anal. Calc. for $C_{104}H_{92}N_{16}O_4Zn$ (1695.355 g/mol): C, 73.68; H, 5.47; N, 13.22; Found: C, 73.62; H, 5.27; N, 13.28; MS (MALDI-TOF): m/z (%) 1603 [M − (N + CH_3+3H$^+$)], 2045 [(M + 4I$^-$) − (CH_3 + CH_3I)].

2.2. Electrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) 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. 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. Electrochemical grade TBAP in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

2.3. *In-situ spectroelectrochemical and in-situ electrocolorimetric measurements*

UV–vis absorption spectra and chromaticity diagrams were measured by an OceanOptics QE65000 diode array spectrophotometer. *In-situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a Pt gauze (semitransparent electrode). 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. For *in-situ* electrocolorimetric measurements, the standard illuminant A with 2° 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 the complexes 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.

3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic procedure as outlined in Fig. 1 started with the synthesis of namely 4-(4-nitrophenoxy)phthalonitrile (**3**) by the

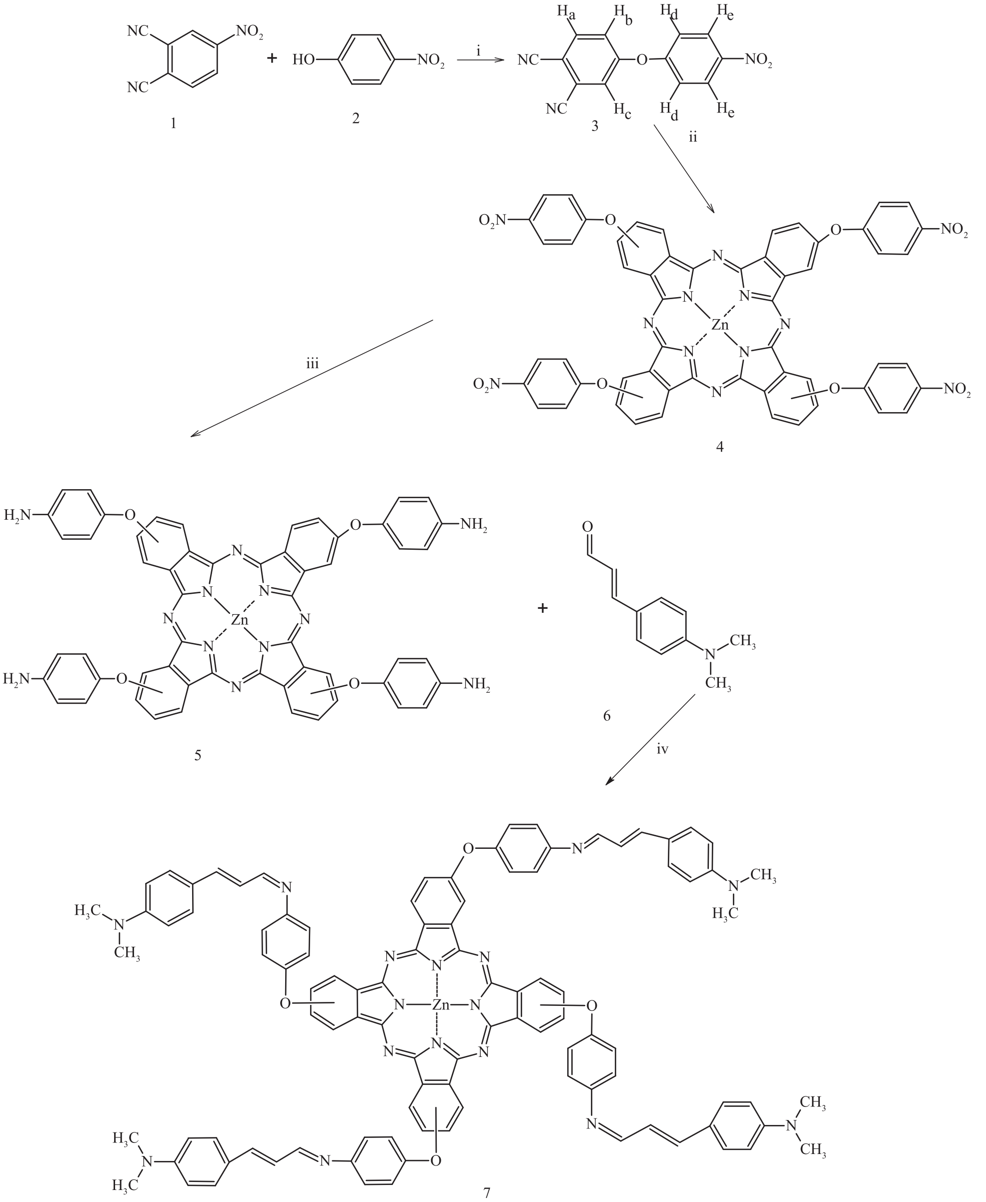

Fig. 1. Synthesis of Pcs.(i) K_2CO_3, DMF, 60 °C; (ii) DBU, DMF, $Zn(OAc)_2$; (iii) Pd/C, hydrazine hydrate, dioxane; (iv) THF, reflux

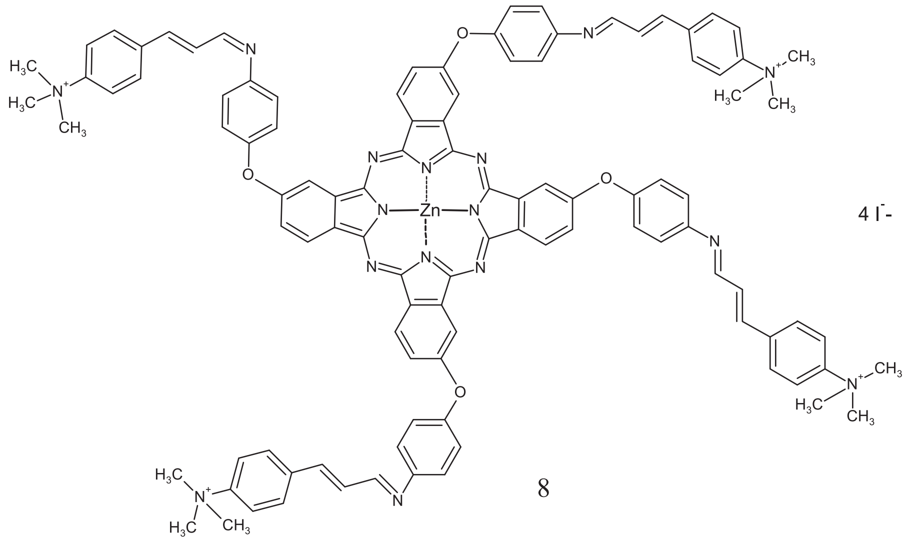

Fig. 2. Quaternized phthalocyanine **8**.

reaction of 4-nitrophenol with 4-nitrophthalonitrile. The reaction was carried out at 50–60 °C in dry DMF with K_2CO_3. This reaction has been frequently used in the preparation of a variety of ether or thioether- substituted phthalonitriles [33,34].

The usual cyclotetramerization reaction of the dinitrile compound (**3**) in the presence of anhydrous metal salt $Zn(CH_3COO)_2$ was used to obtain zincphthalocyanine (**4**) with four nitrophenoxy substituents [31]. Conversion of nitro substituents to amino groups in [2,9,16,23-Tetra-(4-[4-aminophenoxy])-phthtalocyaninatozinc (II)] (**5**) was accomplished with reducing by hydrazine hydrate in the presence of 10% Pd/C as catalyst. This method was found to be more efficient than the reported procedures with $Na_2S\cdot xH_2O$ [31] and tin dichloride ($SnCl_2$) [32]. Then the desired phthalocyanine with unsaturated substituents (**7**) was obtained with moderate yield 37% by the condensation reaction of compound (**5**) and 4-(dimethylamino)cinnamaldehyde (**6**) (Fig. 1). Zn phthalocyanine with four quaternary ammonium groups (**8**) was obtained from the reaction of (**7**) with methyliodide in chloroform (Fig. 2). In the mass spectra of **3** the presence of the characteristic molecular ion peaks at $m/z = 265\ [M]^+$ confirmed the proposed structure.

Cyclotetramerization of the dinitril derivative (**3**) was confirmed by the disappearance of the sharp C≡N vibration at 2233 cm^{-1}. In the IR spectra of **4**, aromatic C–O–C peak was observed at 1248 cm^{-1} and characteristic substituted $-NO_2$ peaks were observed at about 1586 and 1392 cm^{-1}. In the mass spectra of **4** the presence of the characteristic molecular ion peaks at $m/z = 1127\ [M+H]^+$ confirmed the proposed structure. The $-NH_2$ group in **5** was observed at 3339 and 3423 as an intense doublet and observed at 1607.27 cm^{-1} as a strong peak.

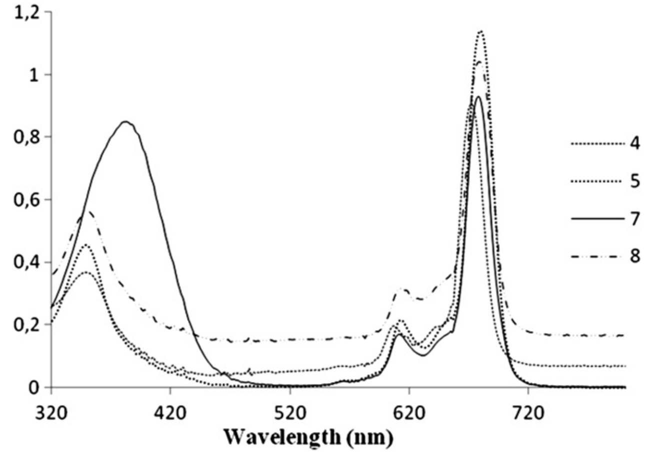

Fig. 3. UV–Vis spectra of phtalocyanines in a THF solution for **4**, **5**, **7**, **8**.

The IR spectrum of the **7** shows characteristic Schiff base stretching band 1599 cm^{-1}. These intense band are assigned to the –C=N stretching frequency of ligand and are characterized for the azomethine moiety of most Schiff base compounds. The absorption band of the C=O in the 4-(dimethyl amino)-cinnamaldehyde disappeared in the infrared spectrum of the 7, which indicates that the condensation has occurred.

In the mass spectrum of compounds **3**, **4**, **5** and **7** the presence of molecular ion peaks at $m/z = 265[M]^+$, 1127 $[M+H]^+$, 1006 $[M]^+$ and 1636 $[M+H]^+$ respectively, clearly indicates the formation of desired products. In the case of quaternized Pc, **8**, the highest values observed in the spectrum correspond to fragment ions 1603 $[M-(N+CH_3{+}3H^+)]$, 2045 $[(M+4I^-)-(CH_3+CH_3I)]$.

The UV–Vis spectra of **4**, **5**, **7** and **8** in THF showed characteristic absorptions between 679 and 607 nm in the Q-band region (Fig. 3). The Q band observed for the compounds was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands (B) in the UV region at 348–383 nm were observed due to the transitions from the deeper π levels to the LUMO [35,36]. Table 1 lists the absorption peaks of the two species from which is evident that the absorption band shifted to longer wavelength as a result of converted $-NO_2$ group into $-NH_2$ on phenoxy groups. Spectra of **5** and **7** in THF are very similar, with intense Q bands at 679 and 678 nm due to a single $\pi \rightarrow \pi^*$ transition with shoulders at 613 and 612 nm, respectively. However, the

Table 1
UV–Vis data for 4, 5, 7 and 8 in THF.

Compound	λ, nm (log ε, M^{-1} cm^{-1})		
4	672 (4.96)	607[a] (4.30)	348 (4.57)
5	679 (5.06)	613[a] (4.34)	349 (4.66)
7	678 (4.97)	612[a] (4.23)	383 (4.93)
8	679 (5.02)	613[a] (4.50)	349 (4.75)

[a] = Shoulder.

Table 2
Voltammetric data of the complexes.

Complex		Oxd.$_{(Subs.)}$[f]	Oxd.$_{(Pc2)}$	Oxd.$_{(Pc1)}$	Red.$_{(Pc1)}$	Red.$_{(Pcs2)}$	Red.$_{(subs)1}$[g]	Red.$_{(subs)2}$[h]	$\Delta E_{1/2}$[d]
4	$E_{1/2}$ vs. SCE[a]	–	0.83	0.65	−0.87	−1.54		−1.19	1.52
	ΔE_p (mV)[b]		80	70	62	80		120	
	I_{pa}/I_{pc}[c]		0.90	0.92	0.72	0.60		0.95	
5	$E_{1/2}$ vs. SCE[a]	0.72[e]		1.03[e]	−0.94	−1.40			–
	ΔE_p (mV) vs. SCE[b]	–		–	69	64			
	I_{pa}/I_{pc}[c]	–		–	0.89	0.85			
7	$E_{1/2}$ vs. SCE[a]		0.76[e]	0.51[e]	−0.91	−1.32[e]	−1.75		1.42
	ΔE_p (mV)[b]		–	–	60	–	100		
	I_{pa}/I_{pc}[c]		–	–		–	0.55		
8	$E_{1/2}$ vs. SCE[a]	0.18	0.76[e]	0.54	−0.98	−1.39	−1.89	−0.57	1.52
	ΔE_p (mV)[b]	346	–	200	70	80	170	347	
	I_{pa}/I_{pc}[c]	0.85	–	0.77	0.95	0.92	0.60	0.90	

[a] $E_{1/2}=(E_{pa}+E_{pc})/2$ at 0.100 V s^{-1}.
[b] $\Delta E_p = E_{pa} - E_{pc}$ at 0.100 V s^{-1}.
[c] I_{pa}/I_{pc} for reduction, I_{pc}/I_{pa} for oxidation processes at 0.100 V s^{-1} scan rate.
[d] $\Delta E_{1/2} = \Delta E_{1/2}$ (first oxidation) − $\Delta E_{1/2}$ (first reduction) = HOMO–LUMO gap for metallophthalocyanines having electro-inactive metal center.
[e] The process is irreversible, thus E_p values were given as $E_{1/2}$.
[f] Oxd.$_{(Subs.)}$ process is the oxidation of the amine groups of the complex **7** and iodide oxidation for the complex **8**.
[g] Red.$_{(subs)1}$ processes are the reduction of the cinnamaldehyde groups for the complexes **7** and **8**.
[h] Red.$_{(subs)2}$ processes are the reduction of the Nitro groups for the complex **4** and triiodide reduction for the complex **8**.

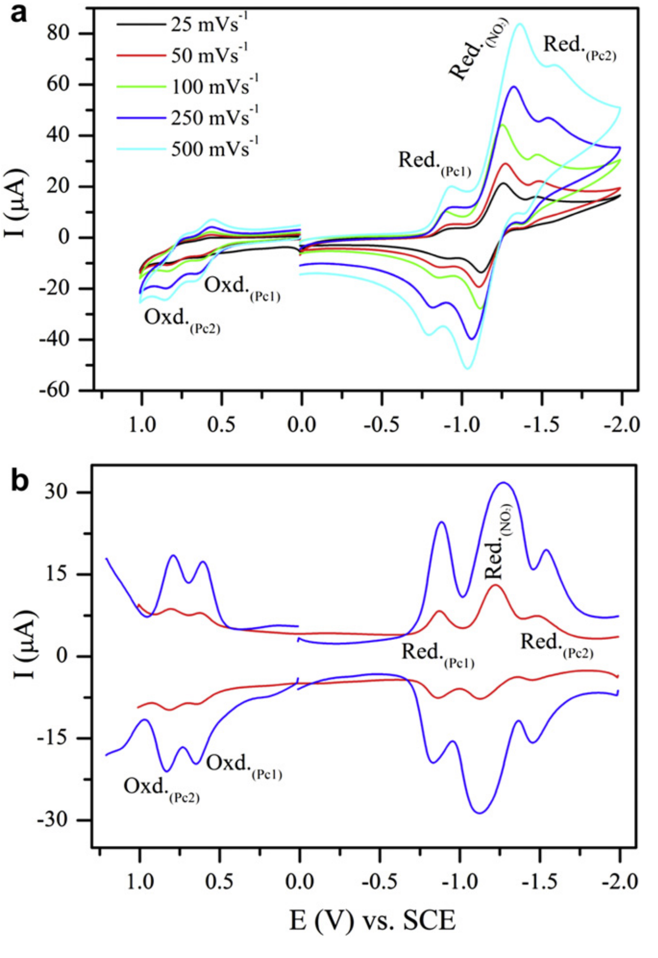

Fig. 4. a) CVs of **4** (5.0 10^{-4} moldm^{-3}) at various scan rates on a Pt working electrode in DMSO/TBAP. b) SWV of **4** recorded different concentrations (blue = 5.0 10^{-4} moldm^{-3}; red = 1.0 10^{-4} moldm^{-3}). SWV parameters:step size = 5 mV; pulse size = 100 mV; Frequency = 25 Hz.

soret (B) bands are observed at different wavelengths as 349 and 383 nm, respectively. The broad absorption in near UV region in the case of **7** is a clear indication of the alkenic substituents in addition to typical B band of Pc core. When the quaternazitaion of **7** was occurred, any difference was not observed in the Q-band region but the B band of compound **8** shifted to blue region at the spectrum.

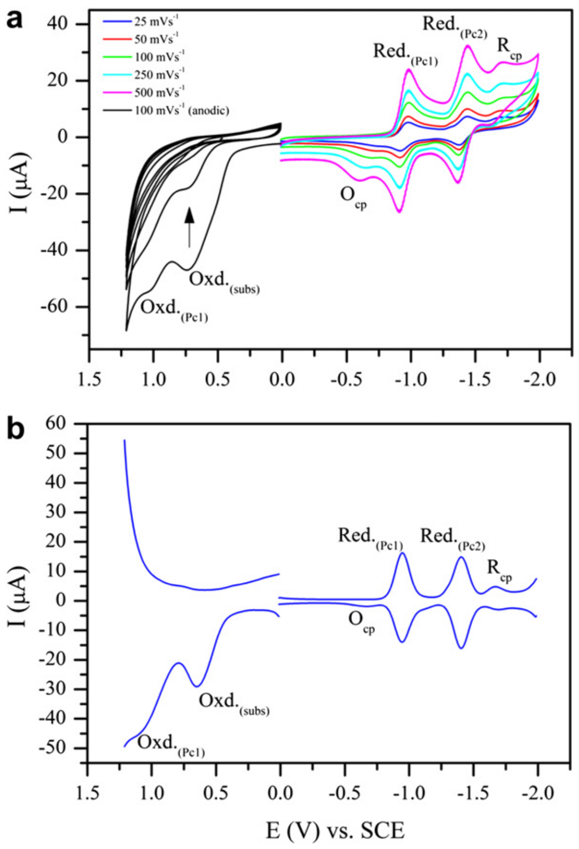

Fig. 5. a) CVs of **5** (5.0 10^{-4} moldm^{-3}) at various scan rates in cathodic side and repetitive CVs in the anodic side at 0.100 V s^{-1} scan rate on a Pt working electrode in DMSO/TBAP. b) SWV of **5**.

Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. A gradual increase in the solubility of **4**, **5**, **7** and **8** has been observed in paralled with the changes in substituents; while nitrophenoxy-substituted pc (**4**) was slightly soluble in DMSO, DMF and THF, aminophenoxy-substituted pc (**5**) showed slight solubility in chloroform in addition to above cited solvents. Addition of unsaturated substituents enabled compound (**7**) to be soluble in most organic solvents. Quaternized complex of zinc (**8**) was soluble in number of organic solvents (e.g. dichloromethane, chloroform, methanol, DMF, THF, DMSO, etc.) and also in water. The high number of polar and bulky trimethylammonium-benzenpropenyliminophenoxy substituents should be responsible for this interesting feature.

3.2. Electrochemical measurements

The phthalocyanine ring often can be reduced to the mono-, di-, tri-, and tetraanionic states or oxidized to the mono- and dicationic states. In addition, Pc's with redox-active metal ions or substituents typically show additional metal-based or substituent-based redox couples [37]. Thus in this study we perform electrochemical characterization of the sequentially synthesized ZnPc complexes bearing redox-active substituents, ZnPc bearing nitrophenoxy (**4**), aminophenoxy (**5**), [4-(dimethylamino)phenyl]prop-2-en-1-ylideneamino)phenoxy (**7**) and quaterner (**8**). CV responses of the complexes were used to support the proposed structures by comparing with each other and with the similar MPc in the literature. Table 2 lists the assignments of the redox couples and estimated electrochemical parameters including the half-wave peak potentials ($E_{1/2}$), ratio of anodic to cathodic peak currents ($I_{p,a}/I_{p,c}$), peak to peak potential separations (ΔE_p), and difference between the first oxidation and reduction processes ($\Delta E_{1/2}$).

Fig. 4 illustrates CVs and SWVs of **4** in DMSO/TBAP electrolyte on a Pt working electrode. Complex **4** exhibits two sequential reversible one-electron Pc ring reductions, $[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-}$ (Red.$_{(Pc1)}$ at $E_{1/2} = -0.87$ V) and $[Zn^{II}Pc^{-3}]^{-}/[Zn^{II}Pc^{-4}]^{2-}$ (Red.$_{(Pc2)}$ at $E_{1/2} = -1.54$ V), and two reversible one-electron ring oxidations, $[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-}]^{+}$ (Oxd.$_{(Pc1)}$ at $E_{1/2} = 0.65$ V) and $[Zn^{II}Pc^{-}]^{+}/[Zn^{II}Pc^{0}]^{2+}$ (Oxd.$_{(Pc2)}$ at $E_{1/2} = 0.83$ V) [38–40]. In addition to the ring-based reduction and oxidation processes, a one-electron reduction of the four nitrophenoxy groups of the substituent environment ($ZnPc\text{-}4[R{-}NO_2]/ZnPc\text{-}4[R{-}NO_2]^{*-}$ (Red.$_{(-NO2)}$ at $E_{1/2} = -1.27$ V)) is recorded between two ring reduction processes. It is well documented that nitrophenoxy groups give a 1-electron reduction processes at around −1.0 V vs. SCE in aprotic media depending on the substituents and electrolyte system [41–43]. Assignments of the redox processes were confirmed with in-situ spectroelectrochemical measurements.

Replacement of the nitrophenoxy groups of the substituents at the ZnPc (**4**) to aminophenoxy (complex **5**) also changes the electrochemical responses of the complex. Fig. 5 gives the CV and SWV response of the complex **4**. In cathodic scans, the complex **5** gives two common 1-electron reversible Pc ring-based reduction processes, Red.$_{(Pc1)}$ ($E_{1/2} = -0.94$ V) and Red.$_{(Pc2)}$ ($E_{1/2} = -1.40$ V). Moreover a cathodic irreversible wave at −1.70 V (R_{cp}) and an anodic wave at −0.64 V (O_{cp}) were observed, which may be due to the electron transfer process of the products of a chemical reaction succeeding the electron transfer processes. In the anodic scans,

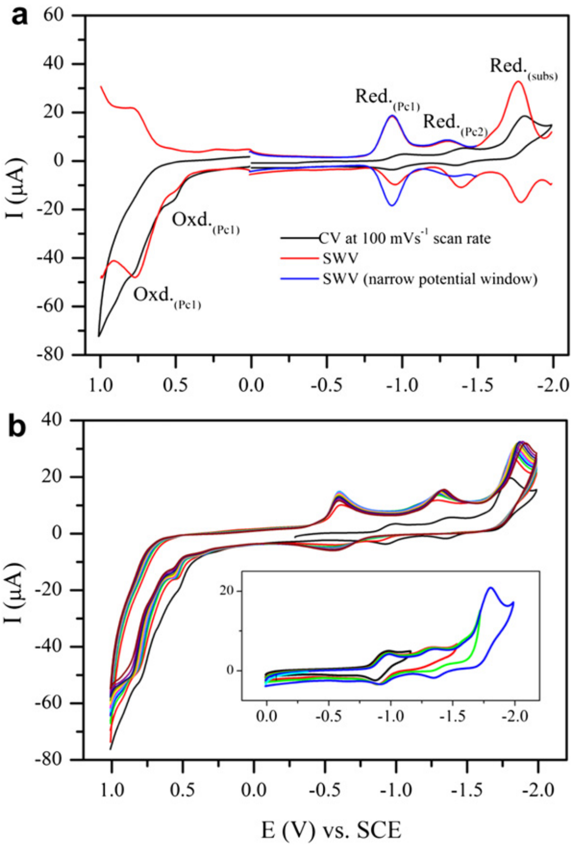

Fig. 6. (a) CVs and SWVs of **7** at 0.100 V s^{-1} scan rate on a Pt working electrode in DMSO/TBAP. (b) CVs recorded with repetitive cycles at 0.100 V s^{-1} scan rate on a Pt working electrode in DMSO/TBAP (inset: CVs recorded with different switching potentials at 0.100 V s^{-1} scan rate).

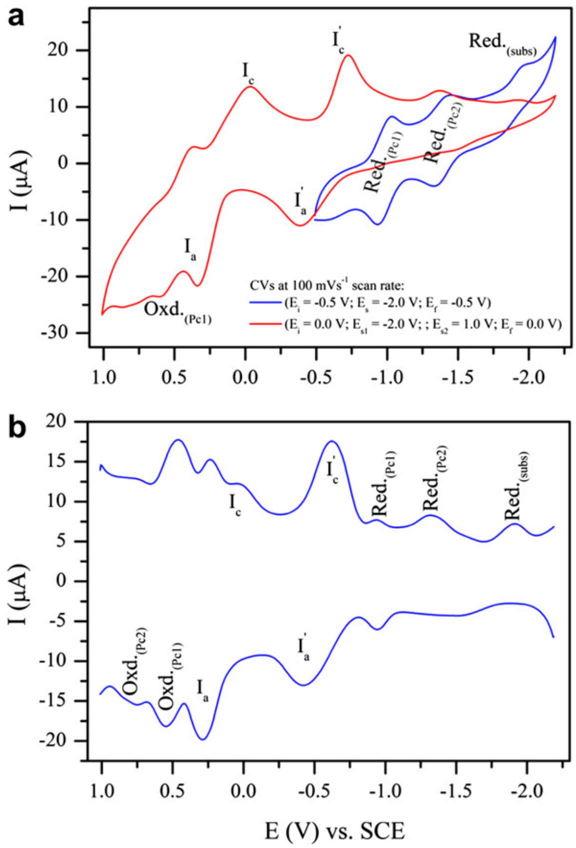

Fig. 7. a) CVs of **8** (5.0 10^{-4} moldm^{-3}) at 0.100 V s^{-1} scan rate on a Pt working electrode in DMSO/TBAP. b) SWV of **8**.

a steady CV response could not be recorded due to the formation of a nonconductive polymer on the working electrode due to the oxidation of the amine groups on the complex **5**. It is documented that amine substituents give oxidation process at around 1.0 V in aprotic media [43,44]. In the first CV cycle, the complex **5** illustrates a huge irreversible wave (Oxd.$_{(subs)}$ at 0.72 V) assigned to the reduction of amine groups and an irreversible Pc-based oxidation wave (Oxd.$_{(Pc1)}$) at 1.03 V. During the continuous cycles this waves get smaller and disappeared after fifth cycle. All waves at the cathodic side disappeared also when the potential is scanned toward the negative potentials after the anodic scans. These behaviors indicate the formation of a nonconductive layer on the electrode which prevents electron transfer reaction of the electrode. Differences between the electrochemical responses given in Figs. 4 and 5 easily characterize the changes of nitrophenoxy groups with aminophenoxy groups to synthesize the complex **5.** Disappearance of the nitro reduction couple also affects the reduction potential of the Pc ring. When nitrophenoxy groups on the complex **4** was changed to a more electron releasing amine groups (complex **5**), the first reduction couple of the complex **5** shift to positive potentials with respect to the complex **4**.

The complex **7** is the products of the reaction between the complex **5** and 4-(dimethylamino)cinnamaldehyde **6** (Fig. 1). Changing of the amino groups (complex **5**) with [4-(dimethylamino)phenyl]prop-2-en-1-ylideneamino (complex **7**) was also monitored electrochemically. Fig. 6 show the CV and SWV responses of the complex **7**. When we compared CV responses of the complex **7** with its starting complex **5**, it is shown that while amine oxidation process of the complex **5** at 0.70 V disappears, a new quasi-reversible 4-electron reduction couples (1-electron for each group) at −1.75 V is observed in addition to the common Pc-based electron transfer processes, reversible first reduction at −0.91 V (Red.$_{(Pc1)}$), irreversible second reduction at −1.32 V (Red.$_{(Pc2)}$), and irreversible oxidations at 0.51 (Oxd.$_{(Pc1)}$) and 0.76 V (Oxd.$_{(Pc2)}$). It is reported that cinnamaldehyde groups gives a 1-electron reduction process at more negative potentials depending on the substituents and the electrolyte systems [45–47]. Assignments of the redox processes were confirmed with in-situ spectroelectrochemical measurements given below. As shown in Fig. 6b, the complex **7** electropolymerizes on the working electrode during repetitive CV cycles. During continuous CV cycles, while Pc-based reduction couples (Red.$_{(Pc1)}$ and Red.$_{(Pc2)}$) disappears, two new couples are gradually enhanced at −0.60 and −1.30 V. Moreover Red.$_{(Subs)}$ couple shifts to negative potentials gradually during the repetitive cycles. At the same time the oxidation processes of the complex decrease in current intensity with shifting to the positive potentials. These electrochemical responses indicate formation of a conductive polymer on the working electrode. This polymerization process is not observed when only the cathodic potentials were scanned, which indicates that oxidation processes of the complex mimic the polymerization process. However without scanning the potential until the Red.$_{(sub)}$ process (−1.80 V), the peaks assigned to this assumed polymer does not increase in current intensity. Switching potential affects the reversibility of the redox processes as shown in Fig. 6b (inset). When the potential is switched just after Red.$_{(Pc1)}$ process (−1.15 V), this process

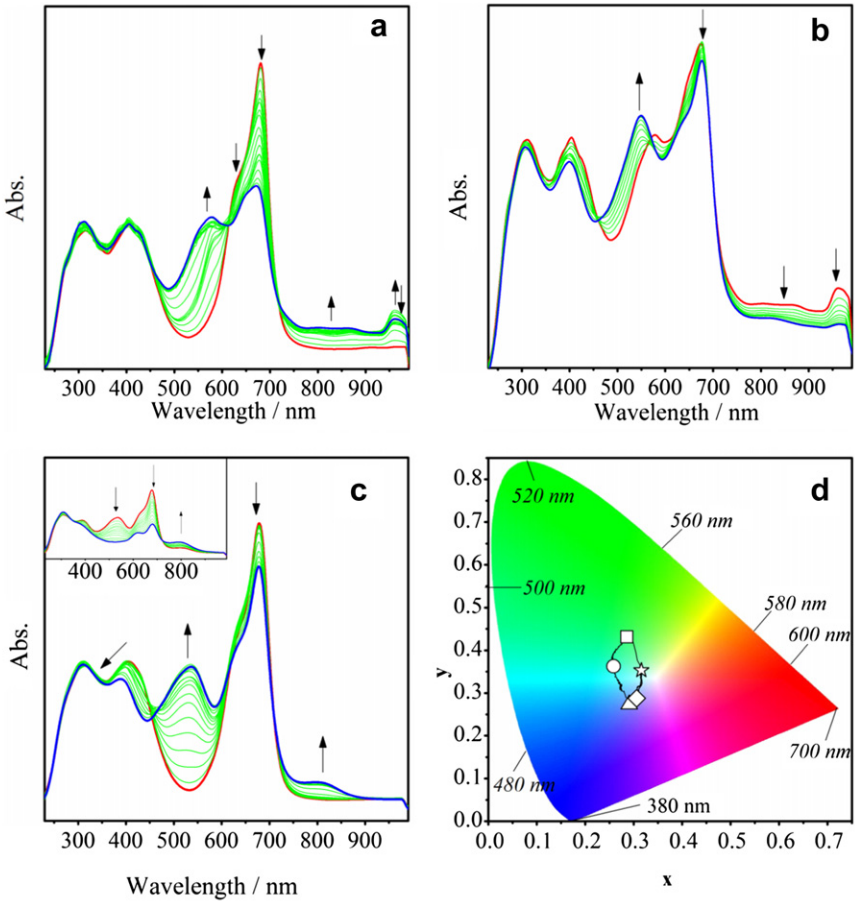

Fig. 8. *In-situ* UV–Vis spectral changes of **7**. a) $E_{app} = -1.10$ V b) $E_{app} = -1.40$ V c) $E_{app} = 0.75$ V (Inset: $E_{app} = 1.10$ V). d) Chromaticity diagram (each symbol represents the color of electro-generated species; □: $Zn^{II}Pc^{-2}$, ○: $Zn^{II}Pc^{-3}$, △: $Zn^{II}Pc^{-4}$, ☆: $Zn^{II}Pc^{-1}$, ◇: $Zn^{II}Pc^{-1}$.

is completely reversible. Reversibility of the first and second reduction processes gets worse when the switching potential shift to the negative potentials. SWVs recorded with different switching potentials also illustrate these effects clearly as shown in Fig. 6a. Basic effects of the replacements of the amino groups (complex **5**) with [4-(dimethylamino)phenyl]prop-2-en-1-ylideneamino (complex **7**) to the peak character of the Pc-based couples are; (*i*) disappearance of the amine oxidation process at 0.70 V, (*ii*) appearance of the [4-(dimethylamino)phenyl]prop-2-en-1-ylideneamino group reduction process at −1.75 V; (*iii*) shifting of the oxidation processes to negative side; (*iv*) second reduction process of the Pc ring reduction at −1.32 V (Red.$_{(Pc2)}$) gets irreversible; (*v*) The complex **7** electropolymerize on the working electrode during repetitive CV cycles.

Fig. 7 shows the CV response of the complex **8**. Quaternization of the complex **7** to form the complex **8** does not affect the electron transfer processes of the Pc-based and the cinnamaldehyde groups considerably. But presence of iodide ions in the complex confuses the CV and SWVs due to the electron transfer processes of the species I^-, I_2 and I_3^- which are present in equilibrium. It is well documented that iodide ions give two redox processes [48,49], which are easily monitored at 0.18 V (I_c/I_a) and −0.57 V (I'_c/I'_a). When the CV is recorded between −0.50 and −1.80V, The complex **8** gives three reversible reduction processes at −0.98 V (Red.$_{(Pc1)}$) and −1.39 V (Red.$_{(Pc2)}$) assigned to the Pc ring reductions and at −1.89 V (Red.$_{(subs)}$) assigned to the cinnamaldehyde groups. However when all available potential window of the electrolyte system is scanned, CV of the complex **8** completely changes due to the electron transfer reaction of the iodide species. Similar CV responses for the effects of iodide were recorded in our previous papers [50]. Addition of iodide ions enhances the peak currents of the relevant peaks, which supported our assignments. When compared with the complex **7**, the Pc ring-based redox processes of the complex **8** shift to negative potentials due to the quaternization process. Assignments of the redox processes were confirmed with in-situ spectroelectrochemical measurements given below.

3.3. Spectroelectrochemical studies

Spectroelectrochemical studies were employed to confirm the assignments in the CVs of the complexes. The complexes **4**, **5**, **7**, and **8** have all redox inactive metal centers. Therefore, in situ UV–vis spectral changes of them indicate the Pc ring-based and/or substituent-based redox characters. All complexes give very similar spectral changes due to the similarity of the redox processes. Fig. 8 shows the in situ UV–Vis spectral changes of **7** under the controlled potential application. During the potential application at −1.10 V, decreasing of the Q band at 680 nm without shift and observation of the new bands in the LMCT region at 578 and 960 nm are characteristics of the ring-based redox processes and assigned to $[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-1}$ (Fig. 8a) [37,51–53]. While the process gives clear isosbestic point at 720 nm in the spectra, isosbestic point at 613 nm tremble which indicate the formation more than one product during the process. Increasing of the band at 960 nm at the beginning of the process and decreasing at the end may also due to the chemical reaction. These products may be the product of

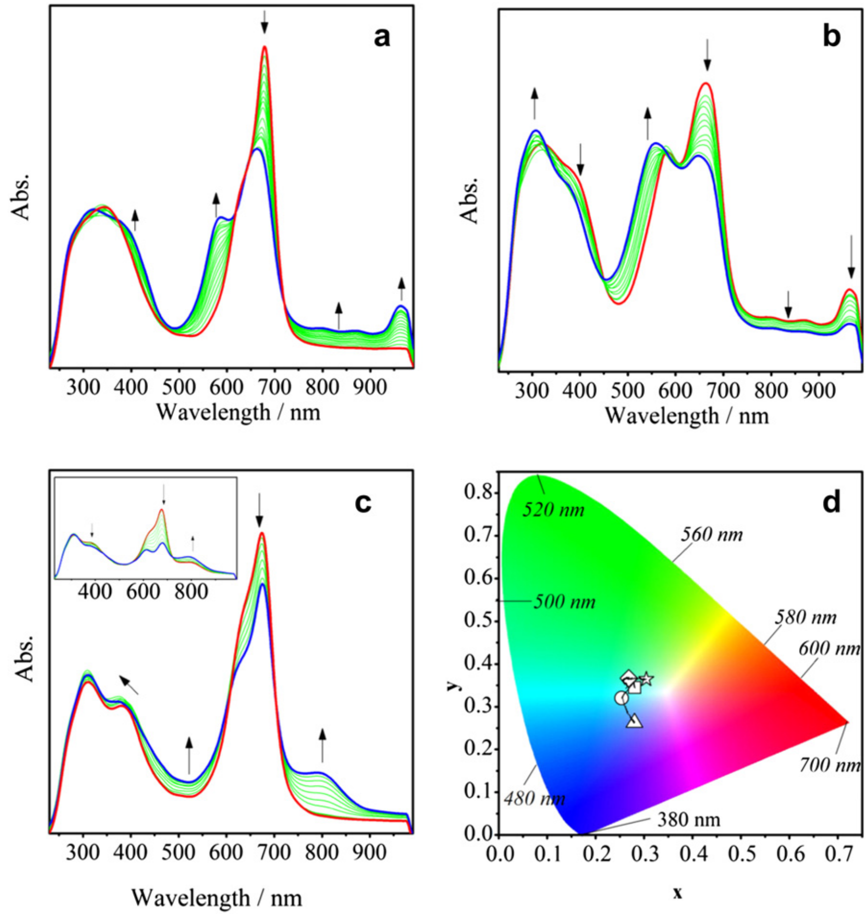

Fig. 9. *In-situ* UV–Vis spectral changes of **8**. a) $E_{app} = -1.10$ V b) $E_{app} = -1.40$ V c) $E_{app} = 0.75$ V (Inset: $E_{app} = 1.10$ V). d) Chromaticity diagram (each symbol represents the color of electro-generated species; □: $Zn^{II}Pc^{-2}$, ○: $Zn^{II}Pc^{-3}$, △: $Zn^{II}Pc^{-4}$, ☆: $Zn^{II}Pc^{-1}$, ◇: $Zn^{II}Pc^{-1}$.

a chemical reaction succeeding the electron transfer reaction in addition to the reduced species.

Then at the -1.40 V potential application, while the Q band at 680 nm, the band at 568 nm, the B band at 404 nm and the band at 960 nm decrease in intensity, a new band is recorded at 550 nm. These spectroscopic changes are easily assigned to the reduction of the monomeric species, $[\mathrm{Zn^{II}Pc^{-3}}]^{-1}$ to $[\mathrm{Zn^{II}Pc^{-4}}]^{-2}$ dianionic species (Fig. 8b) [37,51–54]. When -1.80 V was applied to the working electrode, any considerable spectral change was recorded, which indicate that the process at -1.75 V (V) is not a Pc-based process. Spectroscopic changes given in Fig. 8c are characteristics of the oxidation of $[\mathrm{Zn^{II}Pc^{-2}}]$ to monocationic $[\mathrm{Zn^{II}Pc^{-1}}]^{+1}$ and then to dicationic $[\mathrm{Zn^{II}Pc^{0}}]^{+2}$ species [37,51–54].

The color change of the solution of the complexes during the redox processes were recorded using in situ colorimetric measurements. Fig. 8d gives the chromaticity diagrams of the complex **7** recorded simultaneously during the spectroelectrochemical measurements. Without any potential application, the solution of **7** is green ($x = 0.286$ and $y = 0.431$). As the potential is stepped from 0 to -1.10 V color of neutral **7**, $[\mathrm{Zn^{II}Pc^{-2}}]$ start to changes and greenish blue color ($x = 0.258$ and $y = 0.362$) of monoanionic form of **7** was obtained at the end of the first reduction. Similarly color of the dianionic species was recorded as blue ($x = 0.291$ and $y = 0.274$). Monocationic species, $[\mathrm{Zn^{II}Pc^{-1}}]^{+1}$ has yellowish green color ($x = 0.316$ and $y = 0.353$) and dicationic species has light purple color ($x = 0.306$ and $y = 0.288$).

In situ UV–vis spectral changes of the complex **8** are approximately same with those of the complex 3. Fig. 9 shows the in situ UV–Vis spectral changes of **8** under the controlled potential application. There is no spectral change when the applied potential is between 0.0 and -0.70 V in the cathodic potentials and between 0.0V and 0.50 V in the anodic side, which indicates that the redox processes between $+0.50$ V and -0.70 V (I_c/I_a) and (I'_c/I'_a in Fig. 7)) are not a Pc-based processes. As shown in Fig. 9, the in situ UV–Vis spectral changes under applied potential at -1.10 (Fig. 9a), -1.50 (Fig. 9b), 0.70 (Fig. 9c) and 1.10 V (Fig. 9c inset) are same with the spectral changes of the complex **7**. According to the spectral changes given in Fig. 9, it is easy to assign the redox processes to the electron adding or removing to the Pc ring of the complex **8**. Redox states of the complex **8** have similar colors with those of the complex **7** as shown in the chromaticity diagrams of the complex **8** (Fig. 9d).

4. Conclusion

We have successfully synthesized and characterized a novel Zn phthalocyanine substituted with four dimethylaminocinnamaldiminophenyloxy substituents on peripheral positions and quaternization of its dimethylamino functionality produced cationic Zn phthalocyanine soluble in water and in polar solvents such as methanol, DMSO.

Voltammetric responses of the complexes reveal exchanges of the nitrophenoxy, aminophenoxy, [4-(dimethylamino)phenyl] prop-2-en-1-ylideneamino)phenoxy, and quaternization of the [4-(dimethylamino)phenyl]prop-2-en-1-ylideneamino)phenoxy groups during the synthesis sequences. Presense of electroactive nitro, amine and cinnamaldehyde groups extended the redox richness of the phthalocyanine ring which is one of the desired properties of the metallophthalocyanines in technological applications.

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References

[1] Grund A, Kaltbeitzel A, Mathy A, Schwarz R, Bubeck C, Vermehren P, et al. Resonant nonlinear optical-properties of spin-cast films of soluble oligomeric bridged (phthalocyaninato)ruthenium(II) complexes. Journal of Physical Chemistry 1992;96(18):7450–4.

[2] de la Torre G, Vaquez P, Agullo-Lopez F, Torres T. Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds. Chemical Reviews 2004;104(9):3723–50.

[3] Dini D, Hanack M. Phthalocyanines as materials for advanced technologies: some examples. Journal of Porphyrins and Phthalocyanines 2004;8(7): 915–33.

[4] Snow AW, Barger WR, Klusty M, Wohltjen H, Jarvis NL. Simultaneous electrical-conductivity and piezoelectric mass measurements on iodine-doped phthalocyanine Langmuir-blodgett films. Langmuir 1986;2(4):513–9.

[5] Clasens CG, Blau WJ, Cook M, Hanack M, Nolte RJM, Torres T, et al. Phthalocyanines and phthalocyanine analogues: the quest for applicable optical properties. Monatshefte für Chemie 2001;132(1):3–11.

[6] Guillaud JS, Simon J, Germain JP. Metallophthalocyanines – gas sensors, resistors and field effect transistors. Coordination Chemistry Reviews 1998;178:1433–84.

[7] Duro JA, de la Torre G, Barbera J, Serrano JL, Torres T. Synthesis and liquid–crystal behavior of metal-free and metal-containing phthalocyanines substituted with long-chain amide groups. Chemistry of Materials 1996;8 (5):1061–5.

[8] Clarkson GJ, McKeown NB, Treacher KE. Synthesis and characterization of some novel phthalocyanines containing both oligo(ethyleneoxy) and alkyl or alkoxy side-chains – novel unsymmetrical discotic mesogenes. Journal of the Chemical Society-Perkin Transactions 1 1995;14:1817–23.

[9] Hanabusa K, Shirai H. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 2. New York: VCH Publications; 1993.

[10] Jori G. Photosensitized processes in vivo: proposed phototherapeutic applications. Photochemistry and Photobiology 1990;52(2):439–43.

[11] Moan J. On the diffusion length of singlet oxygen in cells and tissues. Journal of Photochemistry and Photobiology B- Biology 1990;6(3):343–7.

[12] Cook MJ, Chambrier I, Cracknell SJ, Mayes DA, Russell DA. Octa-alkyl zinc phthalocyanines: potential photosensitizers for use in the photodynamic therapy of cancer. Photochemistry and Photobiology 1995;62:542–5.

[13] Ali H, van Lier JE. Metal complexes as photo- and radio sensitizers. Chemical Reviews 1999;99(9):2379–450.

[14] Henari F, Davey A, Blau W, Haisch P, Hanack M. The electronic and non-linear optical properties of oxo-titanium phthalocyanines. Journal of Porphyrins and Phthalocyanines 1999;3(5):331–8.

[15] Eberhardt W, Hanack M. Synthesis of hexadeca alkoxy-substituted nickel and iron phthalocyanines. Synthesis 1995;1:95–100.

[16] Koray AR, Ahsen V, Bekaroglu O. Preparation of a novel, soluble copper phthalocyanine with crown-ether moieties. Chemical Communications 1986;12: 932–3.

[17] Wei S, Huang D, Li L, Meng Q. Synthesis and properties of some novel soluble metallophthalocyanines containing the 3-trifluromethylphenyoxy moiety. Dyes and Pigments 2003;56(1):1–6.

[18] Kocak M, Cihan A, Okur AI, Bekaroglu O. Synthesis and characterization of novel phthalocyanines substituted with 4 tetraaza macrocycles. Chemical Communications 1991;8:577–8.

[19] Kocak M, Gurek A, Gul A, Bekaroglu O. Synthesis and characterization of phthalocyanines containing 4 14-membered tetraaza macrocycles. Chemische Berichte 1994;127(2):355–8.

[20] Bilgin A, Ertem B, Gok Y. Synthesis and characterization of new metal-free and metallophthalocyanines containing spherical or cylindrical macrotricyclic moieties. Polyhedron 2005;24(10):1117–24.

[21] Gursoy S, Cihan A, Kocak MB, Bekaroglu O. Synthesis of new metal-free and metal-containing phthalocyanines with tertiary or quaternary aminoethyl substituents. Monatshefte für Chemie 2001;132(7):813–9.

[22] Kocak M, Okur AI, Bekaroglu O. Novel 2-fold-macrocycle-substituted phthalocyanines. Journal of the Chemical Society-Dalton Transactions 1994;13: 2023.

[23] Kocak M, Cihan A, Okur AI, Gul A, Bekaroglu O. Novel crown ether-substituted phthalocyanines. Dyes and Pigments 2000;45(1):9–14.

[24] Yenilmez HY, Ozcesmeci I, Okur AI, Gul A. Synthesis and characterization of metal-free and metallo phthalocyanines with four pendant naphthoxy-substituents. Polyhedron 2004;23(5):787–91.

[25] Hamuryudan E. Synthesis and solution properties of phthalocyanines substituted with four crown ethers. Dyes and Pigments 2006;68(2–3):151–7.

[26] Dincer HA, Gul A, Kocak MB. A novel route to 4-chloro-5-alkyl-phthalonitrile and phthalocyanines derived from it. Journal of Porphyrins and Phthalocyanines 2004;8(10):1204–8.

[27] Weber JH, Busch DH. Complexes derived from strong field ligands. Inorganic Chemistry 1965;4:469–71.

[28] Kobayashi N, Shirai H, Hojo N. Iron(III) phthalocyanines - oxidation and spin states of iron in iron phthalocyanines with carboxyl groups. Journal of the Chemical Society-Dalton Transactions 1984;10:2107–10.

[29] Derkacheva VM, Bundina NI, Mekhryakova NG, Gulina TY, Kaliya OL, Lukyanets EA. A new method for the preparation of iron phthalocyanines. Zhurnal Neorganicheskoi Khimii 1981;26(6):1687.

[30] Young JG, Onyebuagu W. Synthesis and characterization of di-disubstituted phthalocyanines. Journal of Organic Chemistry 1990;55(7):2155–9.

[31] Shankar R, Sharma P, Cabrera A, Espinosa G, Rosas N. Synthesis and crystal structures of some aryloxy-substituted phthalonitriles. Indian Journal of Chemistry Section B- Organic Chemistry Including Medicanal Chemistry 1996;35B(9):894–9.

[32] Wohrle D, Krawczyk G, Paliuras M. Polymeric bound porphyrins and their precursors.6. Syntheses of water-soluble, negatively or uncharged polymers with covalently bound moieties of porphyrin derivatives. Macromolecular Chemistry and Physics 1988;189(5):1001–11.

[33] Snow AW, Griffith JR, Marullo NP. Syntheses and characterization of heteroatom-bridged metal-free phthalocyanine network polymers and model compounds. Macromolecules 1984;17(8):1614–24.

[34] Wohrle D, Eskes M, Shigehara K, Yamada A. A simple synthesis of 4,5-disubstituted 1,2-dicyanobenzenes and 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines. Synthesis 1993;2:194–6.

[35] Ahsen V, Yilmazer E, Ertas M, Bekaroglu Ö. Synthesis and characterization of metal-free and metal derivatives of a novel soluble crown-ether-containing phthalocyanine. Journal of the Chemical Society-Dalton Transactions 1988;2:401–6.

[36] Özçeşmeci İ, Güney O, Okur Aİ, Gül A. New phthalocyanines containing bulky electron rich substituents. Journal of Porphyrins and Phthalocyanines 2009;13:753–9.

[37] Lever ABP, Milaeva ER, Speier G. Phthalocyanines: properties and applications. In: Leznoff CC, Lever ABP, editors. The redox chemistry of metallophthalocyanines in solution, vol. 3. New York: VCH; 1993.

[38] Arslan S, Yilmaz I. Synthesis, electrochemistry, and in situ spectroelectrochemistry of a new water-soluble zinc phthalocyanine substituted with naphthoxy-4-sulfonic acid sodium salt. Transition Metal Chemistry 2007;32(3):292–8.

[39] Kobayashi N, Ashida T, Osa T. Synthesis, spectroscopy, electrochemistry, and spectroelectrochemistry of a zinc phthalocyanine with D(2h) symmetry. Chemistry Letters 1992;10:2031–4.

[40] Acar I, Bıyıklıoğlu Z, Koca A, Kantekin H. 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. Polyhedron 2010;29:1475–84.

[41] Rodrigues C, Batista AA, Aucelio RQ, Teixeira LR, Visentin LD, Beraldo H. Spectral and electrochemical studies of ruthenium(II) complexes with N4-methyl-4-nitrobenzaldehyde and N4-methyl-4-nitrobenzophenone thiosemicarbazone: potential anti-trypanosomal agents. Polyhedron 2008;27:3061–6.

[42] Pospisil L, Hromadova M, Sokolova R, Bulickova J, Fanelli N. Cationic catalysis and hidden negative differential resistance in reduction of radical anion of nitrobenzene. Electrochimica Acta 2008;53:4852–8.

[43] Carlier R, Raoult E, Tallec A, Andre V, Gauduchon P, Lancelot JC. Electrochemical behavior of mutagenic nitro and amino derivatives of carbazole. Electroanalysis 1997;9(1):79–84.

[44] Kandaz M, Michel SLJ, Hoffman BM. Functional solitare- and trans-hybrids, the synthesis, characterization, electrochemistry and reactivity of porphyrazine/phthalocyanine hybrids bearing nitro and amino functionality. Journal of Porphyrins and Phthalocyanines 2003;7(9-10):700–12.

[45] Gruber J, Camilo FF. Synthesis of novel diaryloxocyclopentanethiocarboxylates by electrochemical reduction of cinnamic acid thioesters. Journal of the Chemical Society-Perkin Transactions 1 1999;2:127–9.

[46] Matesanz AI, Mosa J, Garcia I, Pastor C, Souza P. Synthesis, characterization, crystal structure and electrochemistry of a novel palladium(II) binuclear complex containing 1,2,4-triazole bis(4-phenylthiosemicarbazone) bridges. Inorganic Chemistry Communications 2004;7(6):756–9.

[47] Arquero A, Mendiola MA, Souza P, Sevilla MT. Synthesis, spectral and electrochemical properties of divalent metal complexes containing thiohydrazone and thiosemicarbazone ligands. Polyhedron 1996;15(10):1657–65.

[48] Yaraliyev YA. Oxidation of iodide ions by means of cyclic voltammetry. Electrochimica Acta 1984;29(9):1213–4.

[49] Lopez B, Iwasita T, Giordano MC. Electrochemical behavior of iodide-iodine and bromide-bromine redox systems in nitromethane solutions. Journal of Electroanalytical Chemistry 1973;47(3):469–78.

[50] Dinçer HA, Koca A, Gul A, Kocak MB. Novel phthalocyanines bearing both quaternizable and bulky substituents. Dyes and Pigments 2008;76(3):825–31.

[51] Obirai J, Nyokong T. Synthesis, spectral and electrochemical characterization of mercaptopyrimidine-substituted cobalt, manganese and Zn(II) phthalocyanine complexes. Electrochimica Acta 2005;50:3296–304.

[52] Koca A, Özkaya AR, Selcukoglu M, Hamuryudan E. Electrochemical and spectroelectrochemical characterization of the phthalocyanines with pentafluorobenzyloxy substituents. Electrochimica Acta 2007;52(7):2683–90.

[53] Koca A, Bayar S, Dinçer HA, Gonca E. Voltammetric, in-situ spectroelectrochemical and in-situ electrocolorimetric characterization of phthalocyanines. Electrochimica Acta 2009;54(10):2684–92.

[54] Simicglavaski B, Zecevic S, Yeager E. Spectroelectrochemical in situ studies of phthalocyanines. Journal of the Electrochemical Society 1987;134(3):C130.