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Synthesis and electrochemical properties of a series of novel tetra(4-benzoyl)phenoxyphthalocyanine derivatives

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A novel phthalocyanine, 2,9(10),16(17),23(24)-tetra(4-benzoyl)phenoxyphthalocyanine, and its complexes with Zn(II), Cu(II), Co(II), and Ni(II) have been synthesized and characterized by a combination of elemental analysis, IR, ¹H NMR, UV–vis spectroscopy and mass spectrometry. All of the materials are very soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, *N*,*N*-dimethylformamide and dimethyl sulfoxide. The Q band wavelengths of the complexes decrease in the order: Zn > Cu > Ni > Co. Redox processes were observed at –1.06, –0.74, 0.51 and 0.98 V for the free phthalocyanine, at –0.72 and 1.04 V for the Co(II) complex, at –1.24, –0.77, –0.24, 0.61 and 0.91 V for the Cu(II) complex, and at –0.74 and 1.20 V for the Ni(II) complex. The cyclic voltammograms of the phthalocyanine ring of the four species are similar, with reduction and oxidation couples each involving a one-electron transfer process.

synthesis, electrochemical, (4-benzoyl)phenoxy, phthalocyanine

1 Introduction

Phthalocyanines have a number of applications, such as in chemical sensors, liquid crystals, organic semiconductors, non-linear optical materials, photodynamic therapy, and photovoltaic devices [1–6], due to their good stability, ar-chitectural flexibility, diverse coordination properties and useful spectroscopic characteristics [1, 7]. However, their poor solubility in common organic solvents limits their applications. Introducing bulky substituents or long chain groups, such as alkyl or alkoxy groups, on the periphery of the phthalocyanine framework can enhance their solubility [8]. The introduction of sulfonyl [9], carboxyl [10], pyridine or amino groups [11] gives water-soluble phthalocyanines. Generally, tetrasubstituted phthalocyanines are more soluble than symmetrically octasubstituted ones due to the formation of four positional isomers in the case of the tetrasu-

bstituted analogues [12].

The molecular architecture of a phthalocyanine also plays a significant role in its binding to metal ions. The point of attachment of the substituents to the ring and their relative orientation in space should influence the ease of metal chelation because of the differences in intersubstituent distances [13]. Also, peripheral substitution can be used to change the aggregation behavior. A number of studies of the preparation and properties of phthalocyanine aggregates have been carried out [14, 15]. Aromatic systems with strong electron-donor and -acceptor substituent groups often exhibit solvent-dependent emission properties due to internal charge-transfer processes in the excited state [16]. Phthalocyanines can exhibit electron donating properties and their covalent linking with suitable electron acceptors may offer some interesting possibilities for electronic interaction and modification.

The electrochemical properties of phthalocyanines are very useful in applications as these macrocycles are known to have remarkable properties [1]. In particular, metal-

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lophthalocyanine complexes containing large conjugated substituents often show complicated electrochemistry involving the central metal, the phthalocyanine ring, and the substituents, and hence elucidation of the electrochemical behavior of the large conjugated substituents is of interest [17]. In this regard, the external connection of benzene rings and the presence of electron-withdrawing groups in the periphery should enhance the performance and function of a phthalocyanine, in addition to giving better solubility. Thus, in this work we report the synthesis, characterization, and structural investigation of a metal-free phthalocyanine (H₂Pc) tetrasubstituted at the peripheral positions with (4-benzoyl)phenoxy groups, and its complexes with different metal ions. The nature of the UV-vis spectra and electrochemical properties of the materials are discussed in detail. The materials reported are: 2,9(10),16(17),23(24)tetra(4-benzoyl)phenoxyphthalocyanine (**3a** H_2Pc), 2,9(10), 16(17),23(24)-tetra(4-benzoyl)phenoxyphthalocyanine zinc (II) (**3b** ZnPc), 2,9(10),16(17),23(24)-tetra(4-benzoyl)phenoxyphthalocyanine copper(II) (3c CuPc), 2,9(10),16(17), 23(24)-tetra(4-benzoyl)phenoxyphthalocyanine cobalt(II) (3d CoPc), and 2,9(10),16(17),23(24)-tetra(4-benzoyl) phenoxyphthalocyanine nickel(II) (3e NiPc).

2 Experimental

2.1 Materials and apparatus

All reagents and solvents were commercially available and

used without further purification (unless otherwise stated). All reactions were carried out under a nitrogen atmosphere. IR spectra were recorded on a Magna 560 FT-IR spectrophotometer using KBr pellets. Electronic absorption spectra were recorded on a Cary 500 UV-vis-NIR spectrophotometer. ¹H NMR spectra were recorded on a Varian XL-500 NMR spectrometer in DMSO- d_6 . Mass spectra (MS) were recorded on a MALDI-TOF mass spectrometer. Cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments were performed on a CHI 1120 A electrochemical analysis tester.

2.2 Synthesis of compound 2

(4-Benzoyl)phenoxyphthalonitrile (2) was prepared according to the method of Leznoff [18–20] (Scheme 1). 4-Nitrophthalonitrile (1) (10 mmol, 1.73 g) was dissolved in 60 mL of dimethyl sulfoxide (DMSO) under a N₂ atmosphere and then 4-hydroxybenzophenone (10 mmol, 1.98 g) was added to the solution. After stirring for 15 min, finely ground anhydrous LiOH (25 mmol, 0.60 g) was added portionwise over 2 h with efficient stirring. The reaction mixture was stirred at room temperature for 3 days. Then the solution was poured into 300 mL of NaCl solution (10%), and stirring continued for another 1 h at room temperature. The resulting precipitate was collected by filtration and washed with water, dried and finally recrystallized from ethanol to give a pure white solid powder (2.69 g). The compound was soluble in DMSO, *N,N*-dimethylformamide



Scheme 1 Synthesis of the tetrasubstituted phthalocyanine derivatives.

(DMF), chloroform (CHCl₃), dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), and acetone. Yield: 83.02%. IR [(KBr) v_{max} (cm⁻¹)]: 3098, 3041 (Ar–H), 2229 (C≡N), 1646 (C=O), 1588 (Ar–H), 1482 (Ar–H), 1249 (C–O–C). ¹H NMR (500 MHz, DMSO- d_6) δ (ppm): 8.19–8.17 (d, H, Ar–H), 7.99–7.98 (d, H, Ar–H), 7.87–7.85 (d, 2H, Ar–H), 7.78–7.77 (d, 2H, Ar–H), 7.72–7.69 (t, H, Ar–H), 7.61–7.59 (d, 2H, Ar–H), 7.57 (s, H, Ar–H), 7.33–7.35 (d, 2H, Ar–H).

2.3 Synthesis of compound 3a

A mixture of compound 2 (5 mmol, 1.62 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.40 mmol, 0.70 mL) in 15 mL of dry 1-pentanol was stirred under reflux for 8 h in N₂. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol: H_2O (5:1) and the solid filtered and washed with H_2O . The dark green precipitate was collected, and evaporated under reduced pressure. The resulting dark green product was washed with hot EtOH and dried in vacuum. The compound was soluble in DMSO, DMF, CHCl₃, and THF, slightly soluble in acetone, and insoluble in EtOH, MeOH, and H₂O. Yield: 0.91 g (56%). IR [(KBr) v_{max} (cm⁻¹)]: 3430 (N-H) 3056 (Ar-H), 1656 (C=O), 1594 (Ar-H), 1231(C–O–C). ¹H NMR (500 MHz, DMSO- d_6) δ (ppm): 7.94-7.80 (m, 18H, Ar-H), 7.59-7.56 (m, 18H, Ar-H), 7.54-7.45 (m, 14H, Ar-H, N-H). MS (MALDI-TOF) (THF), m/z: 1298.2 [M+H].

2.4 Synthesis of metal complexes 3b–3e

A mixture of compound 2 (5 mmol, 1.62 g), Zn(CH₃COO)₂·2H₂O (1.25 mmol, 0.275 g) and DBU (0.4 mmol, 0.7 mL) in 15 mL of dry 1-pentanol was stirred under reflux for 8 h in N₂. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol:H₂O (5:1) and the resulting solid was filtered and washed with H₂O to remove unreacted Zn(CH₃COO)₂·2H₂O. The dark green precipitate was collected, and evaporated under vacuum. The resulting dark green product was washed with hot EtOH and dried in vacuum. The compound was soluble in DMSO, DMF, CHCl₃, and THF, slightly soluble in acetone, and insoluble in EtOH, MeOH, and H₂O. Yield: 1.29 g (76%). IR [(KBr) v_{max} (cm⁻¹)]: 3056 (Ar–H), 1653 (C=O), 1594 (Ar-H), 1234 (C-O-C). UV-vis λ_{max} (nm) (log ε) in DMF: 678 (0.98), 609 (0.18), 356 (0.36).¹H NMR (500 MHz, DMSO-*d*₆) δ(ppm): 8.01–7.66 (m, 20H, Ar–H), 7.59–7.56 (m, 16H, Ar-H), 7.54–7.45 (m, 12H, Ar-H). MS (MALDI-TOF) (DMF), *m/z*: 1360.7 [M+H].

Complexes **3c**–**3e** were prepared following the same procedure with CuCl₂·2H₂O, CoCl₂·6H₂O, and NiCl₂·6H₂O precursors, respectively. Complex **3c**: Yield: 1.10 g (65%). IR [(KBr) $v_{\text{max}}/\text{cm}^{-1}$]: 3063 (Ar–H), 1695 (C=O), 1597 (Ar–H), 1235(C–O–C). UV-vis λ_{max} (nm) (log ε) in DMF:

672 (0.13), 607 (0.04), 329 (0.09). MS (MALDI-TOF) (THF), *m/z*: 1359.8 [M+H]. Complex **3d**: Yield: 1.03 g (61%). IR [(KBr) v_{max} (cm⁻¹)]: 3056 (Ar–H), 1655 (C=O), 1593 (Ar–H), 1235 (C–O–C). UV-vis λ_{max} (nm) (log ε) in DMF: 664 (2.16), 602 (0.64), 330 (1.90). ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm): 8.33–7.93 (m, 20H, Ar–H), 7.60–7.47 (m, 16H, Ar–H), 7.30–7.22 (m, 12H, Ar–H). MS (MALDI-TOF) (THF), *m/z*: 1355.1 [M+H]. Complex **3e**: Yield: 1.02 g (60%). IR [(KBr) v_{max} (cm⁻¹)]: 3057 (Ar–H), 1656 (C=O), 1593 (Ar–H), 1237 (C–O–C). UV-vis λ_{max} (nm) (log ε) in DMF: 671 (0.29), 612 (0.20), 333 (0.22). ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm): 7.93–7.80 (m, 20H, Ar–H), 7.60–7.50 (m, 16H, Ar–H), 7.29–7.20 (m, 12H, Ar–H). MS (MALDI-TOF) (THF), *m/z*: 1354.0 [M+H].

3 Results and discussion

3.1 Synthesis and characterization

Compound 2 was prepared via a base-catalyzed (LiOH) nucleophilic aromatic displacement reaction of 1 with 4-hydroxybenzophenone. Compounds 3a, 3b, 3c, 3d and 3e were then prepared by the template reaction of compound 2 with DBU in the presence of the appropriate metal salt precursor (Scheme 1). Relatively good yields (56%-76%) were obtained after purification by recrystallization. Compounds 3a-3e were peripherally (β) substituted and soluble in solvents such as CH₂Cl₂, CHCl₃, toluene, THF, DMSO and DMF.

Compounds 3a-3e were characterized by IR, UV-vis, and ¹H NMR spectroscopy, MS and elemental analysis. The data confirmed the purity of the materials. In the IR spectra, the disappearance of bands due to $-NO_2$ and -OH groups, along with the appearance of the sharp C–O–C, C≡N, C=O vibration absorption peaks at 1249, 2229, and 1646 cm⁻¹ respectively, confirmed the formation of 2. The typical absorption peaks of N-H (3430 cm⁻¹) were observed for **3a** but were absent in the spectra of the metal complexes 3b-3e. The ¹H NMR spectra of the materials showed peaks between 8.33 and 7.20 ppm arising from substituent and ring protons. Although the presence of isomers, as well as Pc aggregation at the concentrations used for the NMR measurements, leads to broadening of the aromatic signals, the observed spectra of all the materials were relatively well-resolved [1, 21]. MS also confirmed the formation of the desired products.

The addition of the aza-linkages and peripheral fused benzene rings to form MPc breaks the accidental degeneracy of the HOMO level in the unsubstituted phthalocyanine so that the $1a_{1u}$ and $1a_{2u}$ orbitals become widely separated, resulting in the observation of a Q band near 670 nm and a B band set near 300 nm [22, 23]. After dissolution in DMF, the well defined Q band maxima observed at 696 nm (**3a**), 678 nm (**3b**), 672 nm (**3c**), 664 nm (**3d**) and 671 nm (**3e**), shown in Figure 1, are typical of monomeric phthalocyanines [24]. The B bands of **3a–3e** are observed at 329, 366, 328, 330 and 333 nm, respectively. The Q and B bands both arise from $\pi \rightarrow \pi^*$ transitions and can be explained in terms of a linear combination of transitions from a_{1u} (Q) and a_{2u} / b_{2u} (B) HOMO orbitals to the doubly degenerate e_g (LUMO) orbitals. The slight broadening of the Q bands for **3a–3e** may be attributed to steric effects of the substituents at the peripheral positions, which result in a slight deviation of the Pc skeleton from planarity [24, 25]. Similar behavior can be found for solutions of 3a–3e in CHCl₃ and THF.

In DMF solution, all the compounds have a weak absorption peak around 610 nm in the vicinity of the Q-band (Figure 2) and the same result also can be observed in other solvents. We assign this band to the absorption of the dimer of Pc, as the absorption peak almost disappeared when the concentration was reduced. This is consistent with previous reports [26, 27].

As shown in Figure 3, the Q-band for **3a** (around 680 nm) is split into two peaks. However, MPc derivatives **3b-3e** show only a single band due to the $\pi \rightarrow \pi^*$ transition of the-



Figure 1 UV-vis spectra of 3a-3e in DMF.



Figure 2 UV-vis spectra of 3b in DMF at different concentrations.

se completely conjugated 18 π electron systems [8] in this region, since they have only twofold symmetry rather than the fourfold symmetry of 3a [28, 29]. Compared with 3a, **3b–3e** exhibit a slightly blue-shifted absorption. The Q band wavelengths of 3b-3e decrease in the order: Zn > Cu > Ni >Co, in accordance with previous reports [30]. Coordination of metallic cations with the four nitrogen atoms of the inner ring, results in a decrease in the charge density of the inner ring. This affects the electron density of the whole Pc ring, leading to an increase in the LUMO energy level of the MPc. Therefore, the absorption wavelength is blue-shifted. Metal ions with different numbers of d-electrons have different effects on the Pc conjugated ring, thus affecting the electronic transition behavior of Pc compounds. The maximum absorption wavelength moves to longer wavelength as the number of d-electrons in the metal ions increases.

3.2 Cyclic and square wave voltammetry

The CV and SWV **3a**, **3c**, **3d** and **3e** were performed in freshly distilled DMF containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte, with a bare glassy carbon electrode as the working electrode, in conjunction with a platinum foil counter electrode and Ag/AgCl reference electrode at a scan rate of 100 mVs⁻¹. The half-wave potential values ($E_{1/2}$), anodic to cathodic peak separation (ΔE_p) and peak current ratios (I_{pc}/I_{pa}) are summarized in Table 1. Figure 4 shows both the CV and SWV of **3a**, **3c**, **3d** and **3e**.

Figure 4 shows the CV and SWV traces of 3a, 3c, 3d and **3e**. Within the -1.6 to +1.5 V potential window, **3a** exhibits two irreversible one-electron oxidation steps, a quasi-reversible one-electron reduction step and an irreversible reduction process at 0.98, 0.51 -0.75 and -1.06 V, respectively (versus Ag/AgCl at a 100 mV s⁻¹ scan rate). The first reduction couple (at -0.75 V) displayed a pair of quasireversible redox peaks with an anodic to cathodic peak separation (ΔE_p) of 113 mV at 100 mV s⁻¹ (the ΔE_p value for the ferrocene standard was 85 mV) [17]. The second reduction couple monitored by CV at -1.06 V was clearly observed during the SWV measurements. Irreversible peaks (the first and second oxidation processes) at 0.51 and 0.98 V were observed in the positive potential scan respectively. These results are essentially in agreement with the literature [31–33]. These redox couples are attributed to the Pc ring. The electrochemical reaction mechanism can be represented as follows:

$$\begin{bmatrix} H_2 Pc(0) \end{bmatrix}^{2^+} \bigoplus_{0.98V}^{e^-} \begin{bmatrix} H_2 Pc(-1) \end{bmatrix}^+ \bigoplus_{0.51V}^{e^-} \begin{bmatrix} H_2 Pc(-2) \end{bmatrix}$$
$$\bigoplus_{-0.74V}^{e^-} \begin{bmatrix} H_2 Pc(-3) \end{bmatrix}^- \bigoplus_{-1.06V}^{e^-} \begin{bmatrix} H_2 Pc(-4) \end{bmatrix}^{2^-}$$

The redox properties of metallophthalocyanines have been studied by many authors [17, 34–36]. All of them



Figure 3 UV-vis spectra of 3a-3e in DMF, CHCl₃ and THF. (a) 3a; (b) 3b; (c) 3c; (d) 3d; (e) 3e.

agree that the reduction and oxidation of MPc are due to the interaction between the phthalocyanine ring and the central metal. According to these studies, the first oxidation and first reduction processes occur on the metal center in metal-lophthalocyanines for Mn, Fe and Co derivatives in polar solvents such as DMF. For Ni, Cu and Zn metallophthalocyanine ring [37, 38]. Thus, redox couples of CuPc (**3c**) should be attributed to the Pc ring. Interestingly, the CV of **3c** dis-

played a reduction peak (at -0.74 V) on sweeping to negative potential with two anodic peaks (AP₁ and AP₂) on the reverse scan. Ozkaya *et al.* [33] reported the same phenomenon. They proposed that the reduction of CuPc by controlled-potential electrolysis at -0.74 V involves a twoelectron redox process. However, the appearance of two reoxidation peaks on the reverse sweep suggests that reduction of CuPc probably occurs in two successive one-electron steps. According to this interpretation, the electrochemical



Figure 4 CV (bottom) and SWV (top) of 3a, 3c, 3d and 3e in DMF containing 0.1 M TBABF₄. Scan rate 0.1 Vs⁻¹. (a) 3a; (b) 3c; (c) 3d; (d) 3e.

Table 1 Voltammetric data for the materials and relevant materials from the literature

	Oxidation 2			Oxidation 1			Reduction 1			Reduction 2			Reduction 3	Def
	$E_{1/2}(V)^{a}$) $\Delta E_{\rm p}({\rm V})^{\rm b}$	$I_{\rm pc}/I_{\rm pa}{}^{\rm c)}$	$E_{1/2}(V)^{a)}$	$\Delta E_{\rm p}({\rm V})^{\rm b}$	$I_{\rm pc}/I_{\rm pa}^{\rm c}$	$E_{1/2}(V)^{a}$	$\Delta E_{\rm p}({\rm V})^{\rm b}$	$I_{\rm pc}/I_{\rm pa}^{\rm c)}$	$E_{1/2}(V)^{a)}$	$\Delta E_{\rm p}({\rm V})^{\rm b)}$	$I_{\rm pc}/I_{\rm pa}{}^{\rm c)}$	$E_{1/2}(V)^{a)} \Delta E_p(V)^{b)}$	$I_{\rm pc}/I_{\rm pa}^{\rm c)}$ KeI.
3a	0.979	0.246		0.505	0.098		-0.738	0.113	0.66	-1.060				Tw
3c				0.919	0.250					-0.718	0.013	0.54		Tw
3d	0.906	0.344		0.607	0.200		-0.243	0.186		-0.770	0.178	0.55	-1.242	Tw
3e				1.204						-0.742	0.134	0.48		Tw
[H ₂ Pc]				0.72			-0.63			-0.88			-1.64	[31]
[CuPc]				1.03			-0.62			-1.17				[44]
[CoPc]				0.46	0.095	0.95	-0.36	0.096	1.00	-1.27	0.103	0.98		[39]
[NiPc]	1.51 ^{d)}			0.89			-0.86			-1.25			-1.65	[36]
[NiPc]				0.14			-1.43			-1.64			-2.54	[45]

Tw = this work. a) $E_{1/2}(V) = (E_{pa}+E_{pc})/2$ at 100 mV s⁻¹ scan rate; b) $\Delta E_p(mV) = E_{pa}-E_{pc}$ at 100 mV s⁻¹ scan rate; c) I_{pa}/I_{pc} values are given for reduction and I_{pc}/I_{pa} values are given for oxidation processes at 100 mV s⁻¹ scan rate; d) the processes were recorded using SWV.

reaction mechanism can be represented as follows:

$$\begin{bmatrix} \operatorname{Cu}(\operatorname{II})\operatorname{Pc}(-1) \end{bmatrix}^{+} \bigoplus_{0.92V}^{e} \begin{bmatrix} \operatorname{Cu}(\operatorname{II})\operatorname{Pc}(-2) \end{bmatrix}$$
$$\stackrel{e}{\longleftrightarrow} \begin{bmatrix} \operatorname{Cu}(\operatorname{II})\operatorname{Pc}(-3) \end{bmatrix}^{-} \bigoplus_{-0.72V}^{e} \begin{bmatrix} \operatorname{Cu}(\operatorname{II})\operatorname{Pc}(-4) \end{bmatrix}^{2-1}$$

Within the electrochemical window of TBABF4/DMF, compound 3d undergoes two irreversible one-electron oxidation steps, a two irreversible one-electron reduction and a quasi-reversible one-electron reduction at 0.91, 0.61, -0.24, -0.77 and -1.24 V, respectively, versus Ag/AgCl at a 100 mV s⁻¹ scan rate [39]. SWV of the materials clearly confirms the recorded redox processes. The first reduction of 3d occurs at -0.24 V, and the first oxidation at 0.61 V (Table 1). The difference between the voltammetric behavior of **3a** and **3d** is due to the fact that metallophthalocyanines such as MnPc, CoPc and FePc, having a metal that possesses energy levels lying between the HOMO and the LUMO of the phthalocyanine ligand, in general exhibit redox processes centered on the metal [31, 37, 41, 42]. The separation between the first oxidation and the first reduction potentials of the metal center for the Co(II) complex, 3d (0. 85 V) agrees with the relevant values in the literature [31, 37, 41, 42], and does not reflect the HOMO-LUMO gap. The process IV (SWV) is not obvious in CV, and it may overlap with process III. The first oxidation (at 0.61 V) and first reduction (at -0.24 V) processes of **3f** can be assigned to the Co(II)/Co(III) and Co(II)/Co(I) redox couples respectively and the remaining processes to the Pc ring. Thus, the electrochemical reaction mechanism for 3d can be described as follows:

$$\begin{bmatrix} \operatorname{Co(III)Pc}(-1) \end{bmatrix}^{2+} \bigoplus_{0.91V}^{e} \begin{bmatrix} \operatorname{Co(III)Pc}(-2) \end{bmatrix}^{+}$$
$$\bigoplus_{0.61V}^{e} \begin{bmatrix} \operatorname{Co(II)Pc}(-2) \end{bmatrix} \bigoplus_{-0.24V}^{e} \begin{bmatrix} \operatorname{Co(I)Pc}(-2) \end{bmatrix}^{-}$$
$$\bigoplus_{-0.77V}^{e} \begin{bmatrix} \operatorname{Co(I)Pc}(-3) \end{bmatrix}^{2-} \bigoplus_{-1.24V}^{e} \begin{bmatrix} \operatorname{Co(I)Pc}(-4) \end{bmatrix}^{3-}$$

For 3e, all the redox processes are assigned to the ring since only ring reduction or oxidation has been documented for NiPc complexes in solution. Within the -1.6 to +1.5 V potential window, complex 3e exhibits an irreversible one-electron reductions processes at 0.92 and -0.72 V. The electrochemical reaction mechanism for 3d can be described as follows:

$$\left[\operatorname{Ni}(\operatorname{III})\operatorname{Pc}(-2)\right]^{+} \bigoplus_{0.92 \,\mathrm{V}}^{\mathrm{e}} \left[\operatorname{Ni}(\operatorname{II})\operatorname{Pc}(-2)\right] \bigoplus_{-0.72 \,\mathrm{V}}^{\mathrm{e}} \left[\operatorname{Ni}(\operatorname{II})\operatorname{Pc}(-2)\right]^{-1}$$

In addition, the oxidation couple monitored by CV is split into two processes during the SWV measurements, especially for 3a, 3c and 3e. This splitting implies that the electron transfer process is associated with aggregationdeaggregation equilibria of these species [43]. The effects of aggregation will be pronounced for CV due to the high concentrations ($>10^{-4}$ M) employed compared to for UV-vis spectroscopy, where low concentrations ($\leq 10^{-5}$ M) are used [17]. Reduction of the Pc ligand is associated with the position of the LUMO, whereas oxidation of the ligand is associated with the position of the HOMO [31]. Thus, the difference between the potentials of the first oxidation and the first reduction processes reflects the HOMO-LUMO gap $(\Delta E_{1/2})$ for free-base phthalocyanines and it is closely related to the HOMO-LUMO gap in metallophthalocyanine species involving redox-inactive metal centers. The $\Delta E_{1/2}$ values recorded for 3a (1.25 V), 3c (1.64 V) and 3e (1.94 V) in our study are in agreement with the values previously reported [31-33, 36, 44].

4 Conclusions

We have synthesized a novel soluble phthalocyanine **3a** and four of its metal complexes **3b–3e** from 4-nitrophthalonitrile and 4-hydroxybenzophenone in two steps and characterized the products by a variety of methods. The results confirm that all the products are formed in excellent purity and have the expected structures. The nature of their UV-vis spectra and electrochemical properties was investigated in detail. The Q band wavelengths of **3b–3e** follow the order: Zn > Cu > Ni > Co. Redox processes at Cu and Ni were observed for CuPc and NiPc. The CV traces of the phthalocyanine ring of the four complexes are similar, with two reduction and two oxidation couples each involving a one-electron transfer process. Redox processes were observed at -1.06, -0.74, 0.51 and 0.98 V for **3a**, at -0.72 and 1.04 V for **3c**, at -1.24, -0.77, -0.24, 0.61 and 0.91 V for **3d**, and at -0.74 and 1.20 V for **3e**. The electrochemical reaction mechanisms for these compounds are also given.

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