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Concise synthesis, electrochemistry and spectroelectrochemistry of phthalocyanines having triazole functionality



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1. Introduction

In recent years, functional phthalocyanines (Pcs) have gained special attention due to their large areas of applications, including diagnostic imaging agents [1], organic photovoltaic devices [2–6], organic field-effect transistors [7] and emerging therapeutics in photodynamic therapy (PDT) [8–13]. In addition, they are similar to the porphyrins seen in biological systems [14]. In spite of their enormous potential, the synthesis of smart Pcs bearing functional groups remains a challenge. Thus, there are many reports on the peripheral modification of Pcs.

The 1,2,3-triazole moiety, having a variety of biological activities, is found in a large number of molecules [15]. The Cu catalyzed 1,3-dipolar cycloaddition reaction between azides and alkynes, named as the "click" reaction [16,17], has recently been demonstrated by a straightforward method for obtaining functionalized Pcs with 1,2,3-triazole groups [18–24]. So far, all attempts at examining Pcs bearing 1,2,3-triazole groups have been for a phthalocyanine post modification approach. The Pcs' cores are obtained first and then post modifications are applied. However, in some cases, extra protection/deprotection steps are required. Moreover, the solubility problem of Pcs with propynyloxy moieties accelerating

ABSTRACT

The synthesis of novel metallophthalocyanines (M = Zn, Ni) bearing substituted benzyl protected 1,2,3triazole moieties at peripheral positions is described for the first time via direct cyclotetramerization. These complexes have been characterized by a combination of FT-IR, ¹H NMR, HRMS and UV–Vis spectroscopy techniques and all the new compounds are highly soluble in most common organic solvents. In addition, the electrochemical and electrochromic behaviors of the complexes are investigated. Cyclic voltammetry and differential pulse voltammetry measurements demonstrate ligand base oxidations and reductions for both the Zn(II) and Ni(II) phthalocyanines by the transfer of one electron in each electrochemical step. The redox couples are identified *in situ* by monitoring the electronic absorption spectral changes during the electrolysis.

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aggregation behavior does not allow triazole formation because of their linear geometry [23]. In order to overcome these problems, a direct approach for Pcs bearing 1,2,3-triazole groups has been examined. We present herein a detailed synthetic, spectroscopic and electrochemical study of metallo (Zn, Ni) derivatives of Pcs, where the bulky and basic character of 1,2,3-triazole type peripheral substitutions on the Pcs core enhances the solubility in organic media and controls the aggregation behaviour [11,12]. To the best of our knowledge, a direct approach has not been previously used for the construction of phthalocyanines bearing 1,2,3-triazole before cyclotetramerization.

2. Experimental

2.1. General

All experiments were carried out in pre-dried glassware (1 h, 150 °C) under an inert atmosphere of argon. The following reaction solvents were distilled from the indicated drying agents: DMAE (CaH₂), DMF (CaH₂). All other chemicals were purchased from commercial suppliers and used without further purification.

Flash column chromatography was performed by using thickwalled glass columns with flash grade silica (Merck Silica Gel 60). The reactions were monitored by thin layer chromatography using precoated silica gel plates (Merck Silica Gel PF-254),





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visualized by UV-light and polymolybdenum phosphoric acid in ethanol as appropriate. All extracts were dried over anhydrous magnesium sulfate and solutions were concentrated under vacuum by using a rotary evaporator.

2.2. Spectroscopy

¹H and ¹³C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 spectrometer. The chemical shifts were expressed in ppm relative to CDCl₃ (δ 7.26 and 77.0 for ¹H and ¹³C NMR, respectively) as the internal standards. Infrared spectra were recorded on a Thermo Nicolet IS10 ATR-FT-IR spectrometer. HRMS spectra were detected on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS at the national nanotechnology research center of Bilkent University (UNAM). UV–Vis spectra were recorded on a VARIAN CARY 100 Bio spectrophotometer.

Voltammetric studies were performed with a Gamry PCI4/3007 Potentiostat–Galvanostat. In this system a platinum bead and a platinum plate electrode (0.5 cm²) were employed as the working and counter electrodes, respectively and an Ag/AgCl electrode was used as a reference electrode. These electrodes were positioned as close as possible to minimize the IR drop. Voltammograms of 0.001 M complex solutions were recorded in DMF containing 0.10 M tetrabutylammonium tetrafluoroborate (TBABF) as the supporting electrolyte under an argon atmosphere, at room temperature. The voltage scan rate during the measurements was kept at100 mV/s.

Constant potential electrolyses, which were followed *in situ* using a UV–Vis HP 8453 A spectrophotometer, were carried out at the peak potentials with an Ag-wire reference electrode, after making the necessary correction between Ag/AgCl and the Ag-wire (about 0.10 V for Ag/AgCl). A platinum gauze (2 cm²) served as the working electrodeand Pt-wire as the counter electrode during the electrolyses.

Color measurement experiments were performed with a Specord S-600 spectrophotometer every 20 min. during the electrolysis in DMF at room temperature.

2.3. Synthesis

2.3.1. Synthesis of 4-(prop-2-ynyloxy)phthalonitrile, 3

Propargyl alcohol (0.26 mL, 4.33 mmol) was added into a stirred mixture of 4-nitrophthalonitrile (0.50 g, 2.89 mmol) and anhydrous potassium carbonate (3.19 g, 23.1 mmol) in DMSO (6 cm³) under an argon atmosphere at room temperature. The mixture was stirred at room temperature for three and a half hour under an argon atmosphere, and then distilled to remove DMSO under reduced pressure. Water (100 cm³) was added to the dried mixture, which was then extracted with DCM. The organic layer was dried over MgSO₄, and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane to afford 3 as a solid (0.49 g, 85% chemical yield). ¹H NMR (400 MHz, CDCl₃) δ : 2.57 (t, *J* = 2.4 Hz, 1H), 4.75 (d, *J* = 2.4 Hz, 2H), 7.25 (dd, *J* = 8.8, *J* = 2.6 Hz, 1H), 7.31 (d, J = 2.6 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 56.6, 76.2, 77.8, 108.2, 115.2, 115.5, 117.4, 119.9, 120.2, 135.2, 160.5. Anal. Calc. for C, 72.52; H, 3.32; N, 15.38. Found: C, 71.94; H, 3.42; N, 15.48%.

2.3.2. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy)phthalonitrile, **4**

3 (0.848 g, 4.65 mmol) was dissolved in DMSO (15 cm^3), then sodium ascorbate (0.9218 g, 0.465 mmol) and CuSO₄·5H₂O (1.1618 g, 0.465 mmol) were added under an argon atmosphere. After stirring for a half hour, benzyl azide was added to the reaction mixture and it was stirred for a further 12 h. Water

(250 cm³) was added to the reaction mixture, which was then extracted with DCM. The organic layer was dried over MgSO₄, and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane to afford **4** as a white solid (0.61 g, 42% chemical yield). ¹H NMR (400 MHz, CDCl₃) δ : 5.21 (s, 2H), 5.47 (s, 2H), 7.18–7.24 (m, 2H), 7.26–7.36 (m, 5H), 7.48 (s, 1H), 7.63 (dd, *J* = 7.6, *J* = 1.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 53.4, 61.5, 106.9, 113.9, 114.3, 116.5, 118.4, 119.3, 122.0, 127.1, 128.0, 128.2, 133.0, 134.2, 141.2, 160.1. *Anal.* Calc. for C, 68.56; H, 4.16; N, 22.21. Found: C, 68.12; H, 4.28; N, 22.34%.

2.3.3. General procedure for the synthesis of phthalocyanines **5a–b** and **6a–b**

Phthalonitriles, **3** and **4**, were dissolved in a mixture of DMEA/ DMF (1:2). After adding the metal salts $(Zn(OAc)_2 \text{ and NiCl}_2)$, stirring was continued at 150 °C for 7 h for the metallophthalocyanines **5a** and **5b** and for 48 h for the metallophthalocyanines **6a** and **6b**. After TLC monitoring, the reaction was stopped by adding a water-methanol (1:1) mixture (100 cm³). The precipitate formed was washed with ether, then extracted with DCM. The organic layer was dried over MgSO₄, and then the solvent was evaporated under reduced pressure [24]. The residue was purified by column chromatography on silica gel eluting with DCM:CH₃OH (95:5 for **6a** and 90:10 for **6b**) to afford the phthalocyanines.

2.3.4. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy substituted Zn phthalocyanine, **6a**

Compound **4** (0.39 g, 1.23 mmol) was reacted with $Zn(OAc)_2$ (0.067 g, 0.31 mmol) and gave **6a** (0.344 g, 20.3% chemical yield). FT-IR (ATR System, cm⁻¹): 2960, 2920, 2850, 1714, 1604, 1485, 1454, 1388, 1334, 1259, 1217, 1182, 1087, 1045, 1024, 1010, 943, 850, 796, 761, 744, 711, 694, 659. ¹H NMR (400 MHz, DMSO) δ : 5.65–5.90 (m, 16H), 7.35–7.85 (m, 24H), 8.34–9.21 (m, 12H). MS(TOF-ESI): m/z [M+Na]⁺ calcd. for C₇₂H₅₂N₂₀NaO₄Zn: 1349.6847; found [M+Na]⁺:1349.3831.

2.3.5. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy substituted Ni phthalocyanine, **6b**

Compound **4** (0.564 g, 1.79 mmol) was reacted with NiCl₂ (0.077 g, 0.595 mmol) and gave **6b** (0.173 g, 20.7% chemical yield). FT-IR (ATR System, cm⁻¹): 2960, 2924, 2852, 1714, 1608, 1531, 1479, 1454, 1415, 1336, 1259, 1226, 1116, 1091, 1047, 1010, 956, 864, 796, 748, 731, 711, 694. ¹H NMR (400 MHz, DMSO) δ : 4.68–6.05 (m, 16 H), 6.75–8.66 (m, 36H). MS(TOF-ESI): *m/z* [M+K]⁺ calcd. for C₇₂H₅₂KN₂₀O₄Ni: 1359.1066; found [M+K]⁺:1359.3773.

3. Results and discussion

3.1. Synthesis

The Huisgen 1,3-dipolar cycloaddition of azides to alkynes has been proven to be versatile for the functionalization of macromolecules, in addition to other applications. The derivatization of metallo Pcs via the click approach will not only pave the way to the rapid and effective synthesis of highly diverse Pcs, but also towards the integration of Pc cores into functional supramolecular systems for harvesting of energy at a molecular level [25–28]. However, as we mentioned above, there are some drawbacks for derivatization. To synthesize the target Pcs **5a**, our first attempt started with the S_NAr type substitution reaction between **2** and 4-nitrophthalonitrile **1** (Scheme 1), resulting in compound **3** in 85% yield. After characterization, completed by NMR spectroscopy, compound **3** was subjected to the appropriate conditions using



Scheme 1. Synthesis of 4-((1-benzyl-1H-1,2,3-triazol-4-yl)methoxy)phthalonitrile 4 and target Pcs scaffolds.

Zn(OAc)₂·2H₂O and DMEA (N,N-dimethylaminoethanol) in a Schlenk tube (Scheme 1). In a short time (7 h), the reaction color turned dark blue and the reaction was stopped. A precipitate was obtained after washing several times with water and methanol mixtures, in different ratios. However, the target Pc-5a, was not detected by spectroscopic techniques because of a solubility problem. It is not soluble in common organic solvents properly. The same result was also observed in the case of the other nickel derivative, Pc-5b. For that reason, our synthetic strategy was changed and triazole formation was sought to apply directly on the cyclotetramerization of monomer 3. In fact, basic nitrogen is known to be detrimental to reactions involving metallic compounds or catalysts. However, previous examples showed that reactions of phthalonitriles containing groups having a basic character had been carried out under common cyclotetramerization conditions to afford the desired Pcs in good yields [29–31]. Therefore, compound **3** was converted to phthalonitrile **4** via click chemistry in 42% yield and the structure of **4** was assigned on the basis of ¹H and ¹³C NMR spectroscopy (Scheme 1). After cyclotetramerization of monomer 4 in the presence of metal salts (Zn(OAc)₂.2H₂O or NiCl₂), using DMAE as the catalyst at high temperature, an isomeric mixture of the desired metallophthalocyanines **6a–b** was obtained in good yield after purification by column chromatography, as expected (Scheme 2). A solubility test of **Pc-6a/b** showed that they are highly soluble in most organic solvents, i.e. CH₂Cl₂, CHCl₃, toluene and THF, but insoluble in water. The structures of the novel Pc compounds **Pc-6a** and **Pc-6b** were characterized by IR, UV, ¹H and ¹³C NMR and LC-HRMS techniques.

The FT-IR spectra of both phthalocyanines **Pc-6a/b** exhibit the disappearance of the characteristic band at 2200 cm⁻¹ assignable to the CN vibration. Absorption bands at 659, 694, 711, 744, 761, 796, 850, 943, 1010, 1024, 1045, 1087, 1182, 1217, 1259, 1334,



Scheme 2. Synthesis of target phthalocyanine structures 6a-b.



Fig. 1. HRMS spectra of (a) Pc-6a and (b) Pc-6b.

1388, 1454, 1485, 1604, 1714, 2850, 2920 and 2960 cm⁻¹ are observed for **Pc-6a**; these can be attributed to phthalocyanine skeletal vibrations [24]. The FT-IR spectrum of **Pc-6b** shows very similar absorption peaks at around 694–2960 cm⁻¹. The mass spectra of phthalocyanines **Pc-6a/b** are shown in Fig. 1. The molecular ion peaks are easily identified at 1349.3831 as the sodium adduct [M+Na]⁺ for **Pc-6a** and 1359.3773 as the potassium adduct [M+K]⁺ for **Pc-6b**.



Fig. 2. Comparison of the electronic absorption spectra in the range (a) 300–750 nm for **Pc-6a** and (b) 250–750 nm for **Pc-6b**.

3.2. UV-Vis absorption spectra

The electronic absorption spectra of **Pc-6a/b** were recorded in CHCl₃ over a wide concentration range $(10^{-6}-10^{-5} \text{ M})$. Fig. 2 compares the electronic absorption spectra in the range 300–750 nm for **Pc-6a** and 250–750 nm for **Pc-6b**.

Both targets, **Pc-6a/b**, exhibit electronic absorptions that are typical for non-aggregated phthalocyanines. As shown in Fig. 2, the absorption spectrum of **Pc-6a** in $CHCl_3$ displays a strong Q band

Table 1

Voltammetry data for the zinc (1) and nickel phthalocyanine (2) using a Pt electrode in DMF at room temperature. VSR = 100 mV/s.

			Ia	II ^a	III ^a	I ^b	II ^b	III ^b	$\Delta E_{1/2}^{c}$
ZnPc	CV	E(V) $\Delta E (mV)^{e}$ $E_{1,2}(V)^{f}$	0.610*	0.980 ^d	1.280	cannot be ob	served		
	DPV	$E(V)$ $\Delta E (mV)^{e}$ $E_{1/2}(V)^{f}$	0.620^{*} 100 0.4975		1.260 100 1.013	-0.475° 45	-0.950* 106	-1.330	1.0675
NiPc	CV	$E(V)$ $\Delta E (mV)^{e}$ $E_{1/2}(V)^{f}$	0.615	0.966 ^{d,vs}	1.160	-0.755 [*] 85 -0.7975	-1.175 [*] 95 -1.2225		
	DPV	$E(V)$ $\Delta E (mV)^{e}$ $E_{1/2}(V)^{f}$	0.656* 135 0.7235		1.176* 76 1.138	-0.760° 63 -0.7915	-1.290* 99 -1.2405	-1.355	1.515

^a Oxidation peak potential.

^b Reduction peak potential.

^c $\Delta E_{1/2} = [\Delta E_{1/2}(\text{first oxidation}) - \Delta E_{1/2}(\text{first reduction})].$

^d Observed due to aggregation potential.

^e $\Delta E(mV) = |E_{pa} - E_{pc}|$.

^f $E_{1/2}$ (V) = $(E_{pa} + E_{pc})/2$.

Reversible peak.

vs Very slightly observable.



Fig. 3. (a) The cyclic voltammogram of 1.0 mM ZnPc solution in a 0. 1 M TBABF-DMF electrolytic solution at a scan rate of 100 mV/s. Inset: Anodic scans recorded at different voltage scan rates (100–700 mV/s). (b) Differential Pulse Voltammogram of ZnPc with the parameters: step size: 5 mV; pulse size: 100 mV; Sample frequency: 25 Hz.

at 696 nm, having a shoulder at 683 nm, together with a Soret band peaking at 358 nm and a weak vibronic band at 625 nm. On the other hand, **Pc-6b** displays a weak Q band at 620 nm with a shoulder at 674 nm and a Soret band at 279 nm. The insets of Fig. 2 show non-aggregation behavior for **Pc-6a/b** solutions.

3.3. Electrochemical measurements

3.3.1. Electrochemisty and spectroelectrochemistry

The electrochemical data for the zinc(II) (**6a**) and nickel(II) phthalocyanine (**6b**) coordination compounds are presented in Table 1.

3.3.2. ZnPc, 6a

Two oxidation peaks are observed in both the cyclic (CV) and differential pulse voltammograms (DPV) of ZnPc in DMF, at around 0.61 (quasi-rev) and 1.28 V versus Ag/AgCl (Fig. 3a). During the anodic scan an additional oxidation peak is also observed in the CV at around 0.980 V, attributed to the aggregation of the complex on the electrode surface [32]. Upon reversal of the scan direction, three reversible reduction peaks appear in the DPV at -0.475, -0.950 and -1.335 V versus Ag/AgCl. Because these cathodic peaks are not observed during the CV studies, reversibility of the



Fig. 4. (a) Variation of the anodic current with the square root of the voltage scan rate for ZnPc. \blacklozenge , first oxidation peak potential; \blacksquare , second oxidation peak potential. (b) Variation of current function $I/(CV^{1/2})$ vs. the voltage scan rate for the oxidation peaks of ZnPc. I (mA) is the current, V (mV/s) is the voltage scan rate and C (mol/L) is the molar concentration. \blacklozenge , first oxidation peak potential; \blacksquare , second oxidation peak potential.

reduction peaks is only illustrated by sweeping forward and reverse DPV scans (Fig. 3b).

Linear dependence, which is observed between the peak current (I_p) and the square root of the voltage scan rate $(V^{1/2})$, indicates a diffusion controlled electron exchange reaction for the anodic peaks (Fig. 4a). The slightly positive slope of the plot of the current function $(I/CV^{1/2})$ (C: Concentration) versus voltage scan rate (Fig. 4b), according to the Nicholson-Shain criteria [33], indicates a reversible electron exchange reaction followed by a reversible chemical reaction for the first oxidation peak. This result is consistent with the voltammetric studies, in which the anodic and cathodic peak separation (ΔE_p) is about 50 mV at 100 mV/s and this value increases to 130 mV as the scan rate is increased (900 mV/s). The peak to peak current ratio of the first anodic peak is almost unity at 100 mV/s, but it goes above unity as the scan rate increases to 900 mV/s. Similarly, the logarithmic plot obtained for the second oxidation peak indicates a reversible oxidation process followed by a catalytic reaction. The absence of the corresponding cathodic peak for the reversible second oxidation is most probably due to the fast catalytic reaction that follows the electrochemical one. Similar analyses are not possible for the cathodic peaks due to their absence in the cyclic voltammograms.

The number of electrons transferred at the first and second oxidation peaks for ZnPc is established to be one by chrono-coulometric methods. Since the area under the second oxidation peak is comparable to that under the first oxidation peak, a one-electron transfer appears to occur for the second process as well.

In order to understand the mechanism of the electrochemical processes and to identify the product species in solution, constant potential electrolysis of solutions of the complexes in DMF was followed by *in situ* UV–Vis. spectroscopy. Electrochemical oxidation was carried out at the consecutive peak potentials in DMF, and the spectral changes were followed in situ by UV-Vis spectroscopy at room temperature. The changes in the electronic absorption spectra of ZnPc during constant potential electrolysis are shown in Fig. 5. The intensity of the characteristic bands of ZnPc at 356, 612 and 679 nm gradually decreases during the electrolysis carried out at the first oxidation peak potential vs. Ag-wire. While the band at 356 nm shifts slightly to 353 nm, a very weak shoulder appears at around 794 nm with an increase in the feature at around 500 nm. During these spectral changes no isosbestic point formation was observed (Fig. 5a). Since the Zn metal center is electrochemically inert, the redox behavior of **ZnPc** is mainly ligand based [34,35]. Decreasing the intensity of the Q band without shifting, with an increase of the spectra in the region 400-600 nm, support the characteristic ring based oxidation process [35] and Refs. thereinl. as well.

These spectroscopic changes clearly suggest the occurrence of a one-step electrode reaction, leading to the formation of $[Zn^{II}Pc^{-1}]^+$, according to Eq. (1).



Fig. 5. The changes in the electronic absorption spectrum of a 3.77×10^{-4} M ZnPc solution in DMF during oxidative electrolysis. (a) after $1e^-$ transfer; (b) after $2e^-$ transfer. (c) The changes in the electronic absorption spectra before the oxidation (BE) and at the end of the oxidation.

$$[\mathbf{Z}\mathbf{n}^{II}\mathbf{P}\mathbf{c}^{-2}] \rightleftharpoons [\mathbf{Z}\mathbf{n}^{II}\mathbf{P}\mathbf{c}^{-1}]^{+} + \mathbf{e}^{-}$$
(1)

Afterwards, the potential was switched to the second oxidation peak potential and the resulting spectral changes, measured in situ during the second electron transfer, are presented in Fig. 4b. The second electron transfer causes a further decrease in the intensity of the bands at 353, 612, 679 and 794 nm. A further decrease in the intensity of the Q band without shifting indicates further ligand oxidation, generating [Zn^{II}Pc]²⁺. However, a slight increase is observed at around 305 nm with two isosbestic points at 297 and 316 nm. Since the electrochemical analysis performed with respect to the Nicholson-Shain criteria [33] denotes that the second electron transfer is followed by a fast catalytic reaction, the decrease in the whole spectrum indicates the decomposition of the electrolysis product and the slight increase at around 305 nm is attributed to the formation of a product at the end of this catalytic process. Based on these results, the following reaction pathways (Eq. 2-3) for the formation and then for the decomposition of the [Zn^{II}Pc] ²⁺ ion can be proposed.

$$[Zn^{II}Pc^{-1}]^{+} \rightleftharpoons [Zn^{II}Pc]^{2+} + e^{-}$$
⁽²⁾

 $[Zn^{II}Pc]^{2+} \rightarrow$ Decomposition to unknown oxidation products (3)

Color changes of the complex in solution during the anodic processes were recorded during *in situ* electrocolorimetric measurements. Before the electro-oxidation, the color of the ZnPc is bluish green (x = 0.2872 and y = 0.3506), which is shown in Fig. 6. As the oxidation is progressively carried out at the peak potentials in DMF, the color of the ZnPc does not change much (x = 0.2900 and y = 0.3508) and a darker green of $[Zn^{II}Pc^{-1}]^+$ ion is obtained at the end of the 1st electron transfer. Further oxidation of $[Zn^{II}Pc^{-1}]^+$, which was carried out at the 2nd peak potential, causes the color of the electrolyte solution to change to grass green (x = 0.3156 and y = 0.3402).

Electrochemical reduction of ZnPc was performed at the peak potentials separately versus an Ag-wire. During the first electron transfer, a decline in the peak intensities is observed for the



Fig. 6. Chromaticity diagram of electrogenerated species during the oxidation of 3.77×10^{-4} M ZnPc in DMF. **II**, Zn^uPc⁻² (BE); **•**, $(Zn^uPc^{-})^*$; **•**, $(Zn^uPc)^{+2}$.



Fig. 7. The changes in the electronic absorption spectra of a 3.77×10^{-4} M ZnPc solution in DMF during reductive electrolysis (a) after $1e^-$ transfer; (b) after $2e^-$ transfer. (c) the changes in the electronic absorption spectra before the oxidation (BE) and at the end of the oxidation.

characteristic bands of the complex, whilst a new band at 797 nm is formed (Fig. 7). As the band at around 288 nm is intensified, an increase in the spectra is also recorded in the region 400–600 nm, with 4 isosbestic points at around 336, 380, 590 and 710 nm. Decreasing the intensity of the Q band without shifting, with an increase in the spectra the region 400–600 nm indicate a characteristic ring base reduction process [[35] and Ref. there in].

Color changes of the complex in solution during the cathodic processes were recorded during *in situ* electrocolorimetric measurements. Before the electro-reduction, the color of the ZnPc is bluish green (x = 0.2872 and y = 0.3506), which is shown in Fig. 6. As the reduction was carried out at the first reduction potential in DMF, the color of the ZnPc changes from bluish green to green (x = 0.3160 and y = 0.3404). The change in color from bluish green to green during the oxidation process reveals the generation of a monoanionic species, $[Zn^{11}Pc^{-3}]^{-}$ (Eq. 4), during the electrochemical reduction process [35].

When the potential was switched to the second reduction peak, further reduction leads to a further decrease in the peak intensity



Fig. 8. Chromaticity diagram of the electrogenerated species during the oxidation of 3.77×10^{-4} M ZnPc in DMF. \blacksquare , $Zn^{u}Pc^{-2}$ (BE); \bullet , $(Zn^{u}Pc^{-3})^-$; \bullet , $(Zn^{u}Pc^{-4})^{-2}$.

of the Q band, whilst a new band is formed at around 310 nm with an isosbestic point at 324 nm. This isosbestic point clearly suggests the occurrence of a one-step electrode reaction, leading to the formation of $[Zn^{II}Pc^{-4}]^{2-}$, according to Eq. (5). During this process, the color of the electrolyte solution starts to change and a yellow color (mx = 0.3171 and y = 0.3352) is obtained; further electrolysis causes a further decline in the whole spectra (Fig. 8). The decrease in the intensity of the characteristic bands indicates the decomposition of the electrolysis product $[Zn^{II}Pc^{-4}]^{2-}$ to an unknown reduction compound (Eq 6).

$$[Zn^{II}Pc^{-2}] + e^{-} \rightleftharpoons [Zn^{II}Pc^{-3}]^{-}$$
(4)

$$[Zn^{II}Pc^{-3}]^{-} + e^{-} \rightleftharpoons [Zn^{II}Pc^{-4}]^{2-}$$
(5)

$$[Zn^{II}Pc^{-4}]^{2-} + e^{-} \rightarrow$$
 Decomposition to unknown reduction products (6)

3.3.3. NiPc, **6b**

The cyclic voltammogram (CV) of NiPc (Fig. 9a) in DMF displays two irreversible oxidation peaks at around 0.615 and 1.160 V versus Ag/AgCl. Upon reversal of the scan direction, two quasi-reversible reduction peaks also appear at around -0.755 and -1.175 V (Fig. 9b). On the other hand, differential pulse voltammograms of NiPc are composed of two quasi-reversible oxidation peaks at 0.656 and 1.176 V and two quasi-reversible cathodic peaks at about -0.760 and -1.290 V versus Ag/AgCl.

As the voltage scan rate increases (Fig. 10a), a linear dependence is observed, both between I_p (peak current) and the logarithm of the voltage scan rates and between E_p (peak potential) and I_p , which suggests a diffusion-controlled electrode exchange reaction [28]. The negative slope of the plot of the current function, $I/(CV^{1/2})$ (C = concentration), versus the voltage scan rate (Fig. 10b) indicates a reversible electron transfer, which is followed by a chemical reaction for the second oxidation and the reduction peaks [33]. Nicholson-Shain plots could not be drawn for the first oxida-



Fig. 9. (a) The cyclic voltammogram of a 1.0 mM NiZnPc solution in a 0.1 M TBABF-DMF electrolytic solution at a scan rate of 100 mV/s. (a) Anodic scan; inset: Anodic scans recorded at different voltage scan rates (100–700 mV/s). (b) Cathodic scan at varius scan rates; (c) Differential Pulse Voltammogram of NiPc with the parameters: step size: 5 mV; pulse size: 100 mV; Sample frequency: 25 Hz.

tion peak because of the disappearance of the first oxidation peak with increasing scan rate. On the other hand, the results obtained from the plots are consistent with our observations in the voltammograms for the other peaks. The reason for obtaining only irreversible oxidation peaks during the anodic scan may be the higher rate of the chemical reaction following the charge transfers [36] and the inconsistence between the voltage scan and the charge transfer rates. The chemical reactions following the electrochemical ones may be attributed to hydrogen ion acquisition or abstraction during the course of the reactions. However, a reversible character of the oxidation peaks is observed in the DPV by



Fig. 10. (a) Variation of the peak current with the square root of the voltage scan rate for NiPc. \blacklozenge , second oxidation peak potential; \blacksquare , first reduction peak potential, \diamondsuit , second reduction peak potential. (b) Variation of current function $I/(CV^{1/2})$ vs. the voltage scan rate for the oxidation peaks of NiPc. I (mA) is the current, V (mV/s) is the voltage scan rate and C (mol/L) is the molar concentration. \diamondsuit , second oxidation peak potential; \blacksquare , first reduction peak potential.

scanning forward and reverse voltammograms (Fig 9c). The reduction peaks of NiPc are quasi-reversible. The anodic and cathodic peak separation (ΔE_p) is about 50 mV at 100 mV/s and this value increases to 100 mV as the scan rate increases (600 mV/s) for both cathodic peaks. The peak to peak current ratio of the first anodic peak is unity at 100 mV/s and stays constant as the scan rate increases to 600 mV/s, unlike the second cathodic peak, for which it is less than unity.

The number of electrons transferred at the oxidation and reduction peaks for NiPc is established to be one by chrono-coulometric methods.

Electrochemical oxidation was carried out at the consecutive peak potentials in DMF, and the spectral changes were investigated *in situ* through UV–Vis spectral changes at room temperature. The changes in the electronic absorption spectra of NiPc during constant potential electrolyses are shown in Fig. 11. While the characteristic bands of NiPc at 280, 305 and 381 nm intensify, the intensity of the bands observed at around 625 and 675 nm gradually decreases. The band at 305 nm slightly shifts to 300 nm and the formation of a new band is observed at around 775 nm, associated with three not so well resolved isosbestic points at 295, 340 and 585 nm at the end of the one-electron transfer. Moreover, an increase in the intensity in the region between 400 and 600 nm is observed during the electrolysis carried out at the first oxidation peak potential vs. Ag-wire as well.

The electrochemical behavior of the complex NiPc is very similar to that of the complex ZnPc, which suggests similar ring-based electrochemical processes. The isosbestic points clearly suggest the occurrence of a one-step electrode reaction and a decrease in the intensity of the Q band without any shift, with an increase at



Fig. 11. The changes in the electronic absorption spectra of a 1.14×10^{-4} M NiPc solution in DMF during oxidative electrolysis. (a) after 1e⁻ transfer; (b) after 2e⁻ transfer. (c) The changes in the electronic absorption spectra before the oxidation (BE) and at the end of the oxidation.

around 400 to 600 nm with newly formed bands, indicate the formation of $[Ni^{II}Pc^{-1}]^+$, according to Eq. (7).

$$[Ni^{II}Pc^{-}2] \rightleftharpoons [Ni^{II}Pc^{-1}]^{+} + e^{-}$$
(7)

Further oxidative electrolysis at the second oxidation peak potential leads to a decrease in the intensity of the whole spectrum progressively, which indicates fast decomposition of the oxidation product [Ni^{II}Pc] ²⁺ to an unknown compound (Fig. 11b).

$$[Ni^{II}Pc^{-1}] \rightleftharpoons [Ni^{II}Pc]^{2+} + e^{-}$$
(8)

$$[Ni^{"}Pc]^{"} \rightarrow Decomposition to unknown oxidation products (9)$$

Color changes of the complex in solution during the cathodic processes were recorded during *in situ* electrocolorimetric measurements. Before the electro-reduction the color of NiPc is blue (x = 0.2710 and y = 0.3349). As the reduction proceeds at the first reduction potential in DMF, the color of NiPc changes slightly and a darker blue color (x = 0.2866 and y = 0.3359) is obtained. When the potential was set to the second peak



Fig. 12. The changes in the electronic absorption spectra of a 1.14×10^{-4} M NiPc solution in DMF during reductive electrolysis (a) after $1e^-$ transfer; (b) after $2e^-$ transfer. (c) the changes in the electronic absorption spectra before the oxidation (BE) and at the end of the reduction.

potential, the color of the electrolyte solution did not change much (x = 0.3004 and y = 0.3341) by the end of the electron transfer.

Electrochemical reduction of NiPc was also carried out at the two peak potentials progressively *vs.* the Ag-wire reference electrode, which is shown in Fig. 12. A decrease in the intensity of the Q band at 675 nm without any shift is observed, with a decrease in the other characteristic band of NiPc at 280 nm, unlike the bands at 305 and 383 nm. While the band at 305 shifts slightly to 301 nm, the region between 400 to 600 nm intensifies. Development of a new band at 775 nm with two isosbestic points at 297 and 338 nm suggests a one-step electrode reaction generating [Ni^{II-}Pc⁻³]⁻, similar to the electro-reduction process of ZnPc. Further electrolysis leads to a decline in the whole spectrum, indicating decomposition of the electrochemical behaviors of ZnPc and NiPc, and based on the spectral findings, the following reaction pathways (Eq. 10–12) can be proposed.

$$[Ni^{II}Pc^{-2}] + e^{-} \rightleftharpoons [Ni^{II}Pc^{-3}]^{-}$$
(10)

$$[Ni^{II}Pc^{-3}]^{-} + e^{-} \rightleftharpoons [Ni^{II}Pc^{-4}]^{2-}$$
(11)

 $[Ni^{II}Pc^{-4}]^{2-} \rightarrow$ Decomposition to unknown reduction products (12)

Color changes in the complex in solution during the cathodic processes were recorded during in situ electrocolorimetric measurements as well. Before the electro-reduction the color of NiPc x = 0.2971 and y = 0.3285). As the reduction was caris blue (ried out at the first reduction potential in DMF, the color of NiPc did not change much again (x = 0.3071 and y = 0.3260). When the potential was switched to the second peak potential, the color of the electrolyte solution did not change (x = 0.3067 and y = 0.3228) by the end of the electron transfer.

4. Conclusion

In this study, we synthesized and characterized novel Zn(II) and Ni(II) phthalocyanines which are substituted with benzyl protected triazole groups. In our synthetic strategy, a direct approach is reported for the first time for the construction of phthalocyanines bearing 1,2,3-triazole before cyclotetramerization. In addition, electrochemical and electrochromic behaviors of the complexes were studied. Voltammetry and spectroelectrochemical studies reveal that ligand base redox couples are generated during the *in situ* electrolysis of the zinc(II) and nickel(II) phthalocyanines. The electrochromic measurements of these new complexes were obtained during the electro-reduction, with the Zn(II) complex providing promising results for photochromic applications.

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