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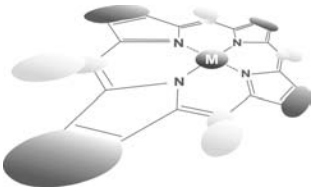

Phosphorus-nitrogen compounds. Part 17. The synthesis, spectral and electrochemical investigations of porphyrino-phosphazenes

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ABSTRACT: The reactions of unsymmetrical porphyrins (**1** and **2**) with $Ni(OAc)_2{\cdot}4H_2O$ in boiling DMF produce porphyrin complexes (**3** and **4**). From the reactions of free porphyrin ligands **1** and **2** with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, the new free porphyrino-phosphazene derivatives (**5** and **6**) are obtained. On the other hand, the reactions of $N_3P_3Cl_6$ with porphyrin complexes (**3** and **4**) afford the new porphyrino-phosphazene complexes (**7** and **8**). In the literature there are a few examples of the porphyrino-phosphazene architectures. The structural investigations of all the compounds have been made by elemental analyses, MS, FTIR, ^{1}H NMR, ^{31}P NMR and UV-visible techniques. The cyclic voltammograms (CVs) are examined in acetonitrile (MeCN) containing 0.1 M tetrabutylammonium-tetrafluoroborate (TBATFB) to investigate the surface attachment properties at the glassy carbon electrode (GCE) and the influence of the presence of metal cations in the porphyrin ring.

KEYWORDS: porphyrino-phosphazenes, synthesis, Ni(II) complexes, spectroscopy, electrochemistry.

INTRODUCTION

Porphyrins with extended chromophores are being investigated for applications that range from material science to medicine [1, 2]. In some cases, ring fusion results in highly red-shifted chromophores that could have value in photodynamic therapy [3–5]. It is known that porphyrin as a photosensitizer can localize on tumor cells and photo-trigger to produce singlet oxygen to cleave DNA and eventually damage the tumor cells [6]. Different structural units are being utilized to act as bridging units in the production of nanoscale systems, including molecular wires and arrays [7, 8]. Porphyrins are also used in different fields of research, including solar energy conversion catalysis, and photocatalytic water splitting is a challenging reaction to supply hydrogen from a sustainable source [9]. Compared to other organic dyes, some metalloporphyrins have advantages in the photo-induced hydrogen evolution systems with polymer solid [10, 11].

Phosphazene chemistry has experienced rapid growth and is a major part of the inorganic non-metallic field [12, 13]. The six-membered cyclotriazaphosphazene, $N_3P_3Cl_6$, is the most investigated phosphorus-nitrogen compound. $N_3P_3Cl_6$ has been used in the preparation of new phosphazene derivatives with different side groups [14]. Recently, chiral functional groups have been introduced onto the cyclic ring to form single diastromers [15]. Reactions of chlorophosphazenes with many mono-, di-, and polyfunctional reagents can lead to the formation of a great variety of products. A review concerning the reactions of chlorophosphazenes has been published [16]. Cyclophosphazene derivatives have found industrial applications in the production of lubricants [17], optical materials [18], inflammable textile polyphosphazene fibers, advanced elastomers with different organic and

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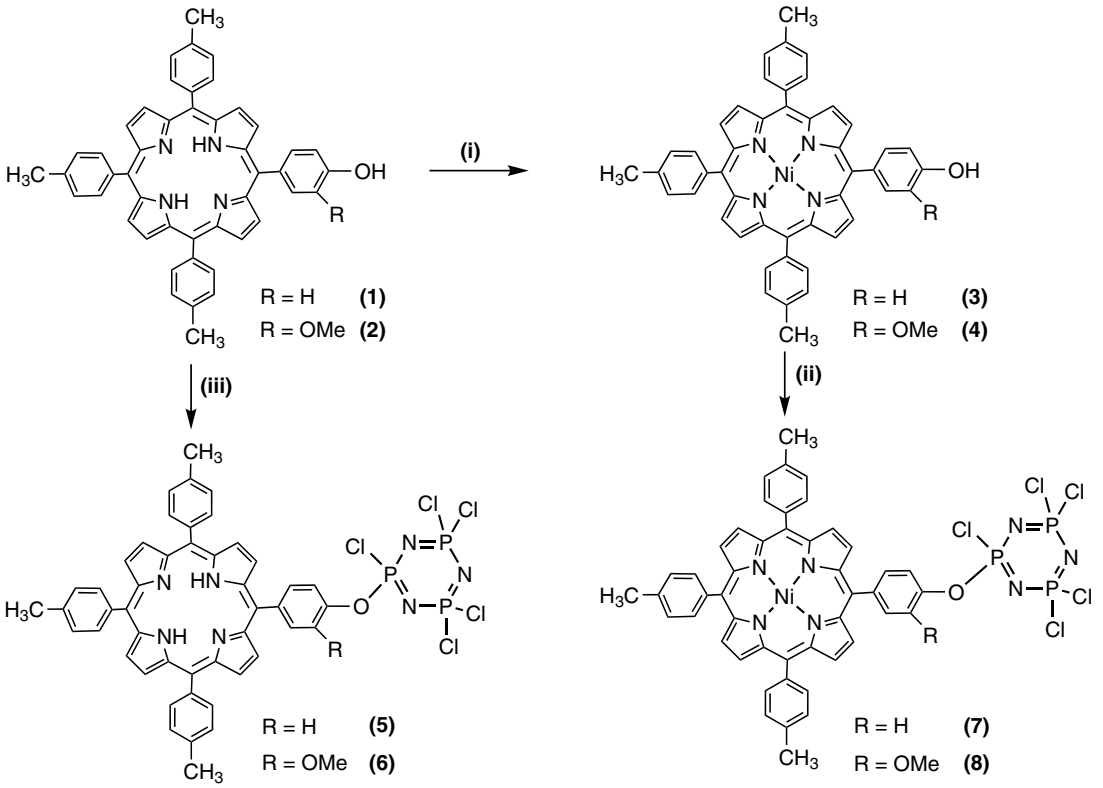


Scheme 1. The synthesis of porphyrino-phosphazene ligands and their Ni(II) complexes. Reagents and conditions. (i) $Ni(OAc)_2{\cdot}4H_2O$, DMF, reflux. (ii) $N_3P_3Cl_6$, NaH, THF, -10 °C. (iii) $N_3P_3Cl_6$, NaH, THF, -10 °C

inorganic side groups [19, 20], and rechargeable lithium batteries [21, 22] and multidimensional use as biomedical materials including synthetic bones [23, 24], selective anti-cancer and anti-bacterial reagents [25].

Interestingly, to date, there is only one report on cyclic-phosphazenes appended with six substited porphyrin rings in order to study physical and chemical properties [26]. In addition, there is also one report on a porphyrin appended with four cyclo-triphosphazene rings [27]. This paper reports (i) the synthesis of two new porphyrino-phosphazene ligands (**5** and **6**) and their complexes of Ni(II) (**7** and **8**) (Scheme 1), (ii) the structures of the free-ligands and their complexes determined by elemental analyses, mass spectrometry (MS), Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{31}P NMR, and UV-visible data, and (iii) cyclic voltammetric studies that have been performed to evaluate the redox potentials.

EXPERIMENTAL

General

The reaction solvents were dried and distilled by standard methods before use. The reagents were of commercial grade and used without further purification. Hexachlorocyclotriphosphazatriene was purchased from Aldrich Chemical Co. (USA). NaH with 60% paraffin was used after it was washed with heptane and then filtered. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX FT-NMR (400 MHz) spectrometer ($SiMe_4$ as internal and 85% H_3PO_4 as external standards). FTIR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr discs and were reported in cm^{-1} units. UV-visible spectra were measured using UNICAM UV2–100 series spectrometer. Microanalyses were carried out by the microanalytical service of TUBITAK (Turkey). Electrospray ionization (ESI) mass spectrometric analyses were performed on the Agilent 1100 MSD spectrometer. Thin-layer chromatography (TLC) was performed on Merck DC Alufolien Kiesegel 60 B_{254} sheets. Column chromatography was performed on Merck Kiesegel 60 (230–400 mesh ATSM) silica gel. Electrochemical experiments were performed using a Gamry Reference 600 workstation (Gamry, USA) equipped with C3 cell stand (BAS, USA). Before electrochemical experiments, solutions were purged with pure argon gas (99.999%) for at least 10 minutes and an argon atmosphere was maintained over the solution during experiments. Working electrode was a glassy carbon disk (BAS) and the counter electrode was a Pt wire. The reference electrode was a Ag^+/Ag (0.01 M) used in MeCN.

Synthesis

5,10,15-tris(4-methylphenyl)-20-(4-hydroxyphenyl) porphyrin (**1**) [28, 29] and 5,10,15-tris(4-methylphenyl)-20-(4-hydroxyphenyl)porphyrinatonickel(II) (**3**) [30] were prepared according to methods reported in the literature. Elemental analyses, mass spectrometry, ESI-MS, FTIR and H NMR data of these compounds have been given for purity and comparison purposes. ^{31}P NMR ($CDCl_3$), ^{1}H NMR ($CDCl_3$) and UV-vis ($CHCl_3$) data of all the compounds are listed in Tables 1, 2 and 3, respectively.

5,10,15-tris(4-methylphenyl)-20-(4-hydroxyphenyl)porphyrin [THP], (1). Yield: 335 mg (3%), mp > 300 °C, R_f = 0.57 (CH_2Cl_2). Anal. calcd. for $C_{47}H_{36}N_4O$: C, 83.90; H, 5.39; N, 8.33%. Found: C, 84.12; H, 5.21; N, 8.22%. IR (KBr): ν, cm^{-1} 3503 (O-H), 3313 (N-H), 3052;3021 (C-H arom.), 2921;2842 (C-H aliph.), 1608 (C=N), 1510 (C=C), 1280 (C-O), 966 (C-N), 796 (β-pyrrole C-H). MS (ESI): *m/z* (%) 673 ([M]$^+$, 100).

5,10,15-tris(4-methylphenyl)-20-(3-methoxy-4-hydroxyphenyl)porphyrin [THMP], (2). 4-hydroxy-3-methoxy benzaldehyde (2.30 g, 15.1 mmol) was dissolved in 500 mL of propionic acid and 4-methylbenzaldehyde (5.30 mL, 45.2 mmol) was added to this. The mixture was heated to 120 °C with vigorous stirring, and then freshly distilled pyrrole (4.18 mL, 60.2 mmol) was added dropwise. The resulting mixture was refluxed for 4 h. Then, the mixture was allowed to cool and was left overnight at room temperature. The separated solid was removed by filtration. The filtrate was washed with hot water to remove the remaining propionic acid and other undesired polymeric tars. Solid lumps obtained thereby were dried and purified by column chromatography with dichloromethane. Purple powder was obtained and was crystallized from dichloromethane/*n*-hexane (1:1). Yield: 320 mg (3%), mp > 300 °C, R_f = 0.54 (CH_2Cl_2). Anal. calcd. for $C_{48}H_{38}N_4O_2$: C, 82.03; H, 5.45; N, 7.97%. Found: C, 81.72; H, 5.33; N, 7.61%. IR (KBr): ν, cm^{-1} 3504 (O-H), 3311 (N-H), 3061;3019 (C-H arom.), 2914;2849 (C-H aliph.), 1598 (C=N), 1508 (C=C), 1261 (C-O), 966 (C-N), 796 (β-pyrrole C-H). MS (ESI) : *m/z* (%) 703 ([M + H]$^+$, 100).

5,10,15-tris(4-methylphenyl)-20-(4-hydroxyphenyl)porphyrinatonickel(II) [THPNi], (3). Yield: 105 mg (96%), mp > 300 °C, R_f = 0.72 (CH_2Cl_2). Anal. calcd. for $C_{47}H_{34}N_4ONi$: C, 77.38; H, 4.70; N, 7.68%. Found: C, 77.53; H, 4.39; N, 7.41%. IR (KBr): ν, cm^{-1} 3508 (O-H), 3050;3019 (C-H arom.), 2918;2848 (C-H aliph.), 1602 (C=N), 1508 (C=C), 1276 (C-O), 961 (C-N), 796 (β-pyrrole C-H). MS (ESI) : *m/z* (%) 730 ([M + H]$^+$, 100).

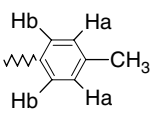
5,10,15-tris(4-methylphenyl)-20-(3-methoxy-4-hydroxyphenyl)porphyrinatonickel(II) [THMPNi], (4). A solution of **2** (0.10 g, 0.15 mmol) in DMF (25 mL) was heated and $Ni(OAc)_2{\cdot}4H_2O$ (0.20 g, 0.75 mmol) was slowly added to this. The mixture was refluxed for 1 h and then cooled. The solvent was evaporated and the solid residue was washed with water to remove the remaining $Ni(OAc)_2$. The residue was filtered, dried, and subjected to column chromatography with dichloromethane. Claret red powder was obtained and was crystallized from dichloromethane/*n*-hexane (1:1). Yield: 108 mg (95%), mp > 300 °C, R_f = 0.71 (CH_2Cl_2). Anal. calcd. for $C_{48}H_{36}N_4O_2Ni$: C, 75.91; H, 4.78; N, 7.38%. Found: C, 76.68; H, 4.56; N, 7.16%. IR (KBr): ν, cm^{-1} 3510 (O-H), 3051;3017 (C-H arom.), 2916;2853 (C-H aliph.), 1598 (C=N), 1504 (C=C), 1256 (C-O), 951 (C-N), 797 (β-pyrrole C-H). MS (ESI): *m/z* (%) 759 ([M + H]$^+$, 100).

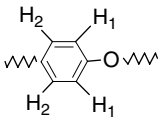
2,4,4,6,6-pentachloro-2-[5,10,15-tris(4-methylphenyl)-porphyrin-20-(4-phenoxy)]-cyclo-2λ^5,4λ^5,6λ^5-triphosphaza-1,3,5-triene [TPPP], (5) and 2,4,4,6,6-pentachloro-2-[5,10,15-tris(4-methylphenyl)-porphyrin-20-(3-methoxy-4-phenoxy)]-cyclo-2λ^5,4λ^5,6λ^5-triphosphaza-1,3,5-triene [TPMPP], (6). To a solution of **1** (0.10 g, 0.15 mmol) in dry THF (20 mL) was added NaH (60% suspension in paraffin oil) (6.0 mg, 0.15 mmol) and the mixture was stirred at room temperature. The red colour of the mixture was changed to green, indicating porphyrin had turned to its Na salt form. A stirred solution of $N_3P_3Cl_6$ (0.05 g, 0.15 mmol) in THF (5 mL) was added and the mixture was stirred at -10 °C for over 1 h. The green colour of the mixture changed to red, indicating that reaction was complete. The solvent was evaporated completely and the residue was subjected to column chromatography first with *n*-heptane and then toluene. Purple powder of compound **5** was obtained and was crystallized from toluene. The same procedure was used for the synthesis of porphyrino-phosphazene ligand (**6**) from free porphyrin ligand (**2**). Yield [**TPPP**], (**5**): 103 mg (70%), mp > 300 °C, R_f = 0.77 (CH_2Cl_2). Anal. calcd. for $C_{47}H_{35}N_7OP_3Cl_5$: C, 57.37; H, 3.59; N, 9.96%. Found: C, 58.21; H, 2.96; N, 10.14%. IR (KBr): ν, cm^{-1} 3317 (N-H), 3053;3024 (C-H arom.), 2920;2851 (C-H aliph.), 1600 (C=N), 1203 (P=N), 1007 (C-N), 798 (β-pyrrole C-H), 590;527 (P-Cl). MS (ESI): *m/z* (based on ^{35}Cl, %) 982 ([M + H]$^+$, 10). Yield [**TPMPP**], (**6**): 114 mg (75%), mp > 300 °C, R_f = 0.73 (CH_2Cl_2). Anal. calcd. for $C_{48}H_{37}N_7O_2P_3Cl_5$: C, 56.85; H, 3.68; N, 9.67%. Found: C, 57.76; H, 3.37; N, 10.01%. IR (KBr): ν, cm^{-1} 3311 (N-H), 3065;3019 (C-H arom.), 2916;2859 (C-H aliph.), 1592 (C=N), 1207 (P=N), 966 (C-N), 798 (β-pyrrole C-H), 598;523 (P-Cl). MS (ESI): *m/z* (based on ^{35}Cl, %) 1012 ([M + H]$^+$, 1).

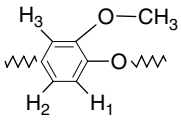
Table 1. ^{31}P NMR spectral data ($CDCl_3$) of **5–8** (δ in ppm, *J* in Hz)

Compound	Spin system	δ_{POCl}	δ_{PCl_2}	$^2J_{PP}$
5	AX_2	P_A 13.33	P_X 20.77	59.5
6	AX_2	P_A 14.27	P_X 22.16	60.5
7	AX_2	P_A 13.12	P_X 22.49	60.2
8	AX_2	P_A 14.25	P_X 21.60	60.7

Table 2. ^{1}H NMR spectral data ($CDCl_3$) of **1–8** (δ in ppm, *J* in Hz, br: broad, s: singlet, d: doublet, dd: doublet-doublet, m: multiplet)







	N*H*	Ar-C*H*$_3$	Ar-O-C*H*$_3$	Ar-O*H*	Ar-*H*$_1$	Ar-*H*$_2$	Ar-*H*$_3$	Ar-*H*$_a$	Ar-*H*$_b$	C*H* (β-pyrr.)
1	-2.73 (s, 2H)	2.73 (s, 9H)	—	5.02 (br, 1H)	7.19 (d, 2H) $^3J_{HH}$ 8.4	8.08 (d, 2H) $^3J_{HH}$ 8.4	—	7.73 (d, 6H) $^3J_{HH}$ 7.7	8.12 (d, 6H) $^3J_{HH}$ 7.7	8.95 (m, 8H)
2	-2.70 (s, 2H)	2.75 (s, 9H)	4.05 (s, 3H)	6.04 (br, 1H)	7.30 (d, H) $^3J_{HH}$ 8.1	7.79 (dd, 2H) $^3J_{HH}$ 8.1 $^4J_{HH}$ 2.0	7.73 (d, H) $^4J_{HH}$ 2.0	7.59 (d, 6H) $^3J_{HH}$ 7.5	8.13 (d, 6H) $^3J_{HH}$ 7.5	8.94 (m, 8H)
3	—	2.71 (s, 9H)	—	5.05 (br, 1H)	7.18 (dd, H) $^3J_{HH}$ 8.2 $^4J_{HH}$ 2.1	7.93 (dd, H) $^3J_{HH}$ 8.2 $^4J_{HH}$ 2.1	—	7.62 (d, 6H) $^3J_{HH}$ 7.8	7.98 (d, 6H) $^3J_{HH}$ 7.8	8.77 (m, 4H) 8.80 (d, 2H) $^3J_{HH}$ 4.7 8.86 (d, 2H) $^3J_{HH}$ 4.7
4	—	2.70 (s, 9H)	4.02 (s, 3H)	6.06 (br, 1H)	7.28 (d, H) $^3J_{HH}$ 8.0	7.61 (dd, H) $^3J_{HH}$ 8.0 $^4J_{HH}$ 2.0	7.50 (d, H) $^4J_{HH}$ 2.0	7.52 (d, 6H) $^3J_{HH}$ 7.6	7.93 (d, 6H) $^3J_{HH}$ 7.6	8.79 (m, 4H) 8.80 (d, 2H) $^3J_{HH}$ 4.9 8.83 (d, 2H) $^3J_{HH}$ 4.9
5	-2.74 (s, 2H)	2.74 (s, 9H)	—	—	7.71 (dd, 2H) $^3J_{HH}$ 8.5 $^4J_{HH}$ 2.1	8.29 (dd, 2H) $^3J_{HH}$ 8.5 $^4J_{HH}$ 2.0	—	7.60 (d, 6H) $^3J_{HH}$ 7.7	8.13 (d, 6H) $^3J_{HH}$ 7.7	8.80 (d, 2H) $^3J_{HH}$ 4.7 8.91 (m, 4H) 8.95 (d, 2H) $^3J_{HH}$ 4.7
6	-2.74 (s, 2H)	2.74 (s, 9H)	4.01 (s, 3H)	—	7.69 (d, H) $^3J_{HH}$ 8.5	7.84 (dd, H) $^3J_{HH}$ 8.5 $^4J_{HH}$ 2.1	7.88 (d, H) $^4J_{HH}$ 2.1	7.59 (d, 6H) $^3J_{HH}$ 7.5	8.13 (d, 6H) $^3J_{HH}$ 7.5	8.84 (d, 2H) $^3J_{HH}$ 4.8 8.90 (m, 4H) 8.93 (d, 2H) $^3J_{HH}$ 4.8
7	—	2.75 (s, 9H)	—	—	7.68 (dd, 2H) $^3J_{HH}$ 8.5 $^4J_{HH}$ 2.1	8.08 (dd, 2H) $^3J_{HH}$ 8.5 $^4J_{HH}$ 2.1	—	7.51 (d, 6H) $^3J_{HH}$ 7.6	7.92 (d, 6H) $^3J_{HH}$ 7.6	8.68 (d, 2H) $^3J_{HH}$ 4.9 8.79 (m, 4H) 8.81 (d, 2H) $^3J_{HH}$ 4.9
8	—	2.77 (s, 9H)	3.99 (s, 3H)	—	7.58 (d, H) $^3J_{HH}$ 7.9	7.62 (dd, H) $^3J_{HH}$ 7.9 $^4J_{HH}$ 2.3	7.66 (d, H) $^4J_{HH}$ 2.3	7.50 (d, 6H) $^3J_{HH}$ 7.8	7.91 (d, 6H) $^3J_{HH}$ 7.8	8.73 (d, 2H) $^3J_{HH}$ 4.9 8.79 (m, 4H) 8.81 (d, 2H) $^3J_{HH}$ 4.9

2,4,4,6,6-pentachloro-2-[5,10,15-tris(4-methylphenyl)-porphyrinatonickel(II)-20-(4-phenoxy)]-cyclo-2λ^5,4λ^5,6λ^5-triphosphaza-1,3,5-triene [TPPPNi], (7) and 2,4,4,6,6-pentachloro-2-[5,10,15-tris(4-methylphenyl)-porphyrinatonickel(II)-20-(3-methoxy-4-phenoxy)]-cyclo-2λ^5,4λ^5,6λ^5-triphosphaza-1,3,5-triene [TPMPPNi], (8). To a solution of **3** (0.10 g, 0.13 mmol) in dry THF (20 mL) was added NaH (60%

Table 3. UV-vis (in $CHCl_3$) data of **1**–**8**

Compound	Colour	λ_{max}, nm ($\varepsilon \times 10^4$ $M^{-1}.cm^{-1}$)				
		Soret band	Q bands			
1	purple	418 (130.0)	518 (4.7)	552 (2.2)	594 (0.8)	650 (0.8)
2	purple	420 (87.0)	518 (4.7)	552 (3.2)	594 (2.4)	648 (2.4)
3	claret red	416 (94.0)	528 (6.6)	—	—	—
4	claret red	416 (92.7)	528 (6.6)	—	—	—
5	purple	418 (110.4)	516 (3.6)	552 (1.5)	594 (0.7)	650 (1.3)
6	purple	420 (130.3)	514 (4.6)	552 (2.0)	592 (0.1)	648 (0.8)
7	claret red	416 (75.0)	528 (4.3)	—	—	—
8	claret red	416 (46.5)	528 (2.5)	—	—	—

suspension in paraffin oil) (5.2 mg, 0.13 mmol) and the mixture was stirred at room temperature. A stirred solution of $N_3P_3Cl_6$ (0.05 mg, 0.13 mmol) in THF (5 mL) was added and the mixture was stirred at -10 °C for over 4 h. The solvent was evaporated completely and the residue was subjected to column chromatography first with *n*-heptane and then toluene. Claret red powder of compound **7** was obtained and was crystallized from toluene. The same procedure was used for the synthesis of porphyrino-phosphazene complex (**8**) from porphyrin complex (**4**). Yield [**TPPPNi**], (**7**): 110 mg (71%), mp > 300 °C, R_f = 0.93 (CH_2Cl_2). Anal. calcd. for $C_{47}H_{33}N_7OP_3Cl_5Ni$: C, 54.24; H, 3.20; N, 9.42%. Found: C, 54.39; H, 3.43; N, 9.29%. IR (KBr): ν, cm^{-1} 3060;3022 (C-H arom.), 2922;2852 (C-H aliph.), 1602 (C=N), 1211 (P=N), 1004 (C-N), 796 (β-pyrrole C-H), 596;525 (P-Cl). MS (ESI): *m/z* (based on ^{35}Cl, %) 1038 ([M + H]$^+$, 0.3). Yield [**TPMPPNi**], (**8**): 117 mg (73%), mp > 300 °C, R_f = 0.86 (CH_2Cl_2). Anal. calcd. for $C_{48}H_{35}N_7O_2P_3Cl_5Ni$: C, 53.84; H, 3.29; N, 9.16%. Found: C, 54.31; H, 3.07; N, 8.82%. IR (KBr): ν, cm^{-1} 3055;3020 (C-H arom.), 2920;2855 (C-H aliph.), 1596 (C=N), 1211 (P=N), 970 (C-N), 798 (β-pyrrole C-H), 604;527 (P-Cl). MS (ESI): *m/z* (based on ^{35}Cl, %) 1068 ([M + H]$^+$, 1).

RESULTS AND DISCUSSION

Synthesis

Preparation of the new porphyrinato-phosphazene-Ni(II) complexes (**7** and **8**) was accomplished in a two-step process (Scheme 1). The first pathway (i) involves the complexation of **1** and **2** with $Ni(OAc)_2$ in boiling DMF to afford the corresponding complexes, **3** and **4**. The second pathway (ii) involves the condensation reactions of **3** and **4** with $N_3P_3Cl_6$ in dry THF at -10 °C to produce new porphyrinato-phosphazene-Ni(II) complexes (**7** and **8**), respectively. On the other hand, the other synthetic route (iii) involves the condensation reactions of **1** and **2** with $N_3P_3Cl_6$ in dry THF at -10 °C to give free porphyrino-phosphazene ligands, **5** and **6**. The crude products after evaporating the solvent in the reduced pressure were purified by column chromatography on silica gel. The synthetic and analytical data of the new compounds **5**–**8** are given in the experimental part. Elemental analyses, FTIR, ESI-MS, UV-vis, ^{31}P and ^1H NMR data are consistent with the proposed structures. The MS spectra of the compounds show molecular ion $[M]^+$ (for **1**) and protonated molecular ion $[M+H]^+$ (for **2**–**8**) peaks.

IR spectra

The FTIR spectra of all the compounds exhibit two weak intensity absorption bands at 3065–3051 cm^{-1} and 3024–3017 cm^{-1}. These are attributed to the asymmetric and symmetric stretching vibrations of the aromatic C-H bonds. All the porphyrino-phosphazene derivatives display the intense characteristic bands between 1211–1203 cm^{-1} and 1007–966 cm^{-1} corresponding to the $\nu_{P=N}$ of the phosphazene skeleton and ν_{C-N} of the porphyrin ring, respectively. The compounds (**1**, **2**, **3** and **4**) and (**1**, **2**, **5** and **6**) exhibit absorption bands for ν_{O-H} and ν_{N-H} in the range of 3510–3503 cm^{-1} and 3317–3311 cm^{-1}, respectively. The characteristic stretching bands for ν_{O-H} disappear in the FTIR spectra of porphyrino-phosphazene derivatives and their complexes (**5**–**8**); ν_{N-H} stretching bands disappear in the spectra of all the nickel(II) complexes (**3**, **4**, **7** and **8**).

^{31}P and ^1H NMR spectra

The ^1H-decoupled ^{31}P NMR data of all the porphyrino-phosphazene derivatives are listed in Table 1. The spin systems are interpreted as simple AX_2 from the ^{31}P NMR spectra. Chemical shifts and coupling constants of free porphyrino-phosphazene ligands (**5** and **6**) and their nickel(II) complexes (**7** and **8**) are very near each other; the average values are 13.74 ppm for δ_{POCl}, 21.76 ppm for δ_{PCl_2} and 60.3 Hz for $^2J_{PP}$.

In all of the new porphyrino-phosphazene ligands and their complexes, the ^1H NMR signals have been assigned on the basis of chemical shifts, multiplicities,

and coupling constants (Table 2). The NH protons of **1**, **2**, **5** and **6** resonate as singlet. The average value is -2.72 ppm. These NH peaks disappear in the spectra of the porphyrinato complexes (**3**, **4**, **7** and **8**). In addition, broad OH peaks at 6.06–5.02 ppm for (**1**–**4**) disappear in the spectra of the porphyrino-phosphazene ligands (**5** and **6**) and their complexes (**7** and **8**).

UV-vis spectra

Figures 1 and 2 depict UV-vis spectra of all the compounds. The UV-vis spectral data are summarized in Table 3. The well-known Soret bands are observed at *ca*. 418 nm, common for all porphyrin derivatives [31]. Of the four less-intensive Q bands at about 517, 551, 592 and 648 nm which are observed in the electronic spectra of the free ligands (**1**, **2**, **5** and **6**), the last three bands disappear in the spectra of the complexes (**3**, **4**, **7** and **8**). In addition, the β-bands characteristic of metalloporphyrins are observed at 528 nm for the Ni(II) complexes (**3**, **4**, **7** and **8**) [32]. It is noteworthy to point out that the UV-vis absorptions of the free ligands are mainly attributable to the porphyrin skeleton. However, one can conclude that no significant changes occur in the free ligands conjugated π-electronic systems. In other words, the phosphazene ring does not affect the porphyrin π-conjugated systems, as is observed in the electrochemical behavior below.

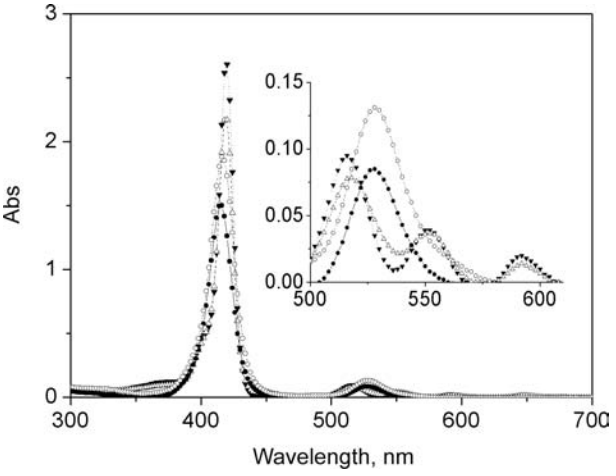


Fig. 1. The UV-visible spectra of **1** (Δ), **3** (○), **5** (▼) and **7** (●)

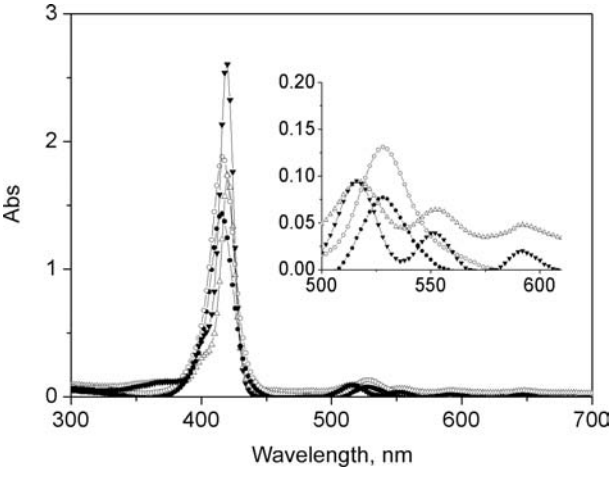


Fig. 2. The UV-visible spectra of **2** (Δ), **4** (○), **6** (▼) and **8** (●)

Electrochemistry of porphyrino-phosphazene derivatives

The anodic oxidation of tetraphenylporphyrins in either free ligand or metalloform leads to the polymerized insoluble thin films on the glassy carbon electrode in MeCN (containing 0.1 M TBATFB). Figure 3(a) shows the consecutive voltammograms of 2,4,4,6,6-pentachloro -2-[5,10,15-tris(4-methylphenyl)-porphyrin-20-(4-phenoxy)]-cyclo-2λ^5,4λ^5,6λ^5-triphosphaza-1,3,5-triene (**5**) (TPPP) as a representative ligand bearing phosphazene ring. The first two irreversible peaks are related to the oxidation of porphyrin ring, forming first π-cation radical (P1) and then the oxidation of π-cation to dication in solution (P2) [33, 34].

To aid understanding of the influence of the presence of metal within the porphyrin ring, the electrochemistry of TPPPNi (**7**) was also investigated. The striking influence of the presence of nickel(II) in the porphyrin ring is the inhibition of P1 and P2 peaks corresponding to the formation of π-cation $[TPPP]^{+\cdot}$ and dication of the free ligand ($[TPPP^{2+}]$), respectively (Fig. 3(a)). The third oxidation peak (P3) around +2.2 V is common in both voltammograms of free ligand and metalloporpyrin. This indicates that the third peak is related to the oxidation of pheripheral phenyl groups rather than the central porphyrin ring, forming cation radicals, $[TPPP^{2+}]^{+\cdot}$ and $[TPPPNi]^{+\cdot}$, for free ligand and nickel(II) complex, respectively. Another common aspect of both voltammograms is the suppression of the wave in the successive scans after the first one, due to the formation of electroinactive film at the GC surface. The suppression of the oxidation wave in the successive scans is a well-known behavior of electroinactive films gradually formed on the conductive substrates [35]. It should be emphasized that electrochemical deposition is not observed when the potential scan is performed in the anodic potential range between 0 V and +0.7 V as well as between 0 V ad +1.3 V, as is shown in the insets of Fig. 3(a). This suggest that covalent bond is not formed until the generation of $[TPPP^{2+}]^{+\cdot}$ and $[TPPPNi]^{+\cdot}$ radicals that attack the graphitic structure of the glassy carbon surface.

This behavior at GC seems contrary to that reported in the literature for a free porphyrin base molecule and metalloporphyrin at the Pt surface [33]. When reaching the P3 peak potential, peripheral phenyl groups of porphyrin are oxidized, leading to the formation of polymer in solution and deposition to the Pt electrodes. In the case of GC surface, a covalent bond is formed by the attack of the cation radicals of ligand and the complex with the graphitic structure of the GC surface. Although the electrodeposited porphyrin polymer is electroactive on the Pt, covalently bonded porphyrin film is not at the GC surface.

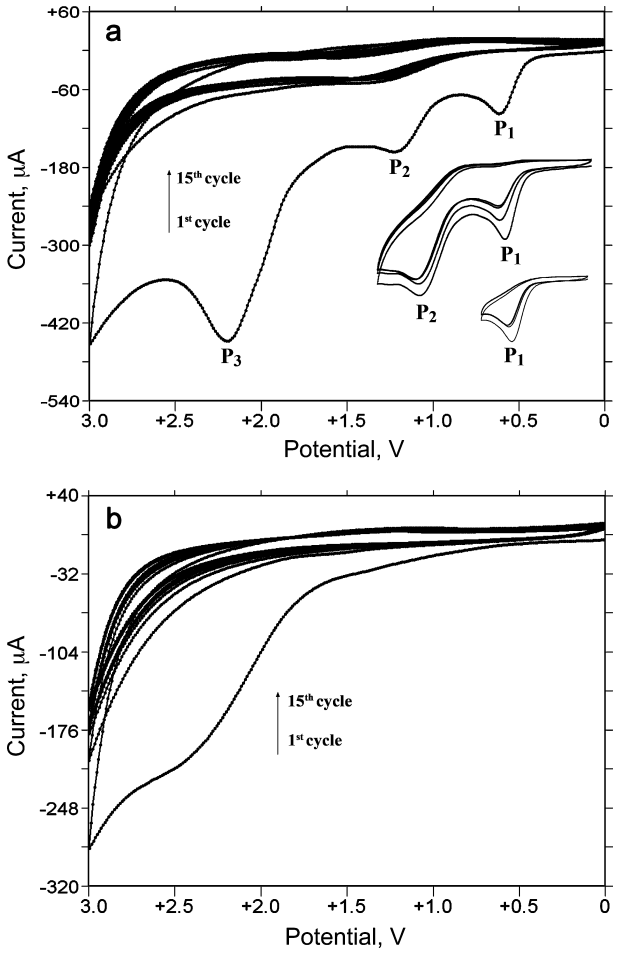


Fig. 3. (a) Cyclic voltammograms of TPPP (**5**) and (b) of TPP-PNi (**7**) on GC in MeCN (0.1 M TBATFB) with 10 cycles *vs.* $Ag/AgNO_3$ (0.01 M). Scan rate is 200 $mV.s^{-1}$

This behavior can be inferred from the blocking effect in the successive scans of anodic oxidation of TPPP (**5**) and TPPPNi (**7**) (Fig. 3) [35].

Another important inference is that the phosphazene substituents do not change the electrochemical behavior of the π-conjugated porphyrin ring, as is observed in the UV-vis spectra as indicated above. Recurrent voltammograms of compounds THP (**1**) (without phosphazene) and TPPP (**5**) (with phosphazene) show three peaks in the same potential range, indicating that kinetics and energetic of the reduction is similar.

CONCLUSION

In this study, new porphyrino-phosphazene ligands (**5** and **6**) and their Ni(II) complexes (**7** and **8**) were obtained. These ligands and the complexes are examples of porphyrino-phosphazene derivatives. The structural investigations of all the compounds have been made by using spectroscopic techniques. Electrochemical behavior of the compounds shows that the presence of metal cation in the porphyrin ring leads to the inhibition of the oxydation of the central porphyrin ring, and that the phosphazene derivative does not influence the oxydation mechanism. The solubility of porphyrino-phosphazene ligands (**5** and **6**) and their complexes (**7** and **8**) in common organic solvents are much higher than the porphyrin ligands (**1** and **2**) and their complexes (**3** and **4**). In the future, many new porphyrino-phosphazenes may be obtained from the chloride replacement reactions of the compounds **5**–**8** with organic substituents, such as primary and secondary amines, diamines, amino alcohols and diols.

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