

A new approach to *N*-phenylquinolino[2,3,4-*at*]porphyrins. Electrochemical and photochemical studies

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Dedicated to Professor Karl M. Kadish on the occasion of his 65th birthday

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ABSTRACT: A new route to *N*-phenylquinolino[2,3,4-*at*]porphyrins is described and the electrochemical and photochemical properties of the synthesized derivatives were investigated. The electrochemical studies (cyclic voltammetry and rotating disk voltammetry) of the free-base and the corresponding Ni, Cu and Pd complexes have shown that the presence of the phenyl group is responsible for the formation of stable radical cations. The capacity of the *N*-phenylquinolino[2,3,4-*at*]porphyrins to generate singlet oxygen was evaluated and some of them have promising features as photosensitizers.

KEYWORDS: π -extended porphyrin, Ullmann conditions, cyclic voltammetry, photosensitizer, singlet oxygen generation.

INTRODUCTION

The synthesis of extended π -conjugated molecules is still a very active field of research [1]. In the particular case of porphyrins, due to their chemical and physical properties, these extended aromatic molecules might be useful in areas such as photodynamic therapy [2], two-photon absorption [3], nonlinear optics [4] or photovoltaics [5]. Therefore, several research groups have focused on the synthesis and chemical transformation of porphyrins into new derivatives with improved features that may turn them into possible candidates for different applications.

Among the available synthetic tools for porphyrin functionalization [6], fusion of aromatic rings with the porphyrin nucleus [7] is the most obvious way to extend the molecule. This can be achieved intermolecularly by directly adding aromatic rings to the porphyrin core [8–12]. In a simpler approach, the *meso* aryl groups already present in the molecule can be fused to the porphyrin macrocycle. This last strategy can be repeated from one up to four times, because there are four *meso* positions available. These reactions have been widely used to introduce functionalities between pyrrole β -positions and *meso* aryl groups [13–16].

In this article, we describe the electrochemical properties of *N*-phenylquinolino[2,3,4-*at*]porphyrin H_2 -4 and of the corresponding complexes M-4 (M = Cu, Ni and Pd) (Chart 1). Their ability to generate singlet oxygen was estimated from the oxidation of cholesterol through UVvis and NMR techniques. These porphyrinic complexes can be obtained by metalation of the known H_2 -4 [15c]. Additionally, an alternative and easier route to those *N*-phenylquinolino[2,3,4-*at*]porphyrins, involving modified Ullmann amination conditions, is also reported.

EXPERIMENTAL

The ¹H NMR spectra were recorded at 300 MHz with a Bruker 300 spectrometer. $CDCl_3$ was used as solvent. The chemical shifts (δ) are expressed in parts per million

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Chart 1. Structures of the synthesized *N*-phenylquinolino-[2,3,4-*at*]porphyrins **4**

(ppm) and the coupling constants (*J*) in Hertz (Hz). The HRMS (ESI) were determined with a MicrOTOF Q spectrometer. The UV-vis spectra were recorded with a Agilent 8453 diode-array spectrophotometer in CH_2Cl_2 . Chromatographic separations were performed with silica gel (Merck, 230–400 mesh) or alumina (Merck, 70–230 mesh). Analytical TLC was carried out on precoated sheets with silica gel (0.2 mm thick, Macherey-Nagel). Dichloromethane and toluene were distilled from calcium hydride and from sodium metal, respectively. All other solvents and reagents were used without further purification.

Synthesis

The known nickel(II) complexes Ni-3 [15c] and Ni-5 [15a] were prepared according to previously published procedures.

Preparation of Ni-4. A solution of Ni-3 [15c] (83.4 mg, 110 μ mol) in nitrobenzene (5 mL) was refluxed for 19 h. After cooling, the reaction mixture was poured on the top of a silica gel column, and the nitrobenzene was eluted with cyclohexane. The reaction products were then eluted using a 2/3 mixture of cyclohexane/dichloromethane. Crystallization from dichloromethane/methanol afforded Ni-4 as a green solid in 79% (65.8 mg). ¹H NMR (300 MHz; CDCl₃; 50 °C): $\delta_{\rm H}$, ppm 7.43 (1H, dd, J = 8.0 and 1 Hz, cyclized Ph), 7.52–7.82 (16+1H, m, H-Ph and H-3), 7.89–7.92 (2H, m, H_{artha}-Ph), 7.96–8.00 (2H, m, H_{ortho}-Ph), 8.03-8.06 (2H, m, H_{ortho}-Ph), 8.53 $(1H, d, J = 5.0 \text{ Hz}, \beta$ -pyrr), 8.58–8.61 (2H, m, β -pyrr), 8.61 (1H, d, J = 5.0 Hz, β -pyrr), 8.85 (1H, d, J = 5.0Hz, β -pyrr), 8.96 (1H, dd, J = 7.7 and 1 Hz, cyclized Ph), 9.48 (1H, d, J = 5.0 Hz, β -pyrr). UV-vis (CH₂Cl₂): λ_{max} , nm (ϵ , M⁻¹.cm⁻¹) 426 (140800), 454 (sh, 118700), 556 (3100), 601 (19500), 633 (34000). HRMS (ESI): m/z 759.1913 (calcd. for NiC₅₀H₃₁N₅ [M]^{•+} 759.1927).

Alternative preparation of Ni-4. A solution of Ni-5 [15a] (54.7 mg, 80 μ mol), iodobenzene (33 μ L, 88 μ mol, 1.1 equiv.), CuI (1.5 mg, 8 μ mol, 0.1 equiv.), L-proline (1.9 mg, 16 μ mol, 0.2 equiv.) and K₂CO₃ (22.1 mg, 160 μ mol,

2 equiv.) in dimethylsulfoxide (3 mL) was heated under argon at 90 °C for 4 h. After cooling, addition of dichloromethane and several washings with water, the solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: cyclohexane/dichloromethane 2/3). Crystallization from dichloromethane/ methanol afforded **Ni-4** as a green solid in 66% yield (39.9 mg).

Demetalation of Ni-4. To a solution of **Ni-4** (82 mg, 110 µmol) in trifluoroacetic acid (1.5 mL) was added concentrated sulfuric acid (1.5 mL). After 45 min of vigorous stirring, the reaction mixture was poured on ice and, after addition of dichloromethane, neutralized with a saturated aqueous solution of sodium hydrogenocarbonate. The organic phase was then washed twice with water and dried on sodium sulfate. Filtration through a short silica gel column and crystallization from dichloromethane/ methanol afforded **H**₂-**4** as a green solid, identical to a pure sample [15c], in almost quantitative yield (78 mg). UV-vis (CH₂Cl₂): λ_{max} , nm (ϵ , M⁻¹.cm⁻¹) 413 (151500), 453 (81900), 594 (20300), 612 (19900), 665 (17700).

Preparation of Cu-4. To a solution of H₂-4 (27 mg, 39 μmol) in toluene (20 mL) was added Cu(OAc)₂ (10 mg, 57 μmol, 1.5 equiv.). This reaction mixture was refluxed under argon for 19 h. The solid residue obtained after evaporation of the toluene was then filtered through a short alumina column (eluent: cyclohexane/dichloromethane 1/1). Crystallization from dichloromethane/ methanol afforded the green solid **Cu-4** in 92% yield (28 mg). UV-vis (CH₂Cl₂): λ_{max} , nm (ε, M⁻¹.cm⁻¹) 405 (76000), 458 (168400), 563 (10100), 606 (14400), 637 (29700). HRMS (ESI): *m/z* 764.1872 (calcd. for CuC₅₀H₃₁N₅ [M]^{*+} 764.1870).

Preparation of Pd-4. A solution of H₂-4 (27 mg, 39 μ mol) and Pd(acac)₂ (19 mg, 62 μ mol, 1.6 equiv.) in toluene (20 mL) was refluxed under argon for 40 h. After evaporation of the toluene, filtration through a short alumina column (eluent: cyclohexane/dichloromethane 1/1) and crystallization from dichloromethane/methanol, the green Pd-4 was isolated in 95% yield (30 mg). ¹H NMR (300 MHz; CDCl₃; 50 °C): $\delta_{\rm H}$, ppm 7.54 (1H, dd, J =8.5 and 1 Hz, cyclized Ph), 7.61-7.92 (16+1H, m, H-Ph and H-3), 8.05-8.08 (2H, m, H_{ortho}-Ph), 8.12-8.16 (2H, m, Hortho-Ph), 8.20-8.23 (2H, m, Hortho-Ph), 8.63 (1H, d, J = 5.1 Hz, β -pyrr), 8.71 (1H, d, J = 5.1 Hz, β -pyrr), 8.70–8.73 (2H, m, β –pyrr), 8.93 (1H, d, J = 5.3 Hz, β -pyrr), 9.38 (1H, dd, J = 8.5 and 1 Hz, cyclized Ph), 9.72 (1H, d, J = 5.3 Hz, β -pyrr). UV-vis (CH₂Cl₂): λ_{max} , nm $(\epsilon, M^{-1}.cm^{-1})$ 409 (112700), 446 (98000), 467 (111300), 527 (6800), 552 (9900), 594 (17700), 627 (33000). HRMS (ESI): *m/z* 807.1631 (calcd. for PdC₅₀H₃₁N₅ [M]^{•+} 807.1609).

Photochemical tests

Using a slide projector lamp (250 W), light was filtered by passing through an aqueous potassium dichromate solution ($\lambda > 510$ nm). A solution of the chromophore (10⁻⁵ M) and cholesterol (2 × 10⁻³ M) in benzene (20 mL) was irradiated for 4 h at room temperature. The porphyrin decomposition was evaluated by comparison of the initial and final electronic spectra of the solution. After evaporation of the benzene and drying, the ¹H NMR spectrum was recorded in CDCl₃ and the amount of oxidized cholesterol was determined by integration of the olefinic protons of the product resulting from the ene reaction *vs.* cholesterol. The initial cholesterol/sensitizer ratio being equal to 200, the turnover number is defined as the number of moles of cholesterol oxidized per mole of sensitizer.

Electrochemical studies

The electrochemical measurements were carried out in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 in a classical threeelectrode cell by cyclic voltammetry (CV) and rotatingdisk voltammetry (RDV). The working electrode was a glassy carbon disk (3 mm in diameter), the auxiliary electrode a Pt wire, and the pseudo reference electrode a Pt wire. The cell was connected to an Autolab PGSTAT30 potentiostat (Eco Chemie, Holland) driven by a GPSE software running on a personal computer. All potentials are given *vs.* Fc/Fc⁺ (ferrocene/ferrocinium) used as internal standard and are uncorrected from ohmic drop. The spectroelectrochemistry was carried out with a homemade electrochemical cell fitted with a thin part allowing recording of the electronic spectra. The working electrode was a platinum grid located in the thin part of the cell.

RESULTS AND DISCUSSION

Synthesis

The *N*-phenylquinolino[2,3,4-*at*]porphyrin H_2 -4 was initially obtained by a synthetic route developed by some of us, involving the following steps: (i) β -pyrrolic nitration of the 5,10,15,20-tetraphenylporphyrin with copper nitrate [17, 18], (ii) synthesis of the corresponding Ni complex, after demetalation of the copper derivative, (iii) reduction of the nitro group with tin powder to afford the (2-amino-5,10,15,20-tetraphenylporphyrinato)nickel(II) [18], (iv) arylation of this amine with bromobenzene using Buchwald-Hartwig conditions, (v) demetalation and (vi) cyclization in nitrobenzene [15c]. Herein, it was verified that the final cyclization reaction might also be performed starting directly from the nickel complex Ni-3 (Scheme 1, route a), giving the Ni-4 porphyrin in excellent yield (79%).



Scheme 1. Preparation of the nickel porphyrin Ni-4



Scheme 2. Cholesterol oxidation by singlet oxygen

Knowing that the treatment of the easily accessible (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) 1 with triethyl phosphite is a very efficient route to prepare the nickel(II) complex Ni-5 [15a] (Scheme 1, route b), prompted us to examine the possibility of using this compound as starting material to obtain N-phe nylquinolino[2,3,4-at]porphyrins. The desired Ni-4 porphyrin was obtained under Ullmann amination conditions [19], by adding copper iodide, L-proline, potassium carbonate [20] and iodobenzene to a solution of Ni-5 in dimethylsulfoxide. Heating this mixture for 4h afforded in a rather good yield (66%) the expected Ni-4 fused derivative (see Scheme 1, route b). Using this alternative approach, Ni-4 can be prepared

in only two steps, just as efficiently as by the formerly published procedure [15c]. All attempts to obtain Ni-4 using the previous Buchwald-Hartwig amination reaction conditions [Pd(II) + rac-BINAP + base] for the arylation of the secondary amine (formally an enamine) Ni-5 were unsuccessful.

The demetalation of Ni-4 by treatment with a trifluoroacetic acid/sulfuric acid solution for less than 1 h gave the free-base H_2 -4 in almost quantitative yield. This free-base was then metalated by standard methods [21], affording the desired Pd-4 and Cu-4 complexes in very good yields.

Photochemical experiments

Since compounds **4** absorb strongly at wavelengths higher than 600 nm (see Fig. 1), we checked their efficiency to generate singlet oxygen by using cholesterol oxidation as a test reaction (see Scheme 2) [22].



The results of these experiments are summarized in Table 1. 5,10,15,20-Tetraphenylporphyrin (H_2TPP) was used as the reference compound. The palladium complex Pd-4 (entry 5: 56 turnovers in 4 h of irradiation) was an excellent singlet oxygen generator when compared to H₂TPP (entry 1: 12 turnovers in 4 h of irradiation). Moreover, Pd-4 is highly stable under irradiation conditions, as shown by the fact that its electronic spectrum taken after irradiation was superimposable with the starting spectrum. Even after 8 h of irradiation, only 8% of decomposition was detected and the turnover number was 104. The results with the copper complex Cu-4 are comparable with those obtained for the reference H₂TPP. The nickel complex Ni-2, as expected, was photochemically inactive. The free-base H_2 -4 (entry 2) was found to be three times more active than the reference H_2TPP ; however, H_2 -4 was less stable than its metallo counterparts under similar irradiation conditions (20% of decomposition after 4 h of irradiation).

Table 1. Photochemical oxidation of cholesterol by different chromophores

Chromophore	λ_{max} (ϵ in benzene)	Turnover number ^a (after 4 h of irradiation)	% chromophore decomposition	
H ₂ TPP	648 (3400)	12	< 2	
H ₂ -4	665 (23000)	31	20	
Ni-4	632 (39000)	0	< 1	
Cu-4	636 (37000)	12	< 3	
Pd-4	626 (39000)	56	< 4	

Experimental conditions: 20 mL benzene, 2×10^{-3} M cholesterol, 10^{-5} M chromophore, 250 W ($\lambda > 510$ nm), 4 h of irradiation, cholesterol/chromophore = 200. ^a The turnover number is defined as the number of moles of cholesterol oxidized per mole of sensitizer.

Compound	E°_{red2}	$\rm E^{\circ}_{red1}$	E° _{ox1}	E° _{ox2}	E° _{ox3}	E° _{ox1} -E° _{red1}
Ni-4	-2.17 (85) ^b	-1.78 (70)	0.16 (75)	0.57 (75)	1.15 (90)	1.94
H ₂ -4	-1.98 (70) ^b	-1.65 (60)	0.17 (75)	0.47 (60)		1.82
Cu-4	-2.15 (90)	-1.79 (70)	0.14 (70)	0.53 (90)		1.93
Pd-4	-2.12 (90)	-1.71 (60)	0.24 (60)	0.65 (60)		1.95
Ni-5°	-2.04	-1.64	0.32	0.63	1.20	1.96

Table 2. Cyclic voltammetry data for the *N*-phenylquinolino[2,3,4-*at*]porphyrin derivatives 4 and Ni-5^a

^a Measured in dichloromethane containing 0.1 M Bu_4NPF_6 . Potentials are given *vs*. the couple Fc/Fc⁺ and in parentheses the peak separation at 0.1 V/s. See Experimental section for details. ^b Reversible if rate > 2 V/s.

° Taken from Ref. 15a.

Electrochemical studies

The structural features shown by the *N*-phenylquinolino-[2,3,4-*at*]porphyrins **4**, namely the presence of a triarylamine partly included in the aromaticity of the porphyrins, prompted us to study the electrochemical properties of this porphyrin series. It is well known that triarylamines give stable radical cations (for example, the tris-4-bromophenylamminium is commercially available). Therefore, all of the derivatives of **4** were studied by cyclic voltammetry (CV) and by rotating disk electrode (RDV). The results of the cyclic voltammetry experiments in dichloromethane are summarized in Table 2. The RDV experiments confirmed the CV data.

Due to the similar electronegativities of Cu and Ni (1.90 and 1.91), the electrochemical behavior of Cu-4 and Ni-4 derivatives were almost identical. However, in the case of Ni-2, a third oxidation was observed at a rather high potential ($E^\circ = 1.15$ V). The first two oxidations are generally assigned to the oxidation of the macrocyclic core [23]: from the neutral species Ni-2 to the radical-cation and then to the dication; the nickel formally stays in the Ni(II) state. The third oxidation might correspond

to the oxidation of Ni(II) to Ni(III), but it was difficult to confirm this spectroscopically due to the proximity to the solvent's oxidation (see Fig. 2). Reversible one-electron transfers were observed, except for the second reduction step of H_2 -4 and Ni-4. At these very cathodic potentials, the generated dianions might react with protons (from residual traces of water present in solution).

At higher scan rates, a reversible behavior was observed, indicative of a chemical follow-up reaction at lower scan rates. The **Pd-4** potential values are anodically shifted, when compared with those of **Ni-4** and **Cu-4**. In fact, for all compounds studied, the HOMO–LUMO gap, measured as the difference between the first reduction and the first oxidation potentials, was in very good agreement with the optical gap obtained from the energy of the lowest energy band from the electronic spectra.

Compounds Ni-4 and Ni-5 are very similar from a structural point of view and, as a consequence, their electronic data are also analogous. However, the addition of the phenyl group on the external nitrogen transforms the secondary amine in Ni-5 into a tertiary amine in Ni-4. This tertiary amine might even be described



Fig. 2. Cyclic voltammetry of Ni-4



Fig. 3. Spectroelectrochemical studies of Ni-4. Changes in absorbance during oxidation of Ni-4 (left side) and evolution observed during reduction of the generated species (right side)

as a triarylamine. During the previous electrochemical studies of **Ni-5**, despite the nice electrochemical reversibility observed in the cyclic voltammetry (at the usual scan rates of 0.1 V/s), the compound underwent chemical follow-up reactions during the spectroelectrochemical studies, making this first oxidation chemically irreversible [24]; the radical cation reacted if the time scale was longer than the CV recording time. Therefore, the first oxidation of compound **Ni-4** was studied carefully by spectroelectrochemistry to see if the addition of the phenyl group affected the electrochemical behavior.

In fact, the behavior was dramatically modified. The presence of a tertiary amine gave a nicely reversible first oxidation step not only on the cyclic voltammetry time scale, but also during the much longer time period needed to record spectroelectrochemical data (see Fig. 3). The chemical reversibility was also checked by thin layer chromatography before and after the oxidationreduction procedure.

Oxidation at a potential higher than that of the first oxidation wave recorded for Ni-4 derivative gave very nice spectral evolution over time. As expected for the generation of a radical cation, the intensity of the Soret band and the Q-bands decreased. Three new bands at lower energy appeared around 695, 750, and 895 nm. The radical-cation generated in this way was stable and the reduction of this species led quantitatively to the starting material Ni-4. The presence of an additional phenyl group on the nitrogen atom (compared to Ni-5 compound) was clearly the stabilizing factor. This observation is in good agreement with the known stability of triarylamminiums. The fact that the radical cation obtained from Ni-4 is stable contrary to the one generated from Ni-5 might be a good indication that the radical cation is localized on the external nitrogen atom or very close to it.

CONCLUSION

In conclusion, we have shown that the nickel(II) porphyrin complex **Ni-5** can be used as an efficient precursor, through a copper-mediated arylation, of the *N*-phenyl-quinolino[2,3,4-*at*]porphyrins **4**. The electronic properties, photostability and the efficiency to generate singlet oxygen suggest that some of these *N*-phenylquinolino[2,3,4-*at*] porphyrins might have adequate features for photochemical applications. The reported porphyrins are functionalized at their periphery by a nitrogen atom that connects the porphyrin core to a neighboring *meso*-phenyl group. A detailed electrochemical study revealed that the stability of the radical cation obtained after oxidation is strongly dependant on the nature of the substituent present on this external nitrogen atom.

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