Molecular Electrochemistry

Electrochemistry as an Attractive and Effective Tool for the Synthesis and Immobilization of Porphyrins on an Electrode Surface

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Abstract: Magnesium(II) 10-phenyl-5,15-*p*-ditolylporphyrin is easily and cleanly transformed by electrolysis. A nitro group is first introduced at the free *meso* position by anodic substitution. Hydrogenation into the amine is then carried out electrocatalytically under ambient conditions with water as a hydrogen supplier. The synthesized porphyrin under the nickel(II) form can be covalently grafted onto a platinum electroce by electrochemical reduction of the diazonium

Introduction

Owing to their essential role in natural processes such as photosynthesis and oxygen transport in blood,^[1] porphyrins have been the subject of intense research for many decades. At the same time, the synthesis of porphyrins still remains a delicate process, particularly in the case of complex substitution patterns. Although electrochemistry presents several advantages as a tool for synthesizing complex organic molecules,^[2] its use in porphyrin synthesis is rather limited and concerns the direct functionalization of the primarily formed macrocycle. Examples of reactions performed electrochemically are the metalation of the porphyrin ring,^[3] the oxidative coupling, which affords diverse types of directly linked polyporphyrins,^[4] or the nucleophilic anodic substitution by which a nucleophile is introduced on a peripheral position of the macrocycle by replacement of a hydrogen atom.^[5] However, none of these examples employs the electrochemical method in successive reactions that comprise a synthetic sequence.

In addition to these aspects of molecular synthesis, there is great interest in the integration of porphyrins into molecular devices designed for energy conversion, molecular electronics,

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201404314. It includes experimental procedures, characterization data, NMR spectra, electrochemical data, and UV/ Vis spectra. cation, generated in situ by a reaction of the nickel(II) aminoporphyrin with sodium nitrite and trifluoroacetic acid. The electrosynthesized thin film gives an electrochemical response typical of a porphyrin material. Films grown under our conditions have a maximum surface coverage of approximately 5×10^{-10} mol cm⁻². The modified electrode exhibits a reproducible electrochemical behavior and a good level of stability over potential cycling and exposition to air.

or sensing.^[6] In this context, the preparation of thin films of porphyrins on solid substrates calls for efficient methods to ensure that the specific properties of the molecule (physical and chemical) are transferred to the material. Among other techniques the electrochemical reduction of aryl diazonium salts has been proven to be efficient in forming organic monolayer films covalently grafted to the electrode surface.^[7] The attractiveness of this approach arises from the strong attachment of the film to the surface, the ability to control the layer thickness, and its tolerance toward other chemical functions on the aryl moiety. Concerning the mechanism, it is generally believed that a one-electron reduction of the aryl diazonium ion and the subsequent elimination of dinitrogen produce aryl radicals prone to attack the electrode material and result in the covalent bonding of the aryl group to the surface.^[7a,8] There are only two reports in the literature on the electrografting of porphyrin from diazonium precursors.^[7d,9] In all of them, the starting compound is derived from tetraphenylporphyrin, to which the N_2^+ function is added onto the *para* position of one or several phenyl substituents. Therefore, in the resulting modified electrode, the porphyrin is not grafted by itself onto the surface, but through a para-phenylene spacer. Starting with this observation, our conviction was that a direct linking could provide unique advantages that result from a more immediate interaction between the porphyrin and the electrode surface (for instance, a faster electron transfer to the electroactive porphyrin moiety). The main objective of the work presented herein was to achieve such a goal.

In this report, we will detail the selective and efficient transformation of a magnesium porphyrin that possesses an unsubstituted *meso* position, magnesium(II) 10-phenyl-5,15-*p*-ditolylporphyrin (Mg(PDTP); see the chemical structure in Scheme 1), into the corresponding amino-functionalized free base. The synthesis operates by nitration and hydrogenation, both of

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Scheme 1. Structure of the synthesized porphyrins. The 10-phenyl-5,15-*p*-ditolylporphyrinyl group is abbreviated as PDTP.

which are carried out electrochemically, with excellent yields. Later on, in the form of the nickel(II) complex, the aminoporphyrin is converted into the corresponding diazonium derivative. In situ reduction of the latter on platinum leads to electrode modification. The modified electrode response favors a direct linking to the surface of the nickel(II) porphyrin through the *meso* position.

Results and Discussion

Nitration at the meso position

Most commonly the nitration of aromatic compounds is realized by means of aromatic electrophilic substitution. The usual reactant is concentrated nitric acid that forms the NO_2^+ ion as the attacking entity.^[10] This reaction can also be performed electrochemically by means of anodic substitution.^[11] The advantages provided by the electrochemical method are the possibility of milder reaction conditions (in particular the use of a nonacidic medium), the minimization of waste (replacement of a chemical oxidizer by the anode), and in certain cases, better selectivities. The use of this method in the porphyrin series has already been reported once. Zinc octaethylporphyrin was converted into a mixture of the meso-mono- and -dinitrated derivatives by means of anodic oxidation in the presence of an excess amount of sodium nitrite.^[12] Thus the rather limited information on this subject led us to study the reaction on Mg(PDTP). The choice of this porphyrin representative was deliberate. In Mg(PDTP) a single meso position is available for reaction, and magnesium as the central metal atom is known to favor oxidation.^[13]

The electrochemical nitration of Mg(PDTP) was carried out at a controlled potential in a separated compartment cell in

the presence of a slight excess amount of NaNO₂ (3.4 equiv versus Mg(PDTP)). Lutidine was also incorporated prior to electrolysis (10 equiv). Indeed, in our recent work on porphyrin anodic substitution, we experienced that this hindered base favors the elimination of the proton at the reactive *meso* position.^[5a, 14] Under these conditions, the working potential was progres-

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sively increased from 0.00 V versus a saturated calomel electrode (SCE), at which point no current flowed through the circuit to 0.70 V, the point at which the reaction proceeded. Finally, the electrolysis was stopped after an uptake of two Faradays per mole of Mg(PDTP), in accordance with the stoichiometry of the expected reaction.

After appropriate treatment of

the crude electrolyzed solution (see all details in the Experimental Section and the Supporting Information), Mg(PDTP-NO₂) was isolated in 91% yield (Scheme 2), which is comparable to what is obtained with classical methods. Nitration at the meso position of porphyrins has been inventoried with a variety of reagents and conditions: concentrated HNO₃ in H₂SO₄, MeOH, or CHCl₃; NaNO₂ in CF₃COOH; NO₂⁻ in combination with an oxidizer, I_2 , Cu^{2+} , or $Ag^{+,[15]}$ Nevertheless, no reagent seems to be appropriate for universal use, and the reaction often lacks selectivity: the mono-nitrated product may be subject to subsequent nitration, either directly on the macrocycle or on peripheral phenyl substituents. Conversely, in the electrochemical nitration of Mg(PDTP), by means of potential control, the reaction is easily constrained at the first degree of substitution, and demetalation (accidental release of the magnesium) does not occur under these basic conditions.

The mechanism of the electrochemical reaction was investigated by voltammetry. Figure 1 shows the cyclic voltammogram of Mg(PDTP) in the potential range in which it is oxidized and its evolution upon consecutive addition of lutidine and NaNO₂.

With only Mg(PDTP) in acetonitrile that contained tetraethylammonium hexafluorophosphate (TEAPF₆) as the supporting electrolyte, two chemically reversible peak systems are observed (solid blue line, Figure 1), which led, respectively, to the cation radical (peak system O1/R1, $E_{1/2}$ =0.68 V) and the dication (peak system O2/R2, $E_{1/2}$ =1.03 V). Thus the response is typical of metalloporphyrins with a non-electroactive metal that undergoes two ring-centered one-electron transfers in oxidation.^[13]

The addition of 10 molar equivalents of lutidine in the analyzed solution induced important modifications in the CV (red dotted line, Figure 1). Although the first oxidation peak (O1')



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Scheme 2. Nitration reaction at the meso position of Mg(PDTP).



Figure 1. Cyclic voltammogram of Mg(PDTP) (0.5 mM) in 0.1 M TEABF₄/ CH₃CN: alone (solid blue line), and after consecutive addition of 10 equiv of lutidine (red dotted line) and 3.4 equiv of NaNO₂ (black dashed line). Working electrode: Pt disk ($\emptyset = 2$ mm); sweep rate: 100 mV s⁻¹; initial potential: 0.00 V versus SCE.

did not change its position, the peak current is multiplied by 1.25. Additionally, in the anodic scan, peak O1' is followed by a partially fused and less intense peak O2' ($E_{p,O2'}=0.80$ V). In fact, this evolution is highly reminiscent of what was previously observed with Zn(PDTP) by the addition of a base.^[4a] The new features on the cyclic voltammogram were proven to have come from the rapid formation of the simply linked dimer at the electrode by oxidative coupling at the hydrogenated *meso* position (see Scheme 3). Although we have no absolute proof



Scheme 3. Dimerization from oxidation at the meso position.



Scheme 4. Mechanistic possibilities for electrochemical nitration of Mg(PDTP) at the meso position.

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(as that is not the purpose of this work), the same electrode reaction seemed to occur with Mg(PDTP). Peak O2' in particular would be the voltammetric trace of the dimer formed near the electrode surface.

Upon supplemental addition of an excess amount of NaNO₂ (3.4 equiv) the cyclic voltammogram of Mg(PDTP) underwent further modifications (black dashed line curve on Figure 1): the first oxidation peak (O1") is slightly shifted towards a lower potential ($E_{p,O1'}-E_{p,O1''}=67$ mV). In fact, NO₂⁻ was oxidized simultaneously to Mg(PDTP) at the potential level of peak O1". Accordingly we have verified that NaNO₂ alone in acetonitrile (ACN) resulted in a chemically irreversible peak at $E_{pa} = 0.54$ V. That is coincident with the shoulder in the increase of peak O1". In agreement with previous reports, this oxidation of NO₂⁻ is expected to produce radical NO₂.^[15d, 16] Moreover, on the basis of the CV in Figure 1, by inverting the potential scan direction after O1", no cathodic peak was detected in the reverse sweep, which indicates a fast reaction of Mg(PDTP*+), but different from dimerization. Conversely, by continuing the oxidative scan after O1", two well-defined reversible peak systems, O2''/R2'' and O3''/R3'', appeared at $E_{1/2}$ =0.89 and 1.20 V. These systems correspond to the stepwise oxidation of Mg(PDTP-NO₂) (see below), which demonstrates that this product was formed instantaneously in the vicinity of the electrode.

As presented in Scheme 4, two mechanisms can be considered for the reaction. These reaction pathways were initially proposed for the nitration of magnesium octaethylporphyrin by nitrite in combination with an oxidant and both were sug-

gested to be relevant.[15d, 17] In path A, the metalloporphyrin is transformed into its π -cation radical Mg(PDTP)^{•+}, on which the addition of NO_2^- proceeds. Subsequent loss of an electron and a proton led to the final meso-nitrated metalloporphyrin Mg(PDTP–NO₂). Path B implies a parallel formation of nitrogen dioxide NO₂ and Mg(PDTP)⁺ by concomitant oxidation of NO2 and Mg(PDTP), followed by the coupling of these two radicals and loss of a proton to give $Mg(PDTP-NO_2)$.

Conversion into amine

Transformation of porphyrins that bear a nitro function in the *meso* position into the corresponding amino derivatives is frequently encountered in porphyrin chemistry. Two main routes are mentioned using: a) NaBH₄ as a reducer with palladium on carbon as a catalyst;⁽¹⁸⁾

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and b) SnCl₂ (reducer) in concentrated HCl.^[19] Furthermore, in the last thirty years, electrocatalytic hydrogenation has been recognized to be an appealing method for the selective hydrogenation of unsaturated organic substrates.^[20] The method provides mild and environmentally friendly conditions. Indeed, the reaction occurs in a mixture of MeOH and H₂O (the latter of which supplies hydrogen) at room temperature and ambient pressure and avoids using costly and/or deleterious metals (Pd, Sn). In particular, nitrated aromatics can be converted into the corresponding amines with competitive chemical and faradaic yields.^[21] The availability of Mg(PDTP–NO₂) provided us with the opportunity to test this electrosynthetic method on nitrated porphyrins as it had never been attempted before.

The conditions chosen for the electrolysis of Mg(PDTP–NO₂) were similar to those reported for the reaction of nitrobenzene,^[21f] among others, Devarda copper constituted the cathode material. The electrolysis was managed in two steps. First, in the pure supporting electrolyte solution the cathode was polarized at -1.20 V versus SCE over 20 min, thus provoking hydrogen evolution and allowing the electrode surface to reach saturation in adsorbed H₂. Then, the porphyrin was added (70 mg, 0.11 mmol) into the cathodic compartment. The working potential was set at -0.96 V, at which point the electrolysis occurred. Finally, the current dropped to zero after a charge of 6 F per one mole of Mg(PDTP–NO₂), as expected for the predicted reaction.

The magnesium aminoporphyrin thus produced has been proven to be sensitive to air. This high susceptibility to oxidation originates both from the peripheric amine and the inner magnesium, which together accentuate the electron-richness of the macrocycle. Therefore, immediately after the electrochemical reaction, Mg(PDTP-NH₂) was converted into the corresponding air-stable free base H₂(PDTP-NH₂) (Scheme 5). De facto, concentrated hydrochloric acid was added to the crude electrolyzed solution and further neutralization with sodium acetate afforded H₂(PDTP-NH₂). After other treatments (washing by liquid–liquid extraction, column chromatography) H₂(PDTP-NH₂) was isolated in its pure state in 80% yield, which is in the same range as the usual synthetic methods. The free base was then treated by nickel acetate in DMF under reflux conditions to afford the nickel(II) aminoporhyrin Ni(PDTP-NH₂) in view of its conversion into the corresponding diazonium derivative, the use of which allowed immobilization of the nickel porphyrin on electrode surfaces.

Thin films of nickel porphyrins have several attractive applications (e.g., microsensors for detection of nitric oxide release from single cells,^[6b] efficient materials for electrocatalytic oxidation of organics^[6a, d] including methanol, ethanol, hydrazine, and formaldehyde). Apart from the diazonium electrografting method, the literature mentions a wide range of approaches for the functionalization of surfaces by porphyrins. That inphysisorption,^[23] self-assembly chemisorption,^[22] cludes through tethered functional groups,^[24] thermolysis,^[25] click chemistry,^[26] oxidation of a peripheric terminal alkyne,^[27] and anodic polymerization.^[28] Otherwise the surface modification by electrochemical reduction of aryldiazonium salts offers several advantages:^[7c, 29] a) the ability to control the deposit (e.g., thickness, mono- or multilayer character of the film); b) compatibility with a wide range of materials and a great variety of reaction media; c) stability of the organic layer provided by the covalent attachment to the surface; d) ease of preparation of the diazonium salt from the amine precursor; and e) tolerance toward many kinds of functional groups on the aryl backbone. Therefore, in view of these advantages, the availability of Ni(PDTP-NH₂) provided the opportunity to test in this manner the direct grafting of the porphyrin onto electrode surfaces.

Electrografting and properties of the Pt-modified electrode

In situ generation of a porphyrin diazonium and subsequent electrografting on Pt

The nickel porphyrin diazonium Ni(PDTP–N₂⁺) was generated in 0.1 \mbox{M} TEABF₄/CH₃CN by reaction of Ni(PDTP–NH₂) with an excess amount of sodium nitrite (2 equiv NaNO₂) in the presence of a strong organic acid (0.5 \mbox{M} trifluoroacetic acid (TFA)). Multiple reaction conditions were attempted before finding the most adequate one (see the Experimental Section for details). In particular, a certain proportion of water (0.5%) must be incorporated to the reaction medium, probably to make NaNO₂ more soluble. The concentration of TFA was adjusted to avoid the possible demetalation of nickel porphyrin by means of acidolysis. The order of the TFA addition is also critical: the reaction worked much better when TFA was added afterwards instead of before or at the same time as NaNO₂.

Once the diazotation reaction was completed, the diazonium cation was reduced on the platinum electrode by means of multiple scan voltammetry. Figure 2b presents the cyclic voltammogram of the in situ generated compound recorded on a platinum electrode at 50 mV s⁻¹ with a potential scan that was initially made to go down.^[30] The first scan shows a sharp peak at E_{pc} =0.20 V that corresponds to the irreversible oneelectron reduction of the in situ generated diazonium cation,



Scheme 5. Electrocatalytic hydrogenation of the nitro group followed by in situ demetalation.

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similarly to what is generally observed for aromatic diazonium

molecules.^[7c] Over the following

scans the cathodic peak current

rapidly decreased in intensity in

accordance with the formation

of an insulating film blocking electron transfer between the

electrode and Ni(PDTP $-N_2^+$) in

solution. Then, after completion of this voltammetric deposition



Figure 2. a) Reaction scheme for in situ generation of the nickel(II) 5-phenyl-10,20-bis-*p*-tolylporphyrin diazonium from Ni(PDTP–NH₂) followed by electrochemical grafting on the platinum surface. b) The first five grafting scans on Pt of 1 mm Ni(PDTP–NH₂) after diazotation in 0.1 m TEABF₄/CH₃CN recorded at 50 mVs⁻¹ at (20±3) °C.

step, the modified Pt electrode was sonicated in DMF, or in CH_2CI_2 , and transferred to a blank electrolyte solution.

Characterization of the Pt-modified electrode

Cyclic voltammetry investigation

After rinsing, the Pt-modified electrode was characterized by cyclic voltammetry. The cyclic voltammograms reproduced in Figure 3a and b show three well-defined and chemically rever-



Figure 3. Cyclic voltammograms of a derivatized electrode a) reduction in 0.1 M TEABF₄/DMF and b) oxidation in 0.1 M TEABF₄/CH₂Cl₂ of Ni(PDTP)/Pt film prepared by thirty grafting cycles at a Pt electrode: second scan (solid line) and fifteenth scan (dotted line). Conditions: $\nu = 1 \text{ Vs}^{-1}$ at (20±3) °C. a', b') Plots of anodic and cathodic peak currents versus scan rate.

sible reduction and oxidation couples centered at $E_{1/2} = -1.35$ and -0.94 in DMF and at +1.28 V in CH₂Cl₂.^[31] In particular, the reductive response (explored in DMF) is not so straightforward, since the redox systems have unequal intensities (peak area ratio $R_{f}2/R_{f}3 = 0.36$ at 1 V s^{-1}). But the sum of the R_f2 and R_f3 peak areas is close to that of peak Of1 (peak area ratio $O_f 1/(R_f 2 + R_f 3) = 1.07)$. These voltammetric features show important similarities to the typical behavior of nickel porphyrins in solution. As a relevant representative, nickel tetraphenylporphyrin, Ni(TPP),^[32] gives rise to a oneelectron oxidation in CH₂Cl₂ $(E_{1/2} = 1.05 \text{ V} \text{ versus SCE})$ and a one-electron reduction in DMF $(E_{1/2} = -1.17 \text{ V versus SCE})$, both chemically reversible.[33] There-

fore, on the basis of the closeness of the potentials, we assume that the integrity of the porphyrin skeleton is retained in the electrodeposited film. Clearly, for the latter, the oxidation potential is higher, but this effect is typically encountered for densely packed porphyrin monolayers.^[34] Considering the splitting of the reduction signal, one possible explanation might be the existence in the film of two different electroactive porphyrin sites, which would be expressed at distinct potentials. As this phenomenon seems to be specific to DMF (no splitting of the oxidation signal in CH₂Cl₂), we suggest that, as a chemical differentiation between the two forms, some of the nickel porphyrins might be axially ligated by DMF and others preserved from this coordination. It is known from literature that nickel porphyrins, and more specifically Ni(TPP), can form adducts with nitrogenous bases,^[35] and the coordinative ability of DMF is well established.[36]

Control experiments were carried out using a polished Pt electrode, which was treated either by depositing $10 \,\mu$ L of a $1 \,m$ M Ni(PDTP--NH₂) solution and then dried under argon, or by soaking the Pt electrode for 24 h in this solution. The resulting electrodes did not show any voltammetric evidence of the attachment of porphyrin.

As expected for surface-immobilized electroactive species, for systems 1, 2, and 3 the peak currents are linearly dependent on the scan rates (see Figure 3a' and b'), and the ratio between the oxidation and reduction peak currents at any given scan rate is close to one. On the first cycle (not shown), the intensity of the reduction peaks is 10 and 12% larger than on the second one, probably because of the desorption of some noncovalently bonded porphyrin molecules. After the first cycle, the voltammograms are persistent for more than 70 cycles. The film redox processes were found to be strongly dependent on both the medium and the scan rate used for anal-

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ysis. The oxidation couple is chemically irreversible in CH₃CN and not observed in DMF, whereas the reduction couple does not appear in CH₂Cl₂ and is chemically irreversible in CH₃CN. Such dependence on the solvent of the modified electrode response was also mentioned by Downard, Moutet, and co-workers in the case of similar covalently bonded Ni-porphyrin films.^[9]

However, when Ni(PDTP) films were subjected to continuous cycling over the range 0.00 to -1.6 V in DMF at scan rate $\geq 1 \; V \, s^{-1},$ the redox system $O_f 2/R_f 2$ progressively decreased in current intensity before completely disappearing after 60 cycles, whereas the redox system Of3/Rf3 remained persistent (see the Supporting Information). This result seems to confirm that systems 2 and 3 are associated to distinct surface-bound species.

The stability of the Pt-modified electrodes when exposed to air was also investigated. As can be seen in Figure 4a, the



Figure 4. a) Cyclic voltammograms of a derivatized electrode in $CH_2CI_2 + 0.1 \text{ M}$ TEABF₄ on a platinum gauze working electrode (geometric area $S = 1 \text{ cm}^2$) recorded at 1 Vs^{-1} at $(20 \pm 3)^\circ \text{C}$: after grafting (solid line) and after two months (dashed line). b) Plots of surface concentration versus number of grafting cycles.

signal of the modified electrode persisted over time. No change could be detected with electrodes left on a laboratory bench top for two months or with electrodes exposed to vigorous ultrasonic cleaning in dimethylformamide, dichloromethane, or acetonitrile. These results point to a strong covalent bonding of the porphyrin moiety on the platinum surface rather than a mere adsorption.

Surface concentrations of electroactive nickel porphyrin groups were estimated on the basis of the charge associated with the film oxidation or reduction, in CH₂Cl₂ or DMF, respectively. Both redox processes gave similar results. The associated surface coverages (Γ) are calculated from Faraday's law [Eq. (1)]:

$$\Gamma = Q/nFS$$

in which Q is the charge obtained from the integration of the baseline corrected area under the oxidation or reduction peak, F is the Faraday constant (96485 $Cmol^{-1}$), n the number of electrons exchanged per electroactive molecule (here n=1 for both oxidation and reduction), and S the geometric area of the electrode (0.031 cm²).

Figure 4b presents the variation of Γ as a function of the number of grafting cycles. The larger increase is obtained on the first deposition voltammetric scan. Thereafter Γ continues to increase, but from scan to scan the variation becomes weaker. Finally, after 40 cycles, Γ reaches a value that nears the limit of $\Gamma_{\rm max}$ = (5.02 ± 0.06) × 10⁻¹⁰ mol cm⁻². This value compares quite well with those reported previously for other electrochemically fashioned covalently bonded porphyrin films.^[37,9,27] With regard to porphyrins grafted on surfaces, a relation has been established between Γ_{\max} and the orientation of the porphyrin plane relative to the surface. $^{\scriptscriptstyle [25,38]}$ In our case, the $\varGamma_{\rm max}$ value is in accordance with a monolayer structure of the film and a roughly perpendicular arrangement of the porphyrin to the surface.

Water contact-angle characterization

The water contact-angle characterization of modified electrodes gave additional evidence of the surface modification.^[39] In our case, the contact angle of a water droplet was increased from 50 to 75° by the electrode functionalization (see Figure 5). This result demonstrates that the porphyrin deposition provides a hydrophobic layer on the platinum substrate.



Unmodified Pt electrode

Figure 5. Photographs of a water droplet (10 µL) on the surface of a platinum plate working electrode before and after electrodeposition. The values of the contact angles are shown inside the images.

Conclusion

We have reported new electrochemical approaches for the functionalization of electrode surfaces by a porphyrin that bears a free meso position. In this manner, the nitro group is first introduced on the macrocyclic ring. In a second step, electrocatalytic hydrogenation affords the corresponding amino derivative. Both reactions are accomplished with competitive yields, thus making the electrochemical method very appealing in such circumstances. The aminoporphyrin, under the form of its nickel complex, is a convenient precursor suited for the electrografting of the porphyrin onto a platinum electrode surface. The process involves converting the aminoporphyrin into its diazonium cation through its reaction with sodium nitrite and trifluoroacetic acid. Further reduction by potential cycling delivers the modified electrode. The grafted film demonstrates

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a well-behaved electrochemical response, which indicates that the porphyrin structure is retained. Although further characterization will be necessary to obtain a formal proof, a direct bonding of the porphyrin to the electrode surface (with no linker between them) has been achieved. The specific electrode properties that are anticipated from such a particularity might be essential for developments in sensing and electrocatalysis.

Experimental Section

Reagents and instrumentation

Tetraethylammonium hexafluorophosphate (TEAPF₆; Fluka puriss., electrochemical grade, \geq 99.0%) and 2,6-lutidine (Aldrich, \geq 99%) were used as received. Tetraethylammonium tetrafluoroborate (TEABF₄) was synthesized by the following method. Typically, in a 500 mL Erlenmeyer flask, tetrafluoroboric acid (84.28 g; HBF₄; Sigma Aldrich, 48% H₂O) was mixed with a solution of tetraethylammonium hydroxide (193.84 g; TEAOH; Alfa Aesar, 35% H₂O). The reaction mixture was continuously stirred under an atmosphere of air. Then, a white precipitate formed after cooling the flask in an ice bucket and was filtered using a Buchner apparatus. Finally, the residue was crystallized from MeOH under reflux conditions, then cooled in a freezer at -18 °C, filtered on a Buchner, and dried at 110 °C in the stove for at least two days before use. CH₂Cl₂ (Carlo Erba 99.5%), CH₃CN (SDS, Carlo Erba, HPLC gradient 99.9%), and triethylamine (99%, Acros) were distilled from P₂O₅, CaH₂, and CaH₂ respectively. H₂(PDTP) was prepared as described in the literature.^[4a, 14]

UV/Vis absorption spectra were recorded using a Varian Cary UV/Vis spectrophotometer 50 scan using quartz cells (Hellma). In the spectroelectrochemical experiments, a UV/Vis immersion probe (Hellma, l=2 mm) was connected through a fiber optic to the same spectrophotometer.

Mass spectra were obtained using a Bruker ProFLEX III spectrometer (MALDI-TOF) with dithranol as a matrix or using a Bruker Micro-ToF Q instrument in ESI mode.

NMR spectra were measured using a Bruker 300 MHz spectrometer (Avance III Nanobay, Avance III, Avance II, respectively). The reference was the residual non-deuterated solvent.

All electrochemical manipulations were performed using Schlenk techniques under an atmosphere of dry oxygen-free argon at room temperature ($T = (20 \pm 3)$ °C). The supporting electrolyte was degassed under vacuum before use. Voltammetric analyses were carried out in a standard three-electrode cell using an Autolab PGSTAT 302N potentiostat connected to an interfaced computer that employed Electrochemistry Nova software. A double-junction SCE with background electrolyte between the two frits was used as reference electrode. The auxiliary electrode was a platinum wire in an independent compartment filled with the background electrolyte and separated from the analyzed solution by a sintered glass disk. For all voltammetric measurements, the working electrode was a platinum disk electrode ($\emptyset = 2 \text{ mm}$). Under these conditions, when operating in CH₃CN (0.1 M TEAPF₆) or in CH₂Cl₂ (0.1 M TEABF₄), the formal potential for the Fc^+/Fc couple was found to be +0.40 or +0.52 V versus SCE, respectively.

Bulk electrolyses were performed in a three-compartment cell separated by glass frits of medium porosity using an Amel 552 potentiostat coupled with an Amel 721 electronic integrator. A platinum grid was used as the working electrode, a platinum wire spiral (l=

53 cm, $\emptyset = 1$ mm) as the counter electrode, and a saturated calomel electrode as the reference electrode. The Devarda working electrode was prepared by co-deposition of Ni and Devarda alloy particles on a stainless-steel grid (3 cm×4 cm).^[40] Electrolyses were followed by TLC and UV/Vis absorption measurements.

Synthesis

Magnesium(II) 5,15-ditolyl-10-phenylporphyrin (Mg(PDTP)): H₂(PDTP) (200 mg, 0.35 mmol) and MgBr₂ (2.60 g) were dissolved in CH₂Cl₂ (50 mL) that contained triethylamine (4 mL, 80 equiv). The reaction mixture was stirred for 10 min at room temperature. The solution was then washed five times with distilled water (250 mL). After evaporation of the solvent, purification by column chromatography (alumina, 0 to 1% MeOH in CH₂Cl₂), and recrystallization from MeOH/H₂O, Mg(PDTP) was obtained in 80% yield (166 mg). ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): $\delta = 2.73$ (s, 6 H; CH₃), 7.59 (d, ³J = 7.8 Hz, 4H; m-tol), 7.71-7.79 (m, 3H; m-and p-Ph), 8.12 (d, ³J= 7.8 Hz, 4 H; o-tol), 8.20–8.23 (m, 2 H; o-Ph), 8.88 (d, ³J=4.5 Hz, 2 H; β-Pyrr), 8.93 (d, ${}^{3}J = 4.5$ Hz, 2H; β-Pyrr), 9.03 (d, ${}^{3}J = 4.3$ Hz, 2H; β-Pyrr), 9.35 (d, ³*J*=4.3 Hz, 2H; β-Pyrr), 10.19 ppm (s, 1H; β-Pyrr); UV/ Vis (CH₂Cl₂): λ_{max} = 420 (100), 558 (4.03), 595 nm (1.73); MALDI-TOF MS (dithranol): *m*/*z*: 587.97 [*M*]^{•+}.

Electrosynthesis

5-nitro-10,20-ditolyl-15-phenylporphyrin Magnesium(II) (Mg(PDTP-NO₂)): The electrolysis was carried out under argon at room temperature in CH₃CN (170 mL) that contained TEAPF₆ (0.1 м), Mg(PDTP) (100 mg, 0.17 mmol), 2,6-lutidine (200 $\mu L,$ 10 equiv), and NaNO₂ (40 mg, 0.58 mmol) under vigorous stirring ($\omega = 1350$ rpm). The applied potential was $E_{app} = 0.70$ V versus SCE. At the end of the electrolysis, 2 Faraday per mole of Mg(PDTP) were transferred. The solution mixture was then evaporated to dryness under reduced pressure. The resulting crude solid was dissolved in a minimum of CH₂Cl₂, and this solution was washed five times with distilled water (750 mL) to remove the supporting electrolyte. The organic phase was evaporated to dryness. The crude product was then purified by column chromatography (alumina, 0 to 2% MeOH in CH2Cl2) and recrystallized from MeOH/H2O to give Mg(PDTP-NO₂) in 91% yield (98 mg). ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): $\delta = 2.72$ (s, CH₃; 6H), 7.59 (d, ³J=7.7 Hz, 4H; *m*-tol), 7.71-7.81 (m, 3H; *m*-and *p*-Ph), 8.08 (d, ³*J*=7.4 Hz, 4H; *o*-tol), 8.16–8.20 (m, 2H; o-Ph), 8.82 (s, 4H; β -Pyrr), 8.98 (d, ${}^{3}J$ = 4.5 Hz, 2H; β -Pyrr), 9.25 ppm (d, ${}^{3}J = 4.5$ Hz, 2 H; β -Pyrr); UV/Vis (CH₂Cl₂): $\lambda_{max} = 426$ (100), 565 (7.97), 619 nm (6.12); MS (ESI-MS): m/z: 634.21 [M+1]⁺.

5-Amino-10,20-ditolyl-15-phenylporphyrin (H₂(PDTP-NH₂)): The synthesis protocol was inspired by the work of J. Lessard et al.^[21d] In practice, the activated Devarda electrode (3 cm×4 cm) was placed in the cell that contained MeOH (170 mL) with H_2O (1.5%) and KOH (0.27 M) under argon. The electrolysis was carried out under argon at room temperature under vigorous stirring ($\omega =$ 1350 rpm). The applied potential was $E_{\rm app} = -1.20 \, {\rm V}$ versus SCE to generate hydrogen at the surface of the electrode for at least 20 min. After the addition of Mg(PDTP-NO₂) (70 mg) in one portion, 6 Faradays per mole of Mg(PDTP-NO₂) were transferred at -0.96 V versus SCE. At the end of the electrolysis, concentrated hydrochloric acid (5 mL) was added, and this mixture was stirred for 1 min. After evaporation of the solvent, the colored residue was dissolved in CH₂Cl₂. The precipitated KCl was then removed by filtration. The green filtrate was evaporated to dryness and neutralized with saturated sodium acetate solution (100 mL). The mixture was extracted with CH₂Cl₂. The organic phase was washed twice



with distilled water (250 mL). After evaporation of the solvent, purification by column chromatography (alumina, CH₂Cl₂), and recrystallization by evaporation of CH₂Cl₂, H₂(PDTP–NH₂) was obtained in 80% yield (51 mg). ¹H NMR (CD₂Cl₂, 300 MHz, 298 K): $\delta = -0.78$ (s, 2H; NH), 2.68 (s, 6H; CH₃), 5.81 (s, 2H; NH₂), 7.51 (d, ³*J*=7.71 Hz, 4H; *m*-tol), 7.62–7.71 (m, 3H; *m*-and *p*-Ph), 7.94 (d, ³*J*=7.92 Hz, 4H; *o*-tol), 8.02–8.05 (m, 2H; *o*-Ph), 8.39 (d, ³*J*=4.53 Hz, 2H; β-Pyrr), 8.40 (d, ³*J*=4.89 Hz, 2H; β-Pyrr), 8.51 (d, ³*J*=4.89 Hz, 2H; β-Pyrr), 8.62 ppm (d, ³*J*=4.62 Hz, 2H; β-Pyrr); UV/Vis (CH₂Cl₂): λ_{max} (log ε)=425 (5.46), 542 (3.83), 580 (4.27), 622 (3.53), 686 nm (4.24); MALDI-TOF MS (dithranol): *m/z*: 581.98 [*M*]⁺.

Synthesis of nickel(II) 5-amino-10,20-ditolyl-15-phenylporphyrin (Ni(PDTP-NH₂)): The porphyrin Ni(PDTP-NH₂) was synthesized by metalation of H₂(PDTP-NH₂) with Ni(OAc)₂·4H₂O according to known procedures.^[19c,22] The porphyrin $H_2(PDTP-NH_2)$ (333 mg, 0.573 mmol) was dissolved in DMF (20 mL), and Ni(OAc)₂·4 H₂O (717 mg, 2.882 mmol) was added in one portion. The reaction mixture was then degassed with argon for 10 min and heated under reflux conditions in a preheated oil bath (170 $^\circ\text{C})$ for 15 min under argon. After cooling at room temperature, deionized water (30 mL) was added, and the resulting solid was isolated by filtration and washed with water. This residue was finally purified by column chromatography (SiO₂, CH₂Cl₂) and recrystallized from a CH₂Cl₂/ MeOH mixture to yield Ni(PDTP--NH_2) in 84\% yield (310 mg, 0.486 mmol). ¹H NMR (CD₃COCD₃, 300 MHz, 300 K): δ=2.60 (s, 6H; CH₃), 7.50 (d, ${}^{3}J = 7.9$ Hz, 4H; *m*-tol), \approx 7.51 (s, 2H; NH₂), 7.66 (m, 3H; m-and p-Ph), 7.79 (d, ³J=7.9 Hz, 4H; o-tol), 7.89 (m, 2H; o-Ph), 8.26 (d, ${}^{3}J = 5.0$ Hz, 2H; β -Pyrr), 8.33 (d, ${}^{3}J = 4.8$ Hz, 2H; β -Pyrr), 8.37 (d, ${}^{3}J = 5.0 \text{ Hz}$, 2H; β -Pyrr), 9.26 ppm (d, ${}^{3}J = 4.8 \text{ Hz}$, 2H; β -Pyrr); $^{13}C{^{1}H}$ NMR (CD₃COCD₃, 125 MHz, 300 K): $\delta = 144.5$, 143.1, 142.9, 140.3, 138.1, 137.9, 137.1, 134.9, 133.7 (two peaks), 133.4, 132.8, 129.3, 128.3, 128.0, 127.7, 127.1, 122.7, 121.5, 21.6 ppm; R_f=0.48 (SiO₂, CH₂Cl₂/*n*-pentane, 50/50 v/v); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 291 (4.24), 359 (3.94), 425 (5.30), 542 (3.92), 599 nm (4.13); HRMS (ESI-MS): *m*/*z* calcd for C₄₀H₂₉N₅Ni: 637.1771 [*M*]⁺; found: 637.1765.

Electrografting of the nickel(II) 10,20-ditolyl-15-phenylporphyrin diazonium generated in situ: Platinum electrodes (Pt disk Ø =2 mm and Pt plate of $S = 1 \text{ cm}^2$, geometric area) were modified by electroreduction of Ni(PDTP-N2+). The porphyrin diazonium was generated in situ from Ni(PDTP-NH2) in acidic aqueous media (TFA) by reaction of the Ni(PDTP-NH₂) (1 mm) with NaNO₂ (2 equiv) in the dark under an argon atmosphere. Typically, in a clean conventional three-electrode cell, appropriate quantities of reactants were placed, namely, Ni(PDTP--NH₂) (6.3 mg) and CH₃CN (1 mL) under argon. After complete dissolution (approximately five minutes), an ice-cold solution (100 µL) that contained NaNO₂ (1.4 mg), H₂O (20 µL), and CH₃CN (80 µL) was added dropwise to the solution under argon. Then, after 15 min, for the following final reaction step, trifluoroacetic acid (170 μ L; TFA) and TEABF₄/CH₃CN (830 μ L, 0.11 M) were mixed, the resulting solution cooled with an ice bath, and it was added in the cell. The working electrode previously polished with diamond polishing slurries, rinsed with distilled water, and dried using argon gas was dipped in this solution. Five minutes after the addition of the TFA solution, a solution of TEABF₄/CH₃CN (7.9 mL, 0.11 м) was added to the cell. The solution was purged with argon for 10 min prior to reductive adsorption, and was kept under a blanket of argon during surface modification. The films were electrografted by cycling between 0.5 and 0.05 V versus SCE for thirty recurrent cycles at room temperature and at 50 mV s⁻¹. After modification, the electrode was sonicated in DMF for 30 s (or CH₂Cl₂ for subsequent analysis using CH₂Cl₂) and dried using argon gas. The modified electrodes were characterized by cyclic voltammetry in $\mathsf{TEABF}_4/\mathsf{CH}_2\mathsf{Cl}_2$ (0.1 m) and $\mathsf{TEABF}_4/$ DMF (0.1 m).

Water contact-angle characterization

This technique allows one to discriminate between the polar or nonpolar nature of the liquid–solid interactions at the interface. One can thus deduce the hydrophilic or hydrophobic character of a surface. The method involves measuring the angle of the tangent of the profile of a drop deposited on the substrate with the substrate surface. In essence, a drop of ultrapure water (10 μ L) is deposited by using a syringe on the surface of the same platinum plate electrode before and after its modification.

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Keywords: diazonium · electrochemistry · electrografting · electrosynthesis · porphyrins

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