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# Recent advances in electrochemical *meso* and $\beta$ -functionalization of porphyrins and electrografting of diazonium-porphyrins

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## Abstract

Recent studies on electrochemical *meso* and  $\beta$ -functionalization of porphyrins and electrografting of diazonium-porphyrin are presented. First the electrochemical oxidative C-C coupling between porphyrins will be presented followed by the inter- and intramolecular *meso* and  $\beta$ -substitutions of porphyrins. Then the latest results on diazonium-porphyrin electrografting will be reviewed.

## Keyword

Organic electrosynthesis; Porphyrin; Anodic nucleophilic substitution; Electropolymerization; Diazonium-porphyrin electrografting.

## Introduction

Porphyrins are ubiquitous in the Nature (heme, chlorophyll) and their physico-chemical properties (UV-Vis, emission, redox...) make them particularly attractive in numerous fields. Their chemical synthesis and more particularly their functionalization in  $\beta$  or *meso*-position(s) are often difficult to handle. An interesting green alternative to common chemical transformations consists in the electrochemical oxidation of the porphyrin ring. Thus, the electrophilic porphyrin cation radical can react with itself leading to polymers or can be substituted by one or several nucleophiles depending on the experimental conditions. In 2011 [1], 2014 [2] and 2016 [3], three book chapters from Ruhlman and co-workers addressed these topics with the description of the electrosynthesis of multisubstituted porphyrins as well as

porphyrin electro(co)polymerization. Contributing to the impressive and exciting renaissance of organic electrosynthesis in the past few years [4–7], this short review presents the last advances on the direct electrochemical *meso* and  $\beta$ -functionalization of the porphyrin ring. Moreover, as not reported before, the electrografting of diazonium-porphyrins will be presented.

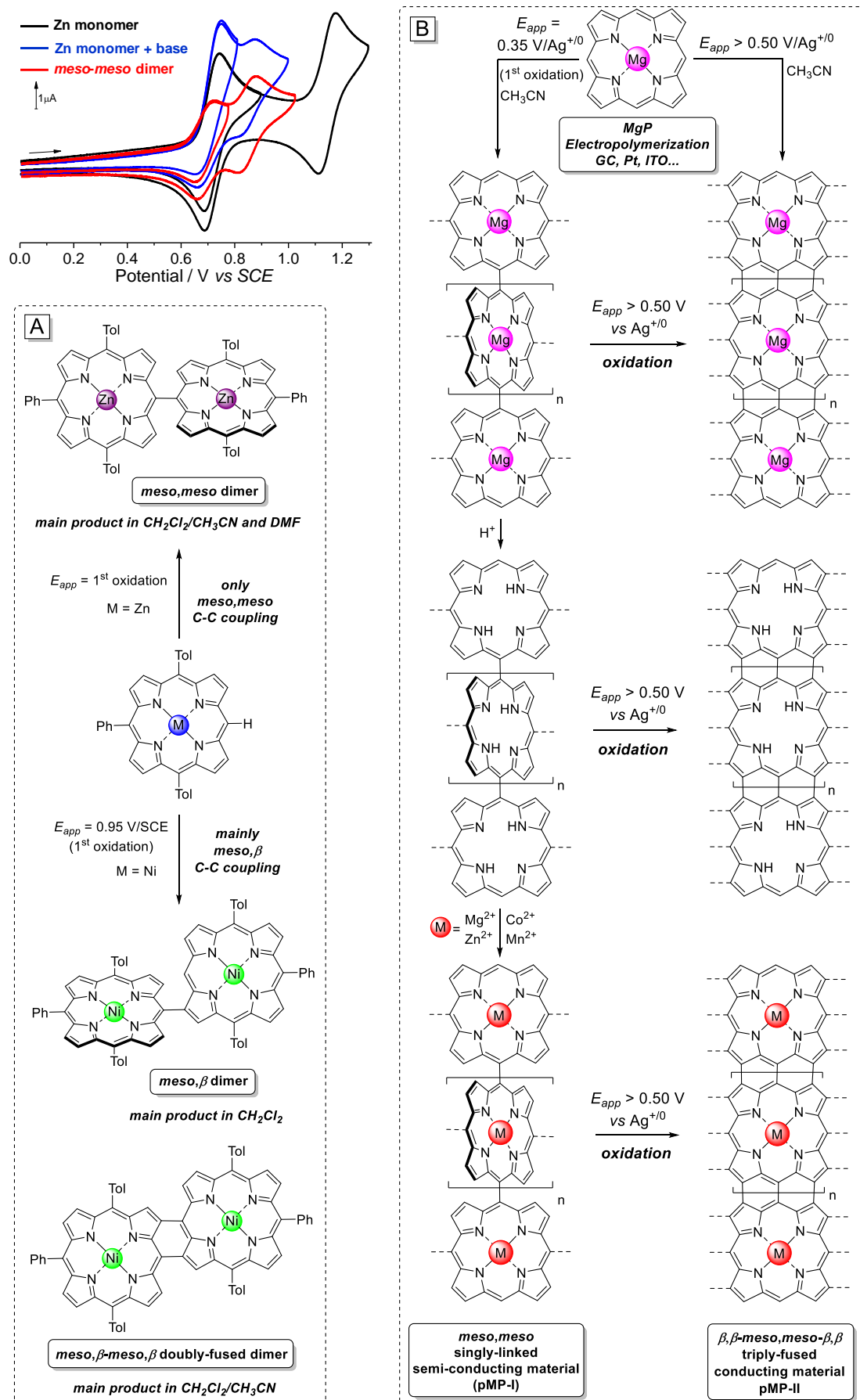
## **1. Electrochemical oxidative C-C coupling between porphyrin units**

### **1.1. Dimerization and oligomerization of porphyrins**

In 2012, Devillers, Lucas and co-workers revisited the pioneer work of the Osuka's group [8,9] with the study of the electrochemical dimerization of the 10-phenyl-5,15-di-*p*-tolylporphyrin Zn(II) complex (Scheme 1A) [10]. The best yield (93%) of *meso,meso* dimer was obtained when the monomer was oxidized to its first oxidation potential in a non-divided cell, in DMF, in presence of 2,6-lutidine. Two years later the same group studied the analogous nickel(II) complex which gave very different results (Scheme 1A) [11]. In particular the C-C coupling occurred preferentially in the *meso*, $\beta$  positions affordind the singly- and doubly-linked dimer. This regioselectivity agrees well with previous results from Osuka and co-workers [9].

### **1.2. *Meso-meso* electropolymerization of porphine**

In 2010, Devillers, Lucas and coll. reported the first detailed electrochemical characterization of magnesium(II) porphine (MgP), the totally unsubstituted porphyrin [12–14]. Electrolysis of MgP at its first oxidation potential led to the formation of the *meso-meso* dimer, trimer, tetramer and pentamer. Pursuing their research on the oxidative reactivity of MgP, Vorotyntsev, Devillers and co-workers reported the first example of *meso-meso* electropolymerization of porphyrin with MgP (Scheme 1B) [15]. The porphine-based polymer was deposited on the electrode surface either by multiscan voltammetry or at applied potential. When the backward potential or the applied potential was low ( $<0.40$  V vs Ag/Ag<sup>+</sup>), a semi-conducting material was obtained (pMgP-I), where the MgP unit was kept intact inside the polymer with the probable formation of only one single *meso-meso* bond between each



Scheme 1. Electrochemical oxidative C-C coupling between tri-*meso*-arylporphyrins (A, [10,11]) and Mg(II) porphine (B, [12,13,15–23]).

monomer unit. For higher potential ( $>0.50$  V) pMgP-I was transformed into another type of polymer, pMgP-II, which was electroactive in the whole available potential range [16]. Considering the different pMgP-II characterizations, it was assumed that the oxidation of pMgP-I at potential beyond 0.50 V leads to the formation of two additional  $\beta,\beta$  bonds between porphyrin units ( $\beta,\beta$ -*meso-meso*- $\beta,\beta$  triply-fused-like polymer [24–26]) leading to a graphene-like totally planar, conjugated and conducting material.

A strong acceleration of the pMgP-I electropolymerization rate was observed upon addition of 2,6-lutidine ( $\geq 1$  eq. *vs* MgP) [17]. The efficiency of the deposit was increased by more than a factor of two while the redox, electric conductivity and spectral properties remained unchanged.

Later, Konev, Lizgina and co-workers published a comparative electropolymerization study focused on MgP and 5,15-bis-(4-methoxyphenyl)porphyrin Mg(II) (MgMPP) [18]. The electrochemical behavior of MgMPP was quite similar to MgP but the polymerization rate and efficiency were much lower due to the fact that only two free *meso* positions are available for polymerization.

Magnesium(II) was efficiently removed from the porphine unit inside pMgP-I by addition of acids, leading to the free base porphine polymer [19]. Metallation of the free base form (pH<sub>2</sub>P-I) was (electro)chemically performed with Zn(II) [19], Co(II) [20–22] and Mn(II) [22]. The first applications of these promising metalated materials concerned sulphite detection [23] and O<sub>2</sub> reduction reaction [22].

## **2. Electrochemical functionalization of porphyrins with nucleophiles**

### **2.1. Electrochemical functionalization with nucleophile(s) at the $\beta$ -position**

Several early examples of electrochemical  $\beta$ -functionalization have been published before 2012 [27–34]. More recently, inspired by Yoshida *and coll.* [35], a new pathway towards the synthesis of amino-porphyrins was developed by Devillers and co-workers [36]. Thus 5,10,15,20-tetraphenylporphyrin (H<sub>2</sub>TPP) was oxidized in presence of a pyridine excess (100

eq.) leading to the  $\beta$ -pyridiniumporphyrin (Scheme 2A). Then the nucleophilic attack of an excess of piperidine on the  $\alpha$ -positions of the pyridinium afforded the  $\beta$ -aminoporphyrin.

## 2.2. Electrochemical functionalization with nucleophile(s) at the *meso*-position

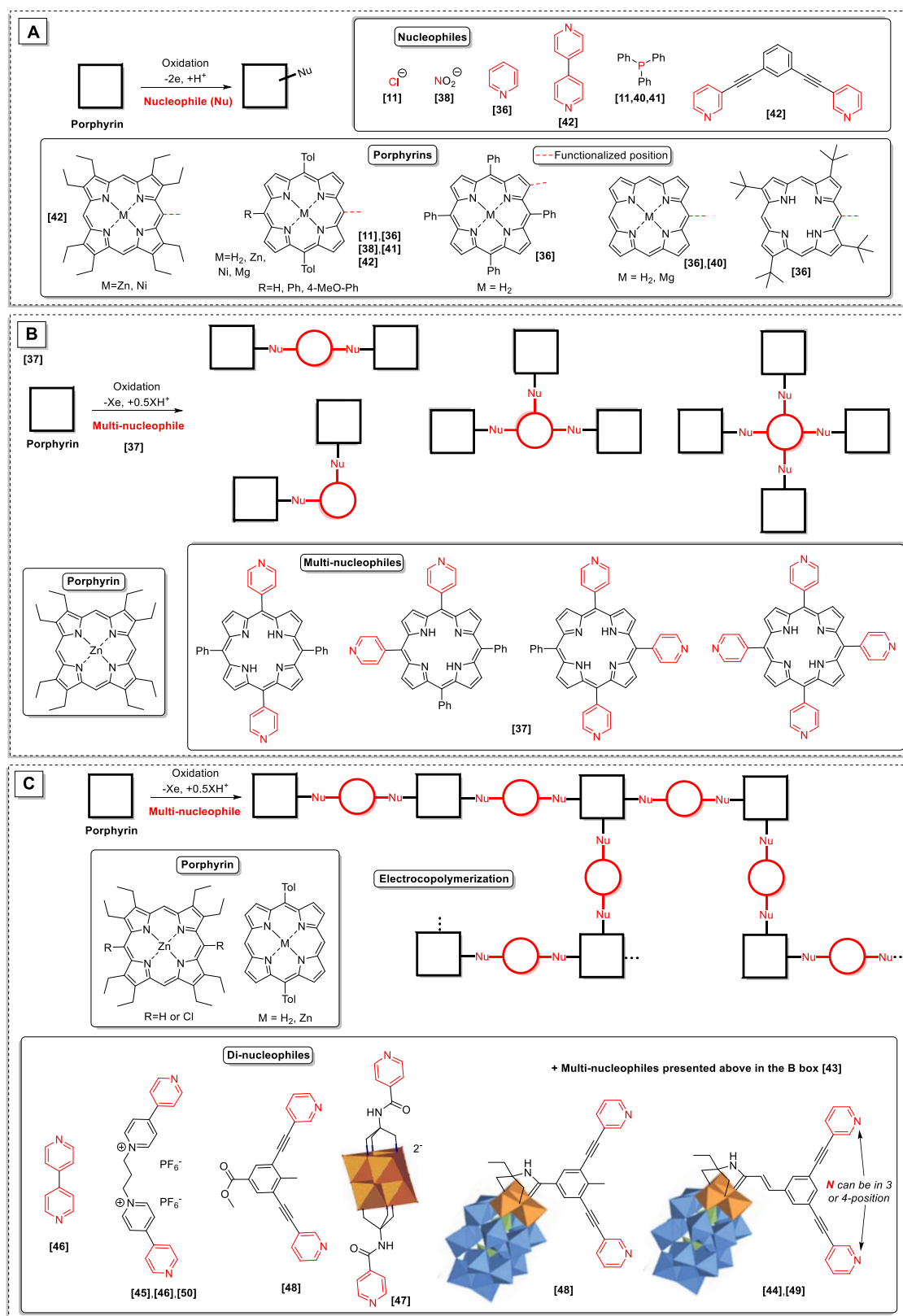
### 2.2.1. Formation of porphyrin monomers and oligomers

In 2013, Ruhlmann and co-workers synthesized porphyrin trimers, tetramer and pentamer starting with (poly(4-pyridinyl))porphyrins as nucleophiles and ZnOEP<sup>•+</sup> as the selectively electrogenerated electrophile (Scheme 2B) [37].

In 2014, Devillers, Lucas and coll. presented the versatile redox reactivity of Ni(II) 10-phenyl-5,15-di-*p*-tolylporphyrin [11]. Depending on the experimental conditions (solvents, divided/non-divided cell), apart from the above-mentioned dimers, different products were produced such as the *meso*-chlorinated porphyrin (in presence of CH<sub>2</sub>Cl<sub>2</sub>, 78% yield) and, in presence of triphenylphosphine, the *meso*-phosphonium porphyrin (72% yield, Scheme 2A).

In 2015, Devillers, Lucas and co-workers published the efficient electrochemical *meso* nitration (91% yield) of the 10-phenyl-5,15-di-*p*-tolylporphyrin Mg(II) complex (Scheme 2A, [38]) as earlier reported by Leung and co-workers for ZnOEP [39]. The electrolysis was performed using 3.4 eq. of NaNO<sub>2</sub> at a potential corresponding to the generation of the porphyrin cation radical. This nitrated porphyrin was then subjected to an electrochemical reduction on Devarda copper electrode in a MeOH/H<sub>2</sub>O/KOH (0.27 M) mixture leading to the free base *meso*-aminoporphyrin in 80% yield.

In 2018, the analogue zinc(II) complex was substituted in *meso*-position with triphenylphosphine using similar conditions as for magnesium(II) porphine [40], *i.e.* 20 eq. of PPh<sub>3</sub>, 10 eq. of 2,6-lutidine, at  $E_{app} = 0.70$  V/SCE [41]. Very recently, Ruppert, Weiss and co-workers presented their porphyrin-tweezer target that they wanted to prepare by electrosynthesis starting with 1,3-bis(pyridin-3-ylethynyl)benzene as the dinucleophilic spacer and 10-(4-methoxyphenyl)-5,15-di-*p*-tolylporphyrin cation radical as the electrophile (Scheme 2A) [42].



**Scheme 2.** Functionalization of porphyrin monomers (A, [11,36,38,41,42]); preparation of oligomers (B, [37]); synthesis of copolymers (C, [43–50]).

With the MOEP (M = Zn and Ni) and 4,4'-bipyridine models, the authors tested the influence of different parameters (solvent, base, oxidant, reaction time, concentration effect, porphyrin

complex). But these optimized conditions did not allowed to reach their initial goal since no porphyrin tweezer dimer was isolated. Nevertheless, the substituted porphyrin monomer was prepared in 17% yield starting with the nickel(II) complex. The authors found that upon oxidation of 10-(4-methoxyphenyl)-5,15-di-*p*-tolylporphyrin in presence of 1,3-bis(pyridin-3-ylethynyl)benzene, the main product of the reaction was the undesired *meso,meso* dimer resulting from the homocoupling of the generated porphyrin cation radical [10,11].

As aforementioned for the  $\beta$ -substitution, Devillers and co-workers reported a new regioselective C–H amination of free base porphyrins via electrogenerated pyridinium-porphyrins [36]. The reaction was successfully tested on free base porphine, 2,7,12,17-tetra-*tert*-butylporphyrin and 5,15-di-*p*-tolylporphyrin providing first the *meso*-pyridinium derivatives (61-85% yield, Scheme 2A) and then the corresponding amino-porphyrins (81-87% yield).

### 2.2.2. Formation of porphyrin copolymers via dinucleophilic spacers

In 2012, a direct "*easy*" electropolymerization method was developed by Ruhlmann by oxidizing ZnOEP in presence of a mixture of di-, tri- and tetrapyridinyl-porphyrins (Scheme 2C) [43]. These polymers were the first bis-porphyrin copolymers reported in the literature.

In 2013, Hasenknopf, Lacôte, Ruhlmann and co-workers published the synthesis of conjugated Dawson-type polyoxometalate-porphyrin copolymers [44] (Scheme 2C). An important synthetic effort was dedicated to the synthesis of organo-POM monomers bearing two pyridinyl fragments based on the 1,3-bis(pyridin-4(or 3)-ylethynyl)benzene substructure.

Still based on the "*easy*" electropolymerization method, Bucher, Ruhlmann and coll. reported the electrocopolymerization of ZnOEP with a flexible dinucleophile (the 1,1'-(propane-1,3-diyl)bis((4,4'-bipyridin]-1-ium)) hexafluorophosphate salt, Scheme 2C) [45,46]. Spectroelectrochemical studies on the material suggested the formation of  $\pi$ -dimers when the viologen moieties were reduced at the first reduction potential. Varying the POM and the porphyrin nature, the "*easy*" electrocopolymerization procedure was extended to Lindqvist-type



polyoxovanadate ( $\text{TBA}_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHCO}(4\text{-C}_5\text{H}_4\text{N})\}_2]$ ) substituted with two pyridinyl groups and ZnOEP or 5,15-ditolylporphyrin free base [47]. It was shown by EQCM measurements that the electrocopolymerization was much more efficient with ZnOEP than with the disubstituted 5,15-ditolylporphyrin. The influence of the attachment of a Dawson-type polyoxometalate on the bipyridinyl spacer was evaluated in another study [48]. The CV analyses of the copolymer material synthesized without preliminary attachment of the POM on the bispyridinyl spacer proved that the porphyrin unit was mainly substituted in *meso* position by four pyridinium groups whereas the second copolymer which contained the POM only showed a reduction signal that matched with the reduction of two pyridinium fragments. These POM-porphyrin copolymers found applications as photovoltaic electrodes where their photovoltaic performance was investigated by photocurrent transient measurements [49]. In particular the control of the film thickness was of utmost importance to keep a good photocurrent-generation efficiency.

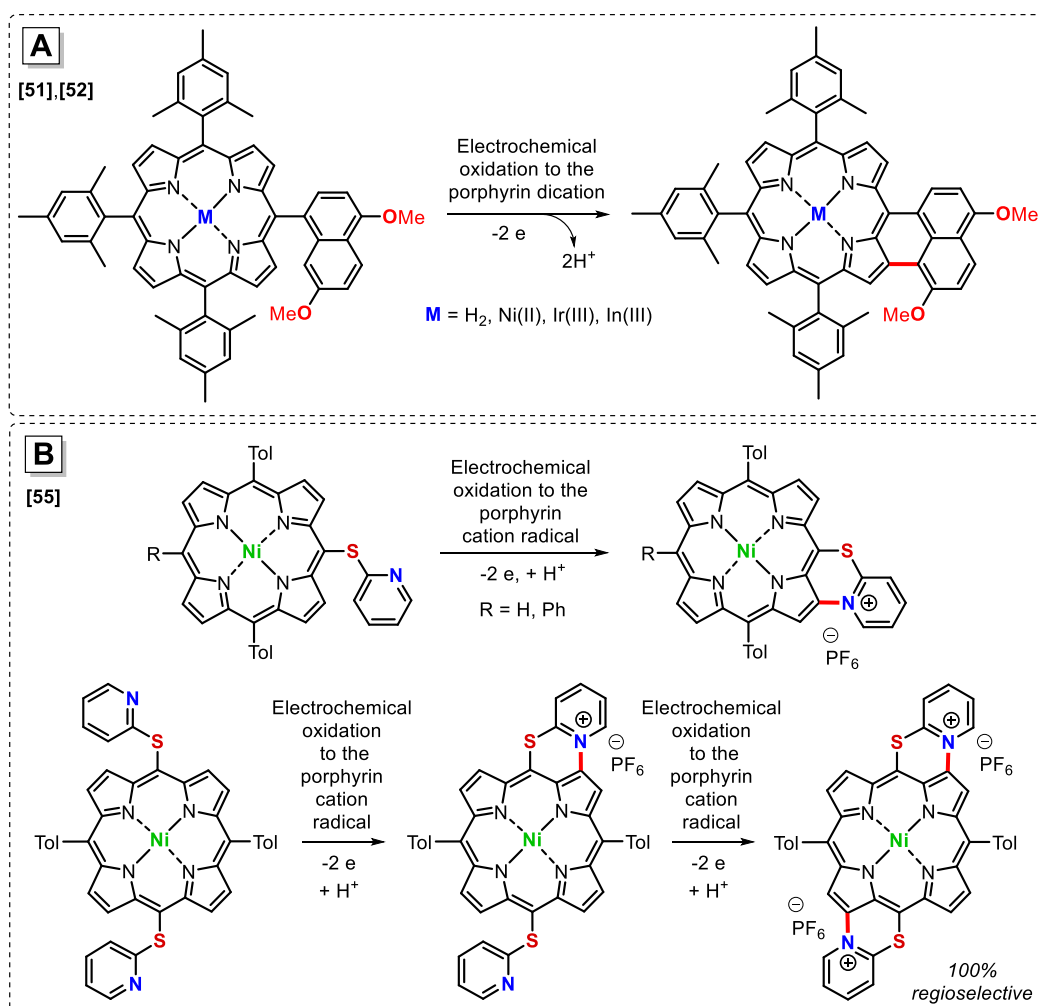
Up to now, all the electrogenerated copolymers have been synthesized by applying a potential that corresponds to the formation of the porphyrin dication. However, in a very recent publication, Ruhlmann and coll. showed that it was possible to generate a copolymer by oxidation of the less hindered zinc(II) 5,15-ditolylporphyrin at its first oxidation step in presence of the flexible 1,1''-(propane-1,3-diyl)bis([4,4'-bipyridin]-1-ium))hexafluorophosphate bis-nucleophile [50]. This new material was compared with the one generated at higher potential (second oxidation of the porphyrin). It was found that the copolymer generated at low potential contained stable isoporphyrin units as proved by ESR measurements.

### 2.3. Intramolecular functionalization of porphyrins

The first electrochemical intramolecular oxidative C-C coupling examples were reported by Kadish, Gryko and co-workers with *meso*-substituted-4,7-dimethoxynaphthalen-1-ylporphyrins (Scheme 3A) [51,52]. In these reports, they showed that the formation of the

dication was necessary to promote the fusion reaction. At this applied potential, the fused product was oxidized to its reactive dication which could lead to further degradation.

In relation with the work of Popp [53] and Yoshida and co-workers [54] which presented the first examples of electrochemical C-N oxidative fusion, Devillers and coll. developed the first chemical and electrochemical oxidative C-N fusion of pyridinyl-substituted porphyrins (Scheme 3B) [55]. Interestingly, the C-N fused (di)cationic compounds exhibited higher oxidation potential than the starting unfused porphyrins thanks to the positive charge(s) generated during the C-N bond formation. Thus overoxidation of the electrogenerated products was prevented which accounted for the high yields obtained for the fusion reaction.



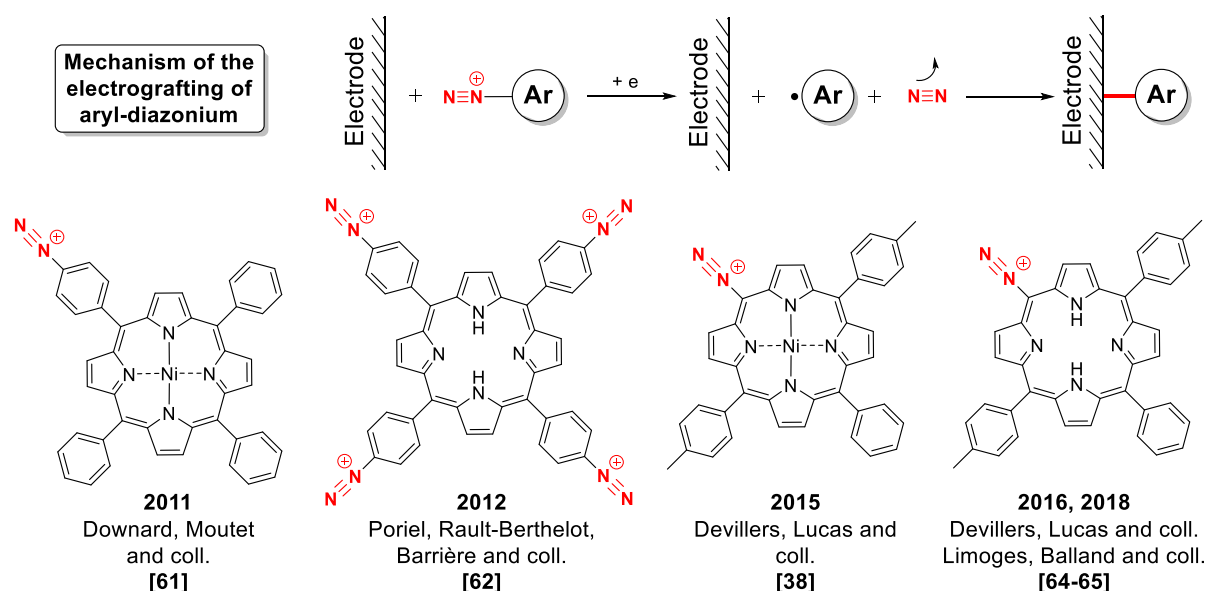
**Scheme 3.** Intramolecular oxidative C-C (A, [51,52]) and C-N (B, [55]) coupling of porphyrins.

### 3. Electrografting of diazonium-porphyrins

Electrografting of aryl-diazonium derivatives is currently an active and competitive research field since various materials may be generated by reduction of the diazonium function. Contrary to the electropolymerization method, the electrografting of aryl-diazoniums affords thin films which spans from mono- to multilayers. Porphyrins entered in this research area quite recently.

#### 3.1. Electrografting of tetraphenylporphyrin-based diazonium

Despite several recent examples of spontaneous grafting of diazonium-porphyrins onto carbon-based substrates (multi-walled carbon nanotubes [56], reduced graphene oxide [57], graphenides  $\text{KC}_8$  [58], GC and carbon cloth [59,60]), the first example of electrografted diazonium-porphyrin was reported by Downard, Moutet and co-workers in 2011 (Scheme 4) [61]. The electroreduction of the 4-(10,15,20-triphenylporphyrin-5-yl)benzenediazonium nickel(II) complex led to a relatively stable deposit on gold, glassy carbon (GC), ITO and PPF (pyrolyzed photoresist film) which showed a similar redox behavior than those observed for solute  $\text{Ni(II)}$  porphyrins. The surface coverage was compatible with the formation of a monolayer on PPF electrode ( $\Gamma = 2.6 \times 10^{-10} \text{ mol cm}^{-2}$ ).



**Scheme 4.** Electrografting mechanism of aryl-diazonium (top) and examples of electrografted diazonium porphyrins (bottom, [38,61,62,64,65]).

One year later, Poriel, Rault-Berthelot, Barrière and coll. presented the reductive electrografting of the 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzenediazonium derivatives that was generated *in situ* in aqueous acidic medium from the corresponding aminoporphyrins [62]. Noteworthy, these authors failed to graft the mono-diazonium-substituted 4-(10,15,20-triphenylporphyrin-5-yl)benzenediazonium in similar conditions.

Very recently, Celik, Ekinici and coll. described the metalation (Mn(II), Fe(III) and Co(II)) and application of these electrografted tetraphenylporphyrin-based diazoniums towards the electrocatalytic reduction of oxygen [63].

### 3.2 Electrografting of *meso*-diazoniumporphyrins

In 2015, Devillers, Lucas and co-workers presented the first example of *meso*-diazonium-porphyrin electrografting (Scheme 4) [38]. The diazonium was generated *in situ* from the corresponding *meso*-aminoporphyrin, in organic medium (CH<sub>3</sub>CN 0.1M TEABF<sub>4</sub>, 2eq. NaNO<sub>2</sub>, 0.5M TFA, 0.5% of water). Though counter-intuitive due to the possible steric hindrance generated by the  $\beta$ -protons surrounding the *meso* position to be coupled with the electrode, the electrodeposition worked well and the nickel(II) porphyrin-based deposit was characterized by electrochemistry. The surface coverage was calculated to be relatively close to a porphyrin monolayer ( $\Gamma = 5 \times 10^{-10}$  mol cm<sup>-2</sup>).

One year later, the same group reported an extension of this preliminary work with the electrografting of the corresponding *meso*-diazonium-porphyrin free base on GC, Pt and ITO [64]. Surprisingly the electrografting was even more efficient and the surface coverage corresponded to multilayers of porphyrins ( $\Gamma = 9\text{-}12 \times 10^{-10}$  mol cm<sup>-2</sup>). To test the robustness of this new free base material, this latter was subjected to a zinc(II) metalation procedure by dipping the modified electrode into a saturated Zn(OAc)<sub>2</sub> CHCl<sub>3</sub>/MeOH solution heated at 60°C. An efficient zinc(II) insertion was demonstrated by electrochemistry and UV-visible absorption spectroscopy and no significant degradation of the porphyrin-based material was

observed. It was even possible to recover the free base form by dipping the metalated zinc(II) porphyrin film into an 0.2 M HCl CH<sub>3</sub>CN solution.

In 2018, Limoges, Balland and coll. presented an efficient and homogeneous functionalization of 3D nanostructured transparent ITO electrodes by electrografting of *in situ* generated free base *meso*-diazonium porphyrin [65]. The authors showed that the obtained material was homogeneous and that the surface coverage can be easily controlled by the number of grafting scans. The porphyrin-based material was quite resistant to desorption/hydrolysis under organic and aqueous conditions whereas its stability was further demonstrated *via* zinc(II) metalation experiments. As mentioned by the authors, this robust functionalization of nanostructured transparent metal oxide electrodes opens new perspectives for the development of more stable dye-sensitized or molecular catalyst-functionalized high surface photoelectrodes.

## Conclusion

Recent progress in porphyrin electrochemical functionalization and electro(co)polymerization as well as in electrografting of diazonium-porphyrins have been summarized. In the porphyrin research field, electrochemical functionalization and electrografting are still underdeveloped though they represent a very powerful surrogate to chemical transformations. Indeed, electrochemistry represents a greener alternate technique which generally affords high control and selectivity, low cost and allows for gram scale reactions. Given the recent revival of organic electrochemistry as well as the current development of porphyrin molecules and materials in different essential applications (photovoltaic, sensors, electrocatalysis...), no doubt that further progress in porphyrinoid electrochemical functionalization will be achieved in the next future.

## Declaration of interest

None

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