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Oxidation of Porphyrins in the Presence of Nucleophiles: From the Synthesis of Multisubstituted Porphyrins to the Electropolymerization of the Macrocycles

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1. Introduction

Porphyrins and porphyrins-containing materials have attracted a considerable attention these last decades, not only because of their roles as biological photosensitizers, redox centers and oxygen carriers, but also because of their attractive chemical properties and potential technological applications (Kadish et al., 2000). In particular, molecular engineering and design of controlled spatial assemblies and architectures of porphyrins are fields undergoing wide growth (Griveau & Bedioui, 2011). For example, macromolecular porphyrins-based systems can potentially mimic natural metalloenzyme structures. Indeed, in such systems, proteins are replaced by metalloporphyrins which can mimic the structure and/or the activity of the prosthetic groups of enzymes (Traylor, 1991). Another area of applications of such assembled porphyrins systems consists in the field of nanomaterials, the electronic communication between the macrocycles allowing developments of molecular photonic, electronic or optoelectronic devices (Jurow et al., 2010). Finally, nanocomposite porphyrins-based materials have also been investigated for applications involving energy storage systems, fuel cells and sensors (Di Natale et al., 2010; Ma et al., 2006).

For this purpose, porphyrins-based polymers have received peculiar attention these last decades. For instance, it has been established that a polymeric matrix may provide the best arrangement for a catalytically active center. The immobilized porphyrins appeared also

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more stable than biomimetic enzymes in aqueous or organic media, particularly at extreme pH and temperature (Griveau & Bedioui, 2011). Finally, conductive porphyrin polymers allow interesting applications for molecular electronics (Wagner & Lindsey, 1994).

Different strategies for the formation of porphyrin polymers have already been described in the literature. A first common method to polymerize porphyrins consists in the use of bridging ligands which can coordinate the metal center of metalloporphyrins. For instance, such coordination polymers have been obtained by coordination of nitrogenous ligands with ruthenium, osmium or iron porphyrins (Collman et al., 1987; Marvaud & Launay, 1993). Nevertheless, more frequently, covalent polymers have been obtained. Generally, the formation of such polymers relies on the use of porphyrins with polymerizable substituents attached on the ring periphery. Even if classical chemical ways can be used to obtain such polymers (Li et al., 2004), electrochemical route appears as an elegant, attractive and easy strategy to perform polymerization.

Indeed, one of the main advantages of electropolymerization lies in the non-manual addressing of polymers allowing formation of films with a good reproducibility and a controlled thickness. Electropolymerization is also an easy way to functionalize conductive surfaces with a good precision. Moreover, electropolymerization of porphyrins provides densely packed layers that facilitate the electron hopping process between macrocycles. Furthermore, the immobilization of such porphyrins-based materials on an electrode is a convenient way to design electrochemical sensing devices, catalytic electrodes, and to study the enzyme reactions by excluding the requirement of a chemical redox mediator to shuttle electrons between the porphyrins and the electrode (Griveau & Bedioui, 2011).

Electropolymerization of porphyrins has been initially developed by Macor and Spiro, who have polymerized vinyl-substituted porphyrins, the coupling occurring after the formation of vinyl radicals by electrooxidation (Macor & Spiro, 1983). Afterwards, other methods of electropolymerization have been published, for example from hydroxy-, amino-, pyrrole- or thiophene-substituted porphyrins (Bedioui et al., 1995; Bettelheim et al., 1987; Li et al., 2005).

In this context, we have developed an original methodology for the electropolymerization of porphyrins, based on nucleophilic attacks of di-pyridyl compounds directly onto electrooxidized porphyrins. This chapter presents an overview of this new method of electropolymerization.

2. Reactivity of porphyrin π-radical cations and dications with nucleophilic compounds

It is well-known that the oxidation of the π-ring of a porphyrin proceeds *via* two one-electron steps generating the π-radical cation and the dication (Fajer et al., 1970). The reactivity of these porphyrin π-radical cations and dications with nucleophilic compounds has been intensively studied. Dolphin and Felton have observed for the first time the reactivity of oxidized porphyrins with nucleophilic solvents or halides (Dolphin & Felton, 1974). In the case of *β*-octaethylporphyrin derivatives, stable *meso*-substituted porphyrins have been obtained. This is the first example of nucleophilic substitution at the periphery of porphyrin nucleus, allowing afterwards the development of a new and simple convenient synthetic route to obtain varied substituted porphyrins. Indeed, several further works report the nucleophilic attack of nitrogeneous, phosphorous or sulphurous nucleophiles (nitrite ion, pyridine, phosphine, thiocyanate…) onto π-radical cations in *meso*-position of *β*-

octaethylporphyrins or in β-position of *meso*-tetraphenylporphyrins (Barnett & Smith, 1974; Barnett et al., 1976; Rachlewicz & Latos-Grażyński, 1995; Shine et al., 1979). However, it must be noted that the π-radical cations have been in most cases prepared by chemical ways, principally by oxidation of macrocycles with iodine, bromine or peroxide.

Giraudeau *et al.* have for the first time investigated the reactivity of the radical cation of the zinc *meso*-tetraphenylporphyrin (ZnTPP), obtained by a direct electrochemical oxidation (electrolysis), in the presence of pyridine as Lewis base, leading to a macrocycle substituted by a pyridinium in β-position (El Kahef et al., 1986). Afterwards, a similar work has permitted to obtain zinc β-octaethylporphyrin (ZnOEP) with pyridinium *meso*-substituted (Giraudeau et al., 1996, 2001) (Fig. 1.a).

When 4,4′-bipyridine is used instead of pyridine, dimers of porphyrins can also be electrosynthesized (El Baraka et al., 1998; Giraudeau et al., 1996). Indeed, 4,4′-bipyridine presents two accessible nucleophilic sites which can both react with porphyrin rings (Fig. 1.b and c).

More recently, dimers of porphyrins with pyridinium spacer have also been synthesized from macrocycles substituted by a pendant pyridyl group which can react with a ZnOEP radical cation (Schaming et al., 2011a) (Fig. 1.e).
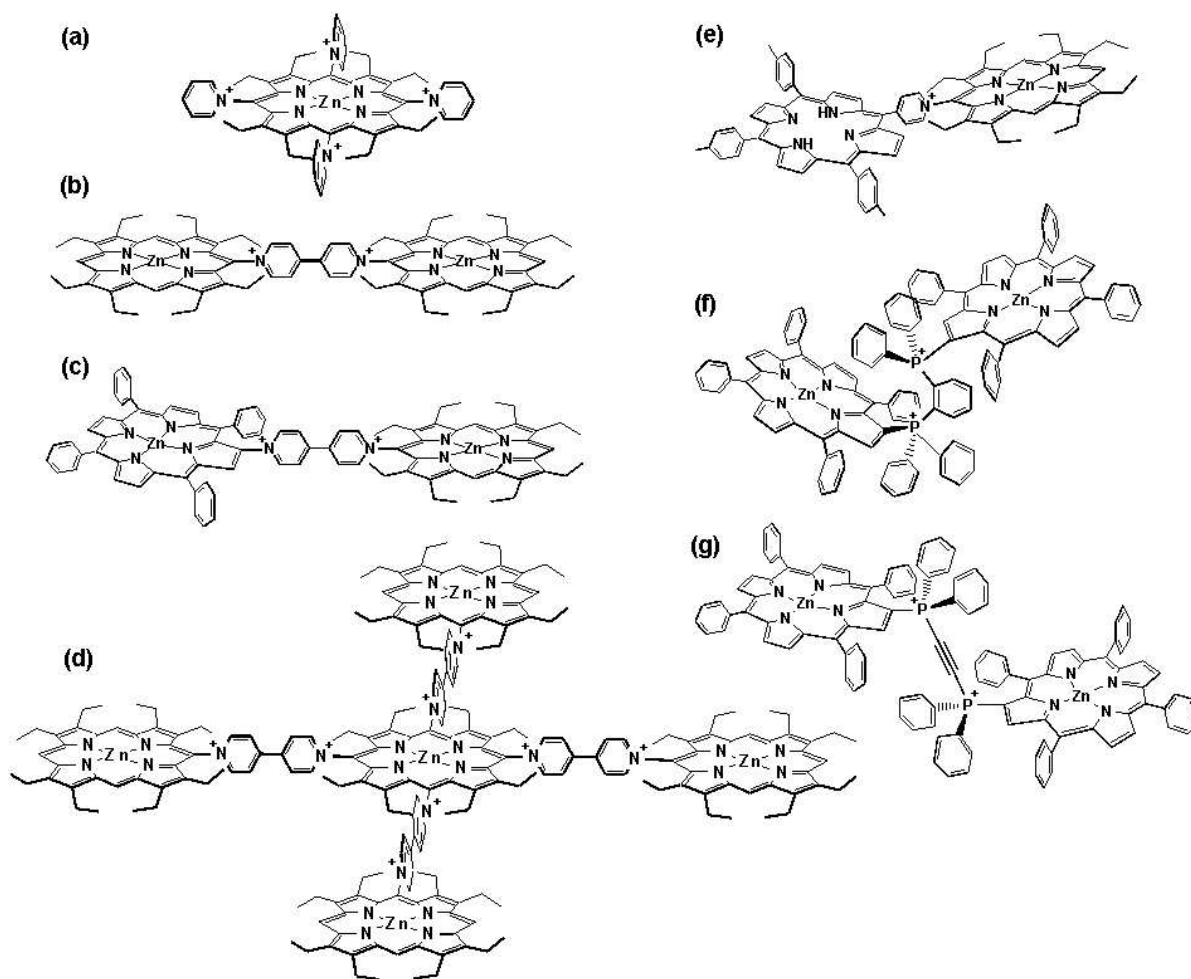

Fig. 1. Examples of a multi-substituted porphyrin (a) and of several oligomers of porphyrins (b-g) obtained from the reactivity of the electrogenerated π-radical cation with Lewis bases such as pyridine-derived species (a-e) or phosphane-derived species (f-g).

To perform all these electrosyntheses, electrolyses at a potential allowing the formation of the radical cation of the porphyrin have been carried out. Nevertheless, an increase of the electrolysis potential can allow multi-substitutions onto macrocycles. Indeed, a judicious control of the applied potential has permitted to obtain di-, tri- and tetra-*meso*-substitutions, leading to the formation of trimers, tetramers and pentamers of porphyrins, respectively (Ruhlmann, 1997; Ruhlmann et al., 1999a) (Fig. 1.d).

Finally, instead of the use of pyridyl-derived compounds as nucleophile, phosphanes have also been used to perform substitutions onto porphyrin rings, allowing the synthesis of dimers or trimers with more flexible di- or tri-phosphonium spacers (Ruhlmann & Giraudeau, 2001; Ruhlmann et al., 2003) (Fig. 1.f and g).

The mechanism of the *meso*-substitutions (onto zinc β-octaethylporphyrin (ZnOEP) for instance) has been described as an $E_1C_{Nmeso}E_2C_B$ process (Giraudeau et al., 1996) (fig. 2). Indeed, after formation of the radical cation (step E_1), nucleophilic attack can occur directly onto the *meso*-position (C_{Nmeso}) where initially a proton is present. After a second oxidation (step E_2), this proton can be removed (step C_B), allowing the re-aromatization of the macrocycle. This mechanism will be more precisely described in the case of the electropolymerization process (see part 3.2).
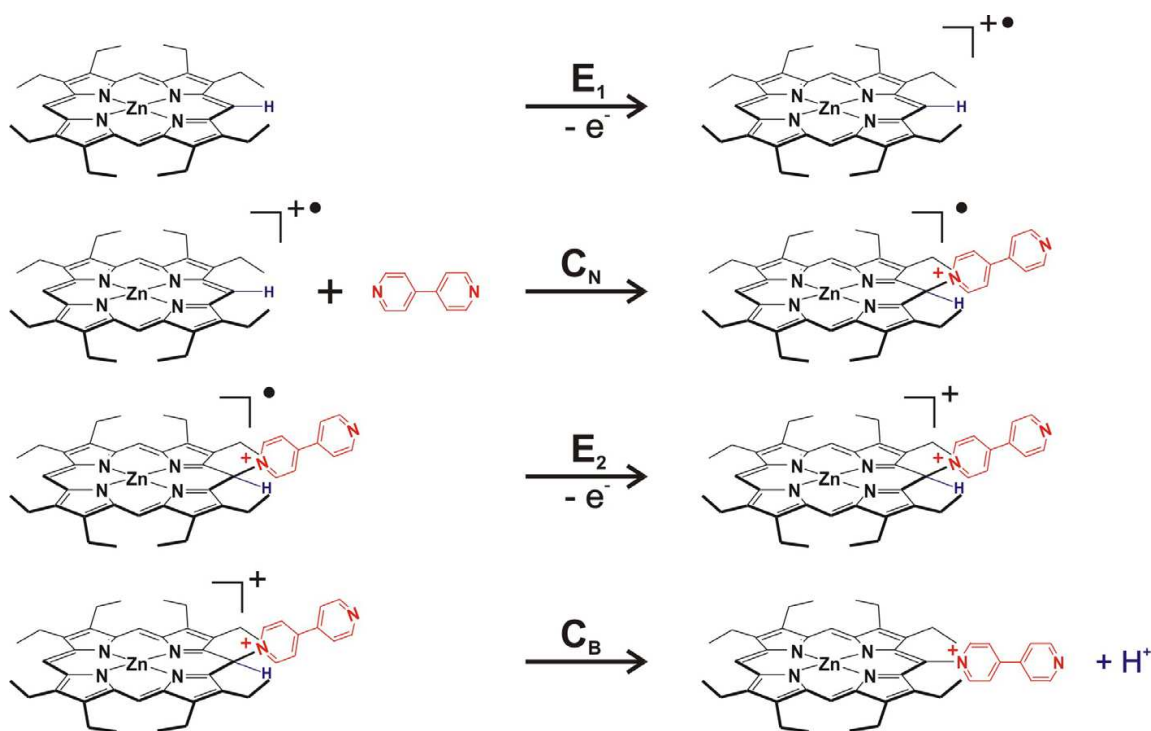

Fig. 2. $E_1C_NE_2C_B$ mechanism explaining the reactivity of a 4,4'-bipyridine (bpy) in *meso*-position of a zinc β-octaethylporphyrin (ZnOEP).

In the case of a nucleophilic substitution in β-position (allowed when *meso*-positions are already substituted as in the case of the zinc *meso*-tetraphenylporphyrin (ZnTPP)), the mechanism is a little bit different. Indeed, an $E_1C_{Nmeso}E_2C_{N\beta}C_B$ process occurs with two different successive nucleophilic attacks (Rachlewicz et al., 1995). First an attack at a *meso*-position (step C_{Nmeso}), which is more favorable, occurs after the electrogeneration of the radical cation (step E_1). After the second oxidation (step E_2), as no proton can be removed from the substituted *meso*-position, a second nucleophilic attack occurs at a β-position of the

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macrocycle (step $C_{N\beta}$) which leads to the loss of the pyridinium attached at the *meso*-position. Then, the spare proton in β-position can be removed (step C_B) in a last step in order to re-aromatize the macrocycle.

3. Towards an electropolymerization process of porphyrins

3.1 Electrochemical investigation of the electropolymerization

During previous electrolyses, electrodes were systematically coated by a thin colored film, ascribed to polymers. Consequently, a more detailed study of these polymers has been investigated.

Thus, in a first report, we have published the formation of a polymer of porphyrins obtained from the electrogenerated dications of ZnOEP macrocycles substituted by a bipyridinium group in *meso*-position (zinc *meso*-bipyridinium-β-octaethylporphyrin, abbreviated ZnOEP(bpy)+) (Fig. 3) (Ruhlmann et al., 1999b, 2008).
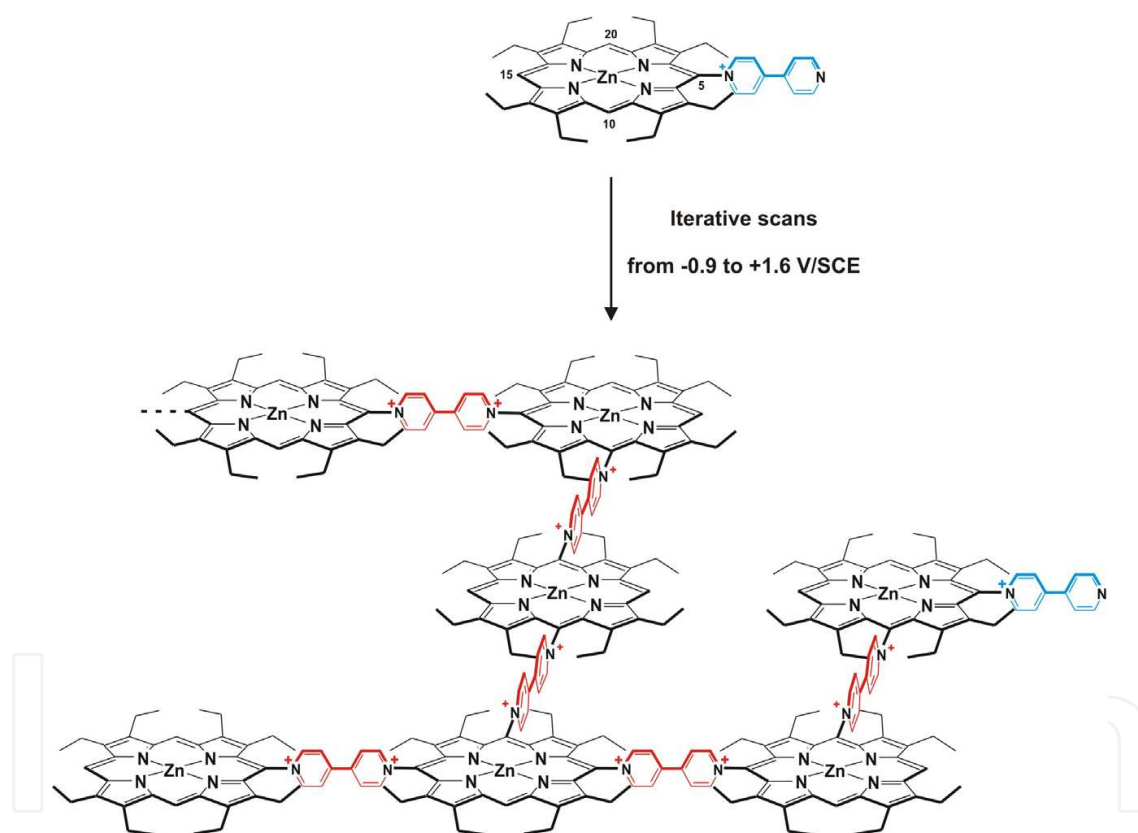

Fig. 3. Electropolymerization scheme of the mono-substituted ZnOEP(bpy)+.

This polymer is obtained with iterative scans by cyclic voltammetry (Fig. 4). During this iterative process, the current increases progressively, showing the formation of a conducting polymer coating the electrode. Moreover, the oxidation waves of the macrocycle become irreversible, suggesting well the reactivity of the dication. Furthermore, these oxidation waves are progressively shifted to higher anodic potential values during electropolymerization. This shift is a consequence of the electron-withdrawing effect of the viologen spacers formed between porphyrins during the polymerization process. These viologen spacers are also responsible of the two reversible reduction waves which appear

and grow around 0.00 and –0.65 V/SCE (peaks a and b in Fig. 4). Indeed, the two pyridiniums of the viologen spacers are reducible in two successive steps due to their mutual interaction (Schaming et al., 2011b).
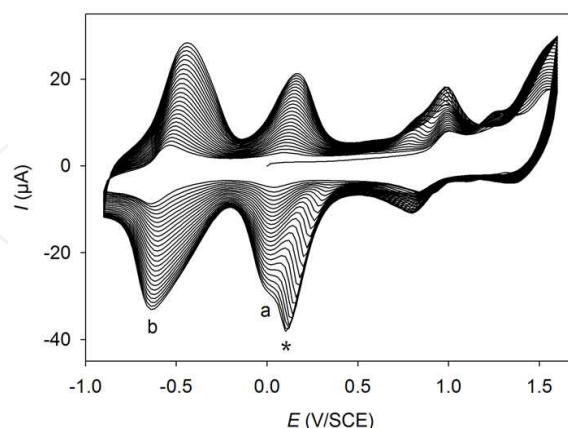

Fig. 4. Cyclic voltammograms recorded during the iterative scans between –0.90 and +1.60 V/SCE of ZnOEP(bpy)$^+$ (0.25 mM) in 1,2-$C_2H_4Cl_2$ and 0.1 M NEt_4PF_6. Working electrode: ITO; S = 1 cm^2; v = 0.2 V s^{-1}.

3.2 Mechanism of the electropolymerization process

The mechanism explaining the formation of polymers is similar to the one proposed for the electrosynthesis of mono-substituted porphyrins, excepted for the first oxidation step. Indeed, for electropolymerization, an $E(EC_NEC_B)_nE$ mechanism can be proposed (Fig. 5), where C_N corresponds to a nucleophilic attack and C_B to an acid-base reaction. Firstly, after formation of the dication (two steps E), the nucleophile (bipyridinium-substituted porphyrin) can react with it in *meso*-position to give an isoporphyrin (step C_N). This result correlates with the previous analysis of the redox behavior of porphyrins in the presence of nucleophiles and in particular the well documented report of Hinman *et al.* (Hinman et al., 1987). This isoporphyrin corresponds in fact to a porphyrin for which aromaticity is broken, because of the simultaneous presence of a pyridinium group and a proton on the same *meso*-carbon. Afterwards, this isoporphyrin can be oxidized again (step E). Finally, this spare proton is lost, leading to the re-aromatization of the macrocycle (step C_B) and allowing the formation of a di-substituted porphyrin. In a similar way, this one can react again, leading gradually to the formation of a polymer. One can also note that the isoporphyrins (which have not lost removable proton) are reduced during the further cathodic scan and conduct to the irreversible wave (peak * in Fig. 4) around +0.10 and +0.40 V/SCE, leading to the regeneration of the porphyrin.

One can notice that if the iterative sweeps are stopped in the anodic part at a potential corresponding to the formation of the radical cation of the porphyrin, no change of the cyclic voltammograms is observed (Schaming et al., 2011b). Moreover, in that case, the oxidation wave of the macrocycle remains reversible, showing that the electrogenerated radical cation does not react further. Thus, these results show that no polymerization occurs when the radical cation is formed. While the formation of the radical cation was sufficient to perform mono-substitutions onto macrocycles, the impossibility to carry out electropolymerization in this case can be explained by a kinetic problem. Indeed, the nucleophilic attack is certainly faster onto the dication than onto the radical cation. Consequently, during
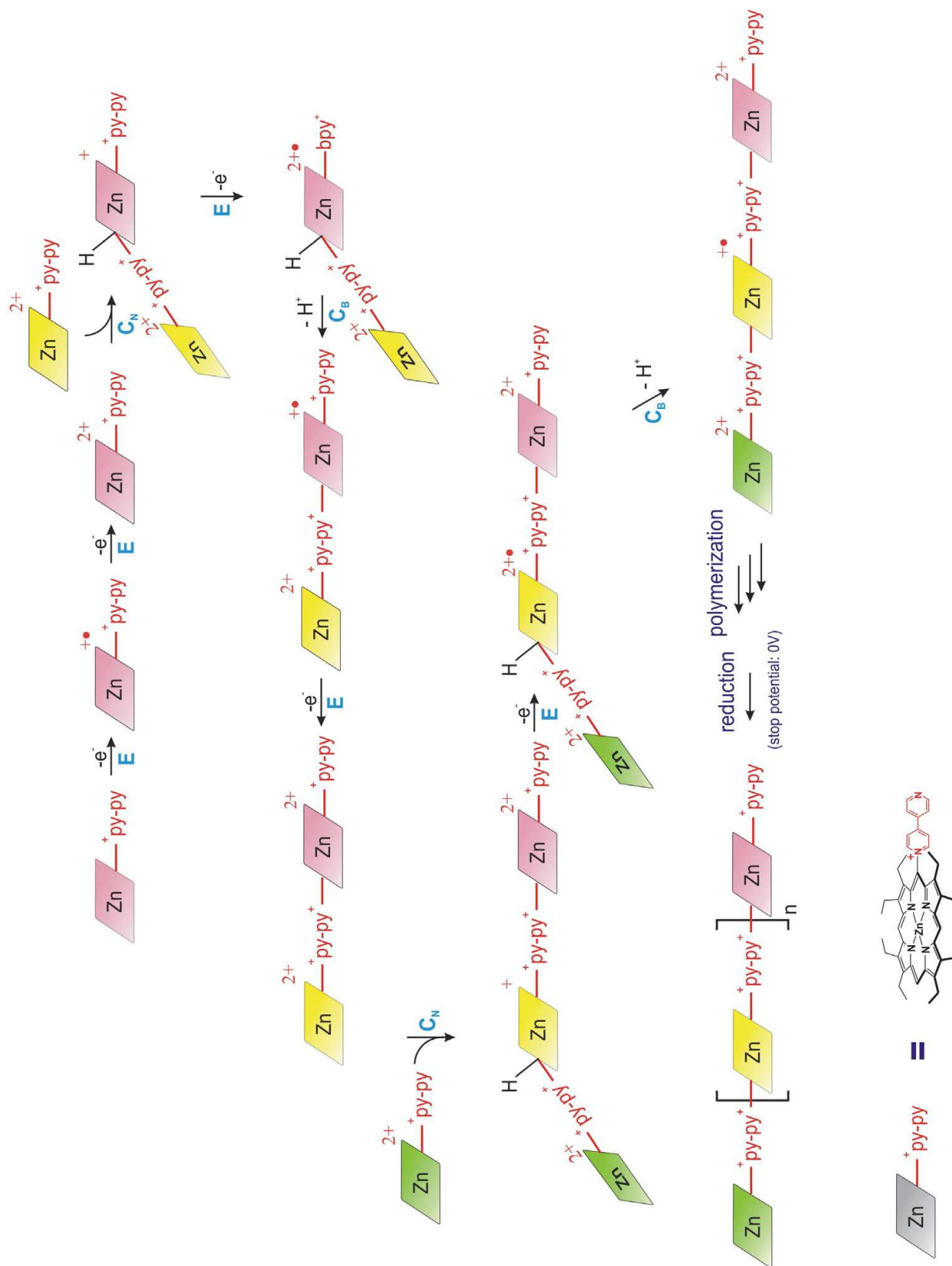
Fig. 5. E(EC$_N$EC$_B$)$_n$E mechanism proposed for the electropolymerization of the mono-
substituted ZnOEP(bpy)$^+$.

electropolymerization, the rate of the sweeps is too fast to perform nucleophilic attacks onto the radical cation, the reverse scan in the cathodic part (leading to its reduction) being too fast. Nevertheless, if an electrolysis is carried out at a potential corresponding to the formation of the radical cation, the electrode is coated, showing also the formation of oligomers and/or polymers. However, this polymeric film formation may also be due to the disproportionation of the radical cation (slow kinetic) leading to the non-oxidized ZnOEP and the porphyrin dication which can be attacked more rapidly by the nucleophile. Nevertheless, the advantage to perform electropolymerization by iterative scans instead of electrolysis at a fixed potential is double: the protons released during the polymerization can be reduced during the cathodic scans, and the iterative scans allow a better homogeneity of the polymeric film deposited onto the electrode, therefore enhancing its conductivity. Another point which can explain the need to apply a higher potential for electropolymerization concerns the degree of substitution of macrocycles. Indeed, into the polymers, porphyrins are at least substituted twice by positively charged groups. Moreover, when the chain of polymer grows, the quantity of positively charged groups increases. Consequently, porphyrins are more and more difficult to oxidize, needing an increase of the oxidative potential to perform the polymerization. This explanation is also supported by the fact that a higher potential has always been required to perform electrosyntheses of multi-substituted porphyrins by electrolysis. As a matter of fact, it can also be noted that the higher the limit potential during the anodic sweeps is, the longer the polymeric chains could be obtained. Otherwise, if the limit potential is too low, only small oligomers can be obtained.

3.3 Control of the geometry of the polymer

The use of ZnOEP(bpy)$^+$ as monomer allows multi-substitutions onto macrocycles because three *meso*-positions remain free (positions 10, 15 and 20, Fig. 3). Thus, nucleophilic attacks can occur on each of them, and consequently that can lead to the formation of zig-zag polymers and eventually of hyper-branched polymers. In order to permit a better control of the geometry of the obtained polymers, porphyrins substituted by two protecting groups as chlorides (zinc 5-bipyridinium-10,20-dichloro-β-octaethylporphyrin, abbreviated ZnOEP(Cl)$_2$(bpy)$^+$) can be used (Ruhlmann et al., 1999b). In this case, linear wires of polymers are obtained because only one *meso*-position remains free. Transmission electron micrographs of this polymer show long wires having length of several micrometers and diameter of about 20 Å (Fig. 6). This is in agreement with the 19 Å molecular width of a ZnOEP molecule.
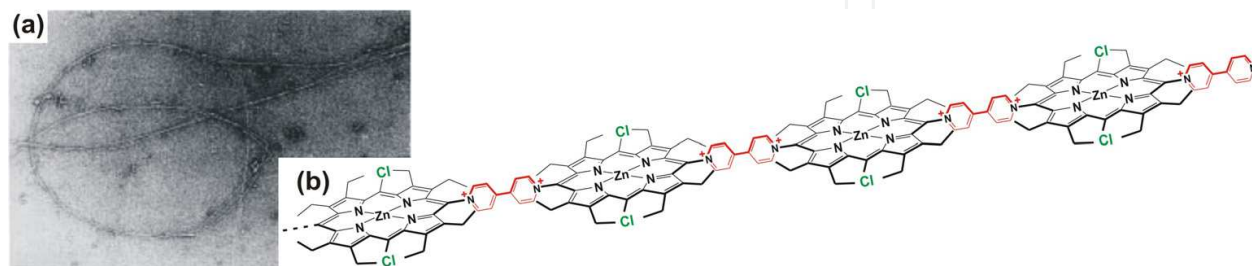

Fig. 6. (a) Transmission electron micrograph of a linear fiber obtained by electropolymerization of ZnOEP(Cl)$_2$(bpy)$^+$. (b) Scheme of the linear chain obtained.

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4. A new process of Easy Polymerization Of Porphyrins (EPOP process)

4.1 A first example

The way of electropolymerization of porphyrins presented above requires a first step consisting in the synthesis of the starting monomeric subunit (ZnOEP(bpy)+). The synthesis of this monomer can be performed by the electrochemical process described before, (reaction of 4,4′-bipyridine with the electrogenerated radical cation of the ZnOEP, see part 2). Even if this synthesis appears easy, the further purification of the obtained compound is more difficult, due to the possibility of multi-substitutions onto the macrocycle. In order to avoid the synthesis of this monomeric subunit, we have recently proposed an alternative method consisting in the direct use of commercial and non-substituted ZnOEP, with the presence of free 4,4′-bipyridine (bpy) in the solution (Fig. 7) (Giraudeau et al., 2010).
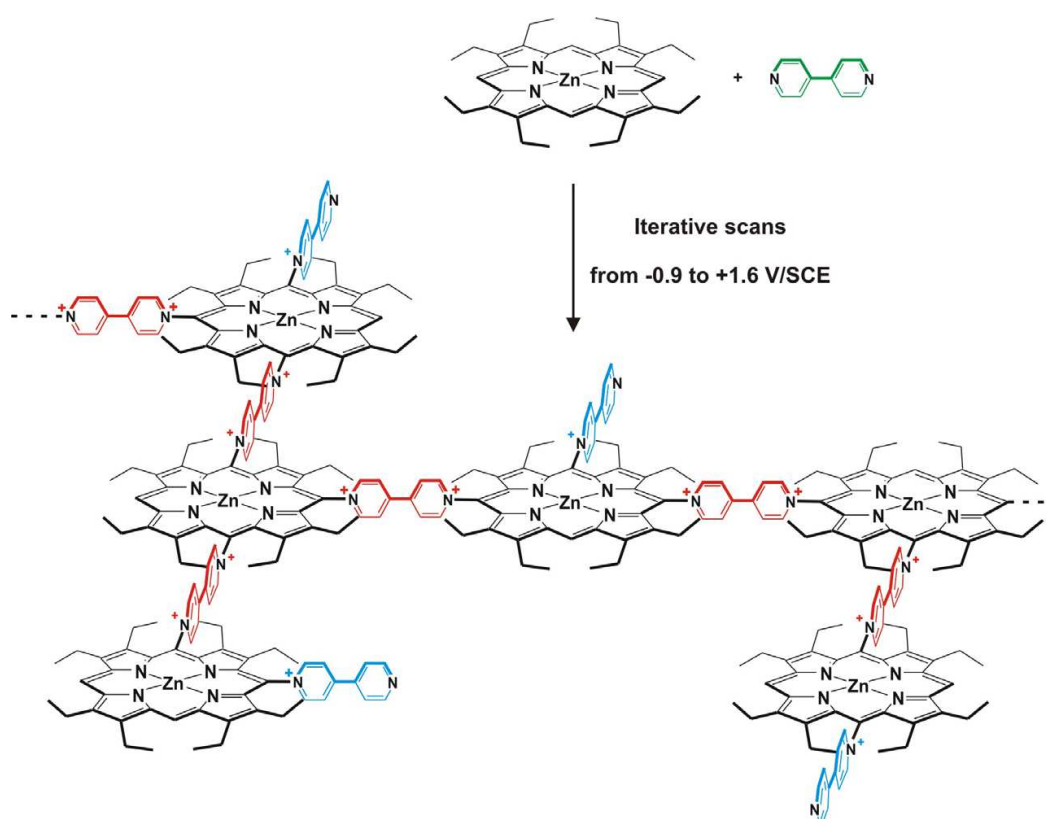

Fig. 7. Electropolymerization scheme of the non-substituted ZnOEP with free bpy.

As previously, electropolymerization can be performed with iterative scans by cyclic voltammetry (Fig. 8). The current increases again during the iterative sweeps. Compared to the cyclic voltammograms obtained in the previous case (Fig. 4), an additional reversible wave is observed at –0.30 V/SCE (peak c in Fig. 8). This additional wave can be attributed to the reduction of the bipyridinium substituents (Schaming et al., 2011b). Indeed, in this case, many bipyridinium groups can be grafted on the macrocycles, without further polymeric chains growth, because of the too important hindrance between the macrocycles. Consequently, the polymer obtained from non-substituted ZnOEP and free bpy can have many bipyridinium groups substituted onto the porphyrins (represented in blue in Fig. 7), leading to the appearance of this new reversible wave corresponding to the reduction of these bipyridinium substituents. On the contrary, when ZnOEP(bpy)+ is used to carry out

the electropolymerization, each chain of polymer can contain only one bipyridinium substituent (at the end of the chain, represented in blue in Fig. 3). In this case, the number of bipyridinium substituents is negligible compared to the number of viologen spacers (present between each macrocycle and represented in red in Fig. 3). As a matter of fact, the signal corresponding to the reduction of these bipyridinium substituents is not observed for the polymer obtained from the substituted monomer ZnOEP(bpy)$^+$.
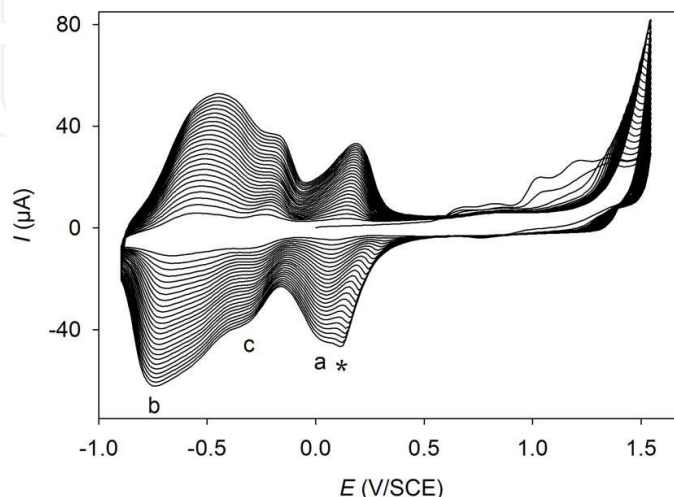
Fig. 8. Cyclic voltammograms recorded during the iterative scans between –0.90 and +1.60 V/SCE of ZnOEP (0.25 mM) in the presence of bpy (0.25 mM) in 1,2-$C_2H_4Cl_2$ and 0.1 M NEt_4PF_6. Working electrode: ITO; S = 1 cm^2; v = 0.2 V s^{-1}.

4.2 Extension to the use of other spacers

As previously said, this second method of electropolymerization allows to avoid the synthesis of the monomeric substituted porphyrin (ZnOEP(bpy)$^+$ for example). Thus, this new way of electropolymerization more conveniently allows the use of the commercial free base porphyrin (H$_2$OEP) or metalloporphyrins (MOEP) with different central metals (M = Co^{II}, Mg^{II}, Ni^{II}, Ru^{II}(CO)…) (Giraudeau et al., 2010). For all of them, an electropolymerization process has been observed, even when porphyrins with oxidable central metal (CoOEP and NiOEP) have been used. Consequently, further applications could be envisaged. For example, polymer with CoOEP could be promising for dioxygen reduction, cobalt porphyrins being known to catalyze this reaction (Chen et al., 2010; Collman et al., 1980).

Moreover, it is also possible to modulate easily the nature of the bridging spacers between the porphyrin macrocycles. Indeed, instead of using free bpy, this process of electropolymerization can be extended to other spacers by varying the nature of the nucleophile, since each compound having two pendant pyridyl groups can be used as spacer. The spacers can be selected for their specific chemical and structural properties: rigid or not; long or short; electron conducting or not; electroreducible or not; with conjugated π bonds (aromatic/alkene/alkyne chains) or successive σ bonds (alkyl chains)… For instance, electropolymerization has been successfully carried out with different nucleophilic compounds (named Py-R-Py) as 1,2-bis(4-pyridyl)ethane (bpe), trans-1,2-bis(4-pyridyl)ethylene (tbpe), but also with reducible spacers as 4,4′-azopyridine (azpy) and 3,6-bis(4-pyridyl)-s-tetrazine (tzpy) (Fig. 9) (Giraudeau et al., 2010; Schaming et al., 2011b).
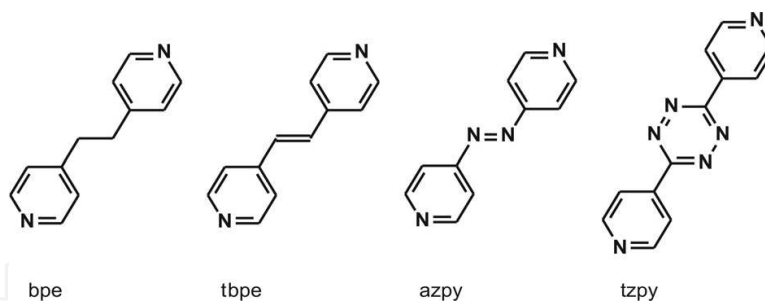
Fig. 9. Several Lewis bases (Py-R-Py) used as spacers: 1,2-bis(4-pyridyl)ethane (bpe), trans-1,2-bis(4-pyridyl)ethylene (tbpe), 4,4'-azopyridine (azpy) and 3,6-bis(4-pyridyl)-*s*-tetrazine (tzpy).

5. Studies of the polymers

When the electropolymerization process is finished (stopped after a pre-defined number of scans: 25 scans for all studies described in this paragraph, unless otherwise indicated), the electrode is removed from the electrochemical cell. Then, the electrode is systematically coated with a brown thin film corresponding to the polymer. In order to study in more details these polymers, it is necessary to previously wash the electrode with CH_3CN or water in order to remove the supporting electrolyte (NEt_4PF_6).

5.1 UV-visible absorption and fluorescence spectroscopies

Firstly, the polymers can be characterized by UV-visible absorption spectroscopy. When an ITO electrode is used to perform the electropolymerization, the spectrum can be recorded directly onto this optically transparent electrode. Whatever the method of electropolymerization, and whatever the spacer presented before, the spectra are similar (blue spectrum, Fig. 10.a). They consist in a large Soret band whose maximum is red-shifted compared to the ZnOEP monomer. Similarly, Q bands are also red-shifted and larger. That can be attributed to the intra- and intermolecular interactions between the porphyrins subunits (Giraudeau et al., 2010; Ruhlmann et al., 2008). The red-shift of the Soret and Q bands can also result from the electron-withdrawing effect of the positively charged pyridinium groups on the macrocycles (Giraudeau et al., 1996, 2010).
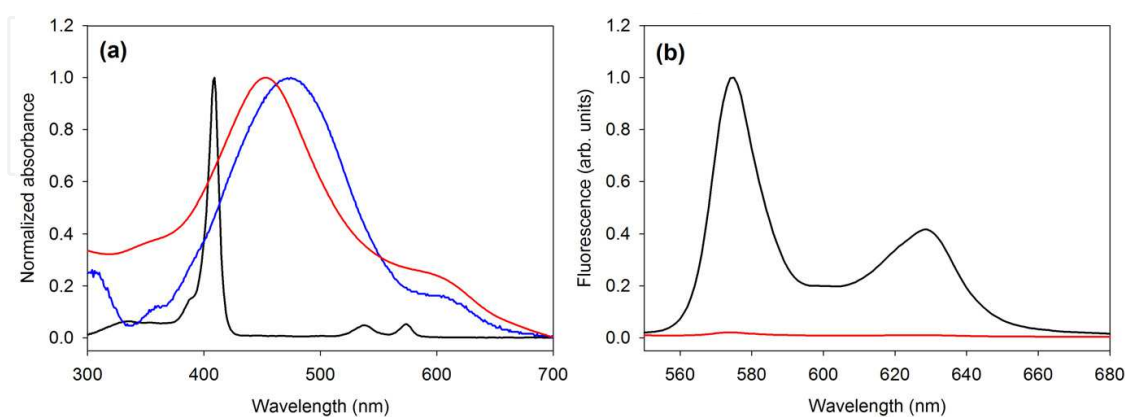

Fig. 10. (a) Normalized UV-visible absorption spectra of ZnOEP in DMF (—), of an ITO electrode modified with the polymer obtained from ZnOEP and bpy after 25 iterative scans (—) and of this same polymer in solution in DMF (—). (b) Luminescence spectra of ZnOEP (—) and of the polymer obtained from ZnOEP and bpy (—) in DMF. λ_{exc} = 420 nm.

Moreover, the polymers can be removed from the electrode by dissolution in dimethylformamide (DMF). That allows to record the spectra of the polymers in solution (red spectrum, Fig. 10.a). Comparing the spectra obtained onto ITO electrodes, the red-shift of the Soret band for spectra recorded in solution appears smaller. Such an evolution can be explained by a decrease of the interactions between the macrocycles when the polymers are in solution. Indeed, in solution, polymeric chains are partially unfolded.

When polymers are in solution, it is also possible to study their luminescence properties: all the investigated polymers show a total quenching (Fig. 10.b).

5.2 Atomic force microscopy (AFM)

The morphology of the polymers can be observed directly onto ITO electrodes by atomic force microscopy (AFM).

Depending on the solvent used to wash the electrode, the morphologies of the deposited polymers appear different (Ruhlmann et al., 2008). Indeed, when water is used to wash the polymer obtained from the mono-substituted porphyrin $ZnOEP(bpy)^+$, this one appears in the form of coils (diameter of *ca.* 50 nm) quasi-packed in the same direction (Fig. 11.a). This orientation effect might be induced by a self-alignment of the polycationic coils in the applied electric field during the electropolymerization. Moreover, after changing of the position of the ITO electrode, the coils cross over each, as shown in Fig. 11.a. That demonstrates the direct influence of the applied electric field onto the polymer arrangement during the electropolymerization process. Nevertheless, when CH_3CN is used instead of water to wash the polymer, a drastic reorganization of these tightly packed coils is observed. Indeed, the alignment of the polymers disappears and a homogeneous dispersion of the coils is observed (Fig. 11.b).
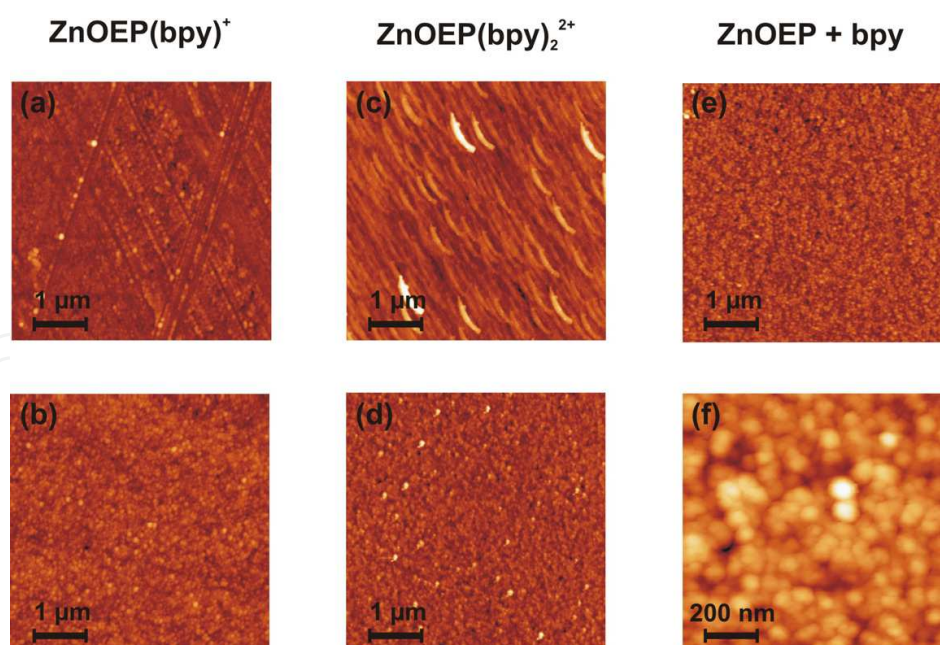

Fig. 11. Atomic force micrographs of different polymers obtained onto ITO electrodes after 25 iterative scans: (a) and (b) polymer obtained from $ZnOEP(bpy)^+$, after washing with (a) water and (b) CH_3CN; (c) and (d) polymer obtained from $ZnOEP(bpy)_2^{2+}$, after washing with (c) water and (d) CH_3CN; (e) and (f) polymer obtained from ZnOEP + bpy, after washing with (e) water and (f) CH_3CN (zoom).

It can be noticed that similar electropolymerization has also been performed from the ZnOEP macrocycles substituted by two bipyridinium groups in *cis*-position (zinc 5,10-dibipyridinium-β-octaethylporphyrin, abbreviated 5,10-ZnOEP(bpy)$_2$$^{2+}$) (Ruhlmann et al., 2008). In that case, a regular arrangement of the coils aggregated in the form of "peanuts" (width of *ca.* 100 nm and length of *ca.* 900 nm), all oriented in the same direction, is observed when the washing is performed with water (Fig. 11.c). This enhancement of the self-alignment of the coils induced by the applied electric field could be explained by the increase of the number of positive charges in this case (because of the presence of two bipyridinium substituents onto each macrocycle) which would induce stronger coulombic repulsions between the different subunits. However a treatment with CH$_3$CN induces also a homogeneous dispersion of the coils (Fig. 11.d) as previously observed for the polymer obtained from the mono-substituted ZnOEP(bpy)$^+$.

In the case of the polymer obtained from the non-substituted ZnOEP with free bpy, tightly packed coils are also observed, but without specific alignment (Giraudeau et al., 2010), whatever the solvent used to wash the electrode (Fig. 11.e and f). That can be tentatively explained by the presence of free bpy which could lead to a disorganization of the film. Moreover, the free bpy can also axially coordinate the Zn central metal of the macrocycles (Giraudeau et al., 2010) which increases the distance between the macrocycles and consequently could lead to a decrease of the electrostatic effect between the macrocycles. As a result, effect of the applied electric field should be lesser onto the electropolymerization process, the orientation effect disappearing in this case.

5.3 Scanning Electrochemical Microscopy (SECM)

Scanning electrochemical microscopy (SECM) in feedback mode has also been used to investigate electronic and permeation properties of the polymeric films obtained from the mono-substituted ZnOEP(bpy)$^+$ and the non-substituted ZnOEP in presence of free bpy, in order to compare these two different electropolymerization ways allowing the formation of similar polymers (Leroux et al., 2010). Briefly, the SECM principle is based on the interaction of the polymeric film (deposited onto ITO electrode) under investigation with a redox probe (the mediator) that is electrogenerated at a microelectrode. This interaction is followed through the analysis of the current flowing at the microelectrode while it approaches the substrate. Depending on the nature of the mediator, the study of either the permeability or the reactivity is possible.

Firstly, ferrocene (Fc) and tetrathiafulvalene (TTF), which work in oxidation, have been chosen as mediator (Fig. 12.b). According to their redox potentials, their oxidized forms (Fc$^+$ and TTF$^{\bullet+}$, respectively) cannot react with the polymeric films (their redox potentials do not permit the oxidation of the porphyrin macrocycles) (Fig. 12.a). Thus, they are good candidates to probe the permeability of the polymeric films, because they can rapidly exchange electrons with the non-coated ITO substrate (positive feedback). Whatever the polymer studied as substrate onto the ITO electrode, a negative feedback is observed. These negative feedback characters are less important in the case of the polymer obtained from the non-substituted ZnOEP, showing that this polymer is more permeable than the one obtained from the mono-substituted ZnOEP(bpy)$^+$. That can be explained by an increase of the distance between the macrocycles due to the formation of bipyridine-bridged zinc porphyrins (bpy axially ligated to Zn) mentioned before (see part 5.2).

Secondly, tetracyanoquinodimethane (TCNQ) and 4-nitrobenzonitrile (4NB), which work in reduction, have been chosen as mediator (Fig. 12.b). Their redox potentials are sufficiently negative to permit to the reduced forms (TCNQ$^{\bullet-}$ and 4NB$^{\bullet-}$, respectively) to reduce the viologen spacers of the polymers (Fig. 12.a). Thus, they are good candidates to probe the reactivity of the polymeric films, because their electron exchanges with the non-coated ITO substrate are negligible (negative feedback). Nevertheless, a more important positive feedback is observed when the ITO electrodes are coated with a polymeric film, showing well the predicted reactivity of the polymers with these two mediators. But the positive feedback characters are lower in the case of the polymer obtained from the non-substituted ZnOEP. That can be explained by a lower conductivity of this polymer compared to the other one, because of an increase of the distance between the redox active centers also due to the formation of bipyridine-bridged zinc porphyrins.
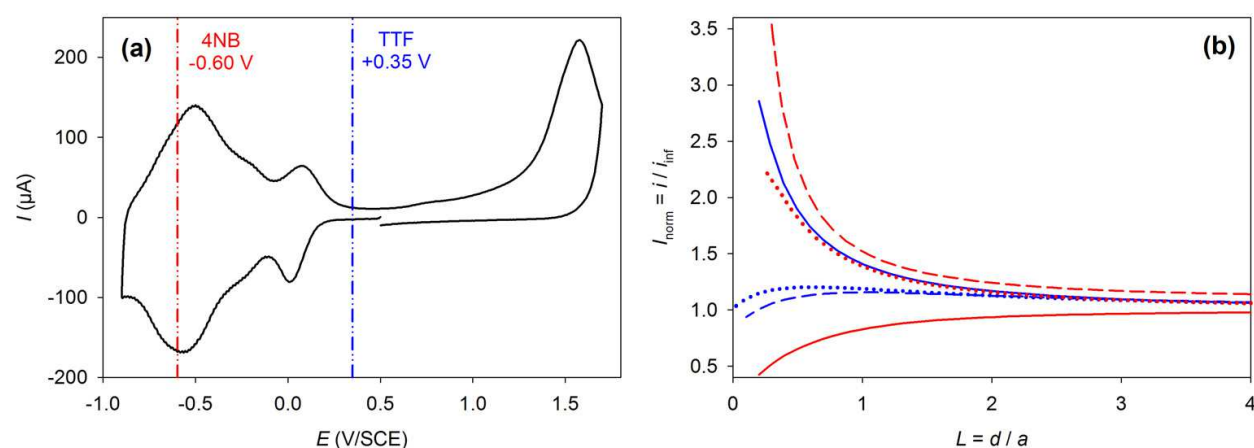

Fig. 12. (a) Cyclic voltammogram of the polymer obtained from ZnOEP and bpy after 25 iterative scans onto ITO electrode in CH$_3$CN and 0.1 M NBu$_4$PF$_6$ (v = 0.2 V s^{-1}), with indications of the redox potential values of several mediators used. (b) SECM approach curves, in CH$_3$CN and 0.1 M NBu$_4$PF$_6$ on non-coated ITO electrodes (full lines), ITO electrodes coated with the polymer obtained from ZnOEP(bpy)$^+$ after 25 iterative scans (dashed lines) and ITO electrodes coated with the polymer obtained from ZnOEP and bpy after 25 iterative scans (dotted lines), with TTF (—) and 4NB (—) used as redox mediators. L is the normalized distance and I_{norm} is the normalized current, where i corresponds to the current at a platinum microelectrode (with a radius a equal to 5 µm) localized at a distance d from the substrate and i_{inf} corresponds to the steady-state current when the microelectrode is at an infinite distance from the polymeric substrate.

5.4 Control of the polymeric film thickness

It is also interesting to note that electropolymerization allows easily to control the thickness of the polymeric film deposited onto the electrode (Schaming et al., 2011b).

As represented Fig. 13, plot of the absorbance of the polymer at the maximum of the Soret band as a function of the number n of iterative scans shows a linear increase. The thicknesses of the films determined from AFM confirm this point since a linear increase of the thickness with the value of n is observed (Fig. 13, inset).
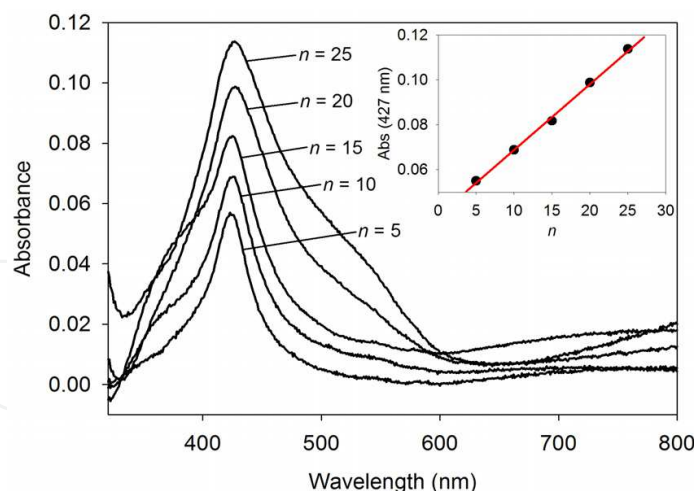
Fig. 13. UV-visible absorption spectra of ITO electrodes modified with the polymer obtained from ZnOEP and tzpy after different numbers n of iterative scans. Inset: absorbance at 427 nm *vs. n*.

6. Formation of original copolymers from the EPOP (Easy Polymerization Of Porphyrins) process

As previously explained, all compounds having two pendant pyridyl groups can play the role of spacers between macrocycles. Consequently, more original organic or inorganic compounds, with specific interesting properties, can be used, if two pendant pyridyl groups are present. Thus, this novel easy way of electropolymerization of porphyrins appears as a promising approach to elaborate new functional materials.

6.1 Porphyrin–porphyrin copolymers
6.1.1 Electropolymerization

In a first example, porphyrins having two pendant pyridyl groups have been used in order to obtain copolymers of porphyrins containing two different types of macrocycles. (Xia et al., 2012)

Fig. 14.b illustrates the cyclic voltammograms obtained in the case of the use of the 5,15-dipyridyl-10,20-diphenyl free base porphyrin (5,15-$H_2Py_2Ph_2P$) in the presence of zinc 5,15-dichloro-β-octaethylporphyrin (5,15-$ZnOEP(Cl)_2$). These two macrocycles have been chosen in order to allow the formation of a linear copolymer as represented in Fig. 14.a.

As expected, the current increases progressively during the iterative scans. The new reduction processes appearing around –0.40 and –0.60 V/SCE (peaks *) can be attributed to the reduction of the pyridinium spacers.

One can underline that even if the 5,15-$H_2Py_2Ph_2P$ porphyrin is oxidized during the iterative scans, no substitution in β-positions of this macrocycle by a pyridyl group of another 5,15-$H_2Py_2Ph_2P$ macrocycle could occur. Indeed, the kinetic of a nucleophilic substitution in β-position is too slow compared to the kinetic of a substitution in *meso*-position (see part 2). Consequently, while mono-substitutions are possible in β-position of porphyrins (Giraudeau et al., 1996), electropolymerization is very difficult and even impossible, because the rate of the iterative sweeps is too fast to let enough time for the β-substitutions in such experimental conditions.
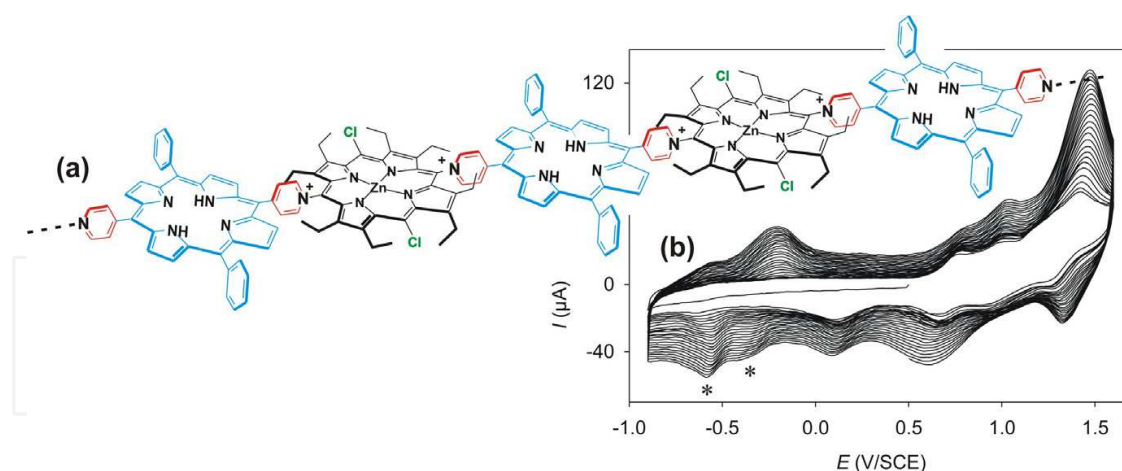
Fig. 14. (a) Scheme of the linear bis-porphyrin copolymer obtained. (b) Cyclic voltammograms recorded during the iterative scans between –0.90 and +1.60 V/SCE of 5,15-ZnOEP(Cl)$_2$ (0.25 mM) in the presence of 5,15-H$_2$Py$_2$Ph$_2$P (0.75 mM) in 1,2-C$_2$H$_4$Cl$_2$/CH$_3$CN (4:1) and 0.1 M NBu$_4$PF$_6$. Working electrode: ITO; S = 1 cm^2; v = 0.2 V s^{-1}.

6.1.2 Characterization

The characterization of this copolymer has also been performed by UV-visible absorption spectroscopy and by atomic force microscopy. No important change in comparison with the previous polymers has been observed. Indeed, its spectrum is red-shifted and larger compared to the ones of the porphyrins alone (Fig. 15.a). Furthermore, the copolymer appears as tightly packed coils without alignment (Fig. 15.b).
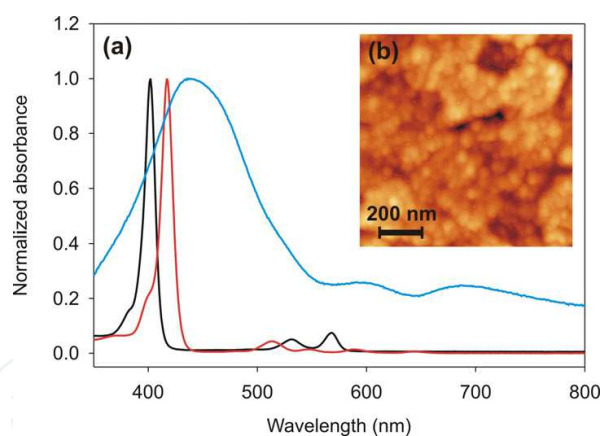

Fig. 15. (a) Normalized UV-visible absorption spectra of ZnOEP in 1,2-C$_2$H$_4$Cl$_2$ (—), of 5,15-H$_2$Py$_2$Ph$_2$P in 1,2-C$_2$H$_4$Cl$_2$ (—) and of an ITO electrode modified with the copolymer obtained from ZnOEP and 5,15-H$_2$Py$_2$Ph$_2$P after 25 iterative scans (—). (b) Atomic force micrograph of the same copolymer after washing with water.

6.2 Porphyrin–polyoxometalate copolymers

Polyoxometalates (POMs) are well-defined metal-oxygen cluster anions constituted of early metal elements in their highest oxidation state with a wide variety of structures and properties (Jeannin, 1998; Katsoulis, 1998). They have particularly attractive catalytic, electrocatalytic and photocatalytic applications. For instance, POMs are known to photocatalyze the reduction of noble or heavy metal cations (Costa-Coquelard et al., 2008; Troupis et al., 2001, 2006).

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Nevertheless, POMs are efficient only under UV light, which is a drawback for environmental applications. Indeed, it seems preferable to use solar light, principally in the visible domain. The development of photosensitized systems could overcome this issue. For instance, {POM–porphyrin} systems appear interesting for photocatalytic applications in the visible domain (Schaming et al., 2010a, 2011c; Schaming, 2010c). In these hybrid organic-inorganic systems, porphyrins act as photosensitizers able under visible illumination to transfer electrons to POMs, which are known to be good electron acceptors. Thus, the excitation of the porphyrins leads to their oxidation and to the simultaneous reduction of the POMs. Then, the reduced POMs are able to transfer electrons to M^{n+} cations to give M^0.

Using an Anderson-type POM substituted by two pendant pyridyl groups ($[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$, abbreviated py–POM–py), we have recently obtained a porphyrin–POM copolymer by the method of electropolymerization presented before (Fig. 16) (Schaming et al., 2010b).
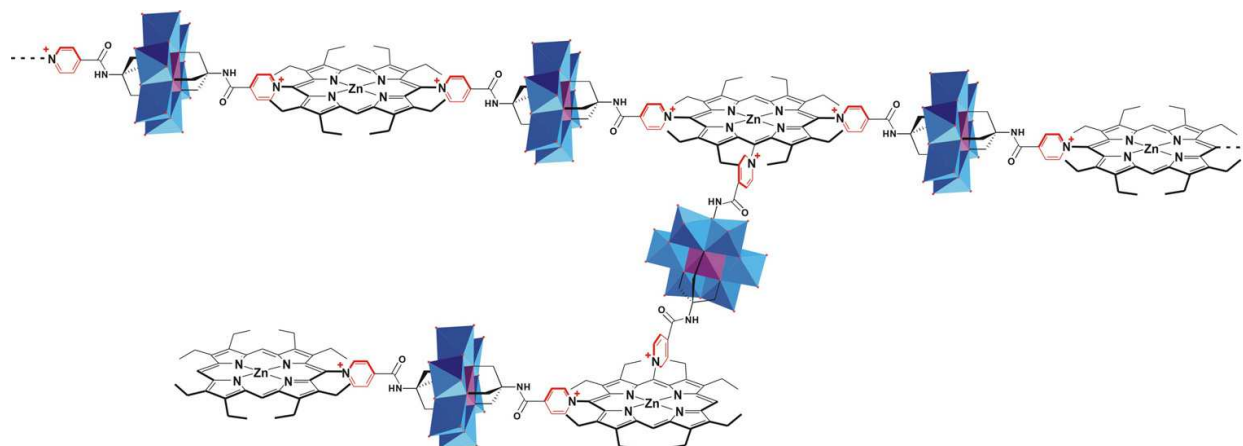

Fig. 16. Scheme of the porphyrin–POM copolymer.

6.2.1 Electropolymerization

Fig. 17.a shows the cyclic voltammograms obtained in the case of the use of the non-substituted ZnOEP macrocycle in the presence of the py–POM–py compound. As previously, the current increases progressively during the iterative scans. As already described, the new peak appearing around –1.00 V/SCE (peak *) can be attributed to the reduction of the pyridinium spacers. Nevertheless, one can also notice the appearance of a new peak around +0.20 V/SCE (peak •) during the anodic scans. This one could be assigned to the oxidation of the adsorbed H_2 formed upon the reduction of the protons during the cathodic scans, these protons being formed during the nucleophilic substitution onto the porphyrins. To explain the presence of this additional anodic peak (not observed previously), one can suggest that it is due to the presence of POMs which can be easily protonated and consequently the released protons are not dispersed in the solution but remain close to the electrode. As a matter of fact, they can be easier and in bigger quantity reduced during the cathodic scans, and the H_2 formed can be further re-oxidized.

In order to confirm the assignment of this wave, the electropolymerization process has also been carried out with iterative scans performed only in the anodic part (scans stopped at 0 V/SCE), in order to avoid the reduction of the protons. As expected, the signal assigned to the oxidation of the adsorbed H_2 disappears (Fig. 17.b). Surprisingly, in this case, the current decreases during the iterative scans. Thus, the copolymer obtained by this way seems less conductive. This decrease in the conductivity can be tentatively explained by the fact that

when the electropolymerization is performed by oxidative and reductive scans, the film should be more organized and consequently more conductive than when performed only by oxidative scans.
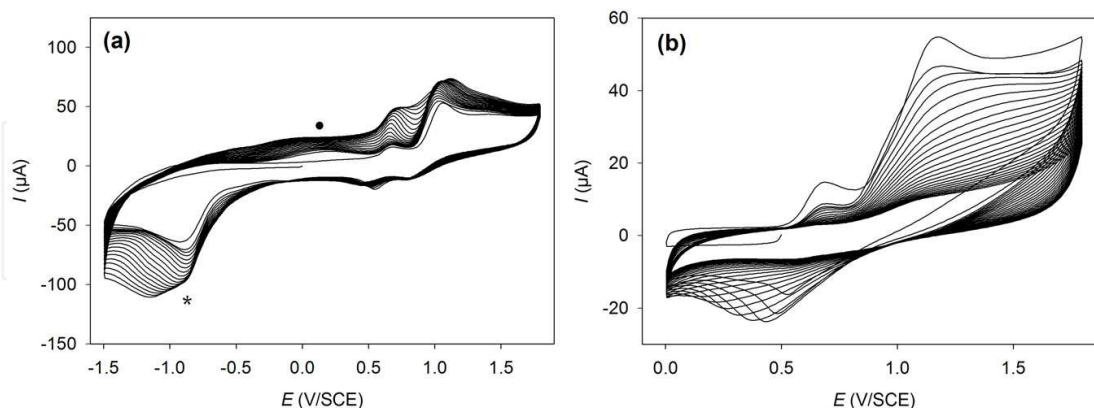

Fig. 17. Cyclic voltammograms recorded during the iterative scans (a) between –1.50 and +1.80 V/SCE and (b) between 0 and +1.80 V/SCE of ZnOEP (0.25 mM) in the presence of py–POM–py (0.25 mM) in 1,2-$C_2H_4Cl_2$/CH_3CN (7:3) and 0.1 M NBu_4PF_6. Working electrode: ITO; S = 1 cm^2; v = 0.2 V s^{-1}.

6.2.2 Characterization

Compared to the previous polymers, the UV-visible absorption spectrum of the porphyrin-POM copolymer appears less large and more structured (Fig. 18.a). That can be attributed to the presence of POM between each macrocycle, which avoids interactions between adjacent porphyrins. Concerning its morphology, this copolymer appears again as little coils (Fig. 18.b).
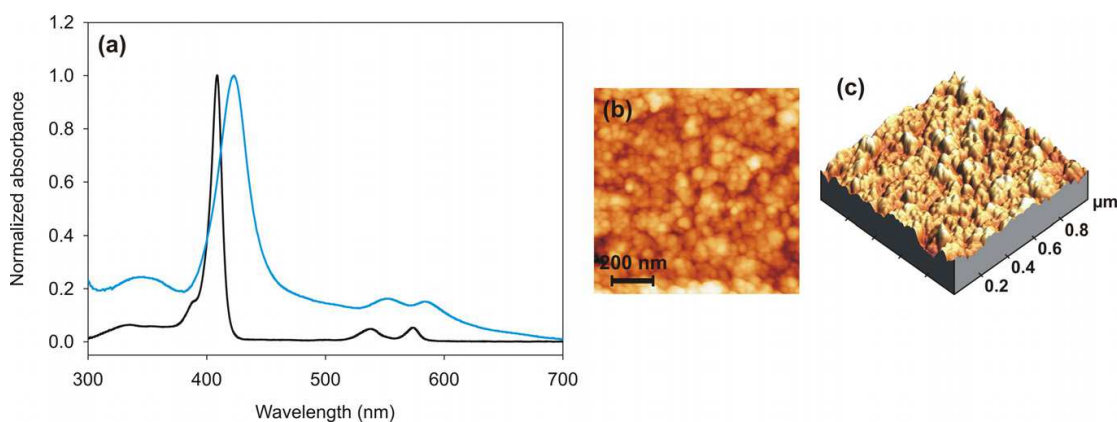

Fig. 18. (a) Normalized UV-visible absorption spectra of ZnOEP in DMF (—) and of an ITO electrode modified with the copolymer obtained from ZnOEP and py–POM–py after 25 iterative scans performed between –1.50 and +1.80 V/SCE (—). (b) 2D and (c) 3D atomic force micrographs of the same copolymer.

6.2.3 Use of di-substituted ZnOEP porphyrins

Different di-substituted ZnOEP macrocycles have also been used in order to control the geometry of the copolymers. As previously explained, 5,15-ZnOEP(Cl)$_2$ allows the formation of linear polymers. But it can be noticed that the zinc 5,15-dipyridinium-β-octaethylporphyrin (5,15-ZnOEP(py)$_2$$^{2+}$) can also be used in the same purpose. It is

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interesting to note that in this case the morphology of the obtained copolymer is quite different. Indeed, the coils appear more agglomerated (Fig. 19.b), while in the case of the use of 5,15-ZnOEP(Cl)$_2$, non-agglomerated coils are observed (Fig. 19.a).
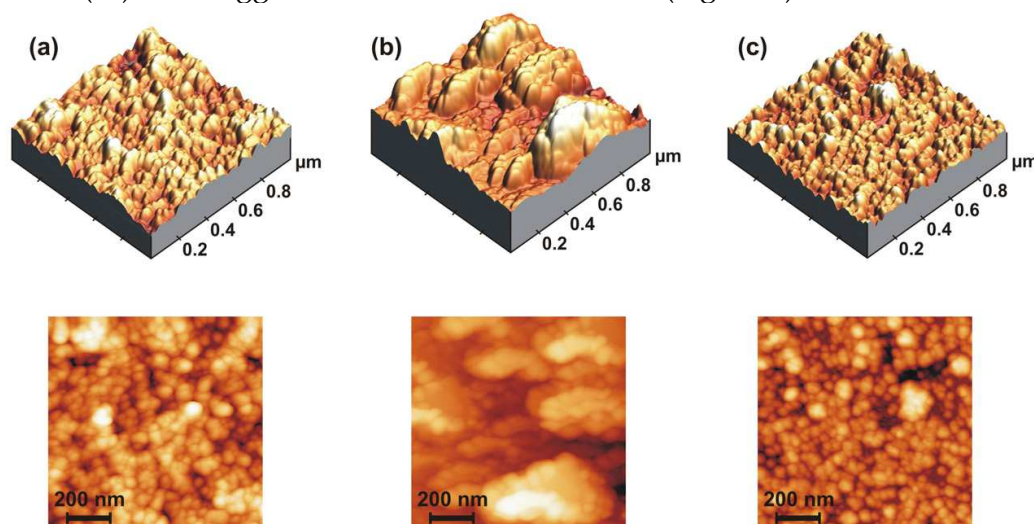

Fig. 19. 2D and 3D atomic force micrographs of different porphyrin–POM copolymers obtained onto ITO electrodes after 25 iterative scans: (a) polymer obtained from 5,15-ZnOEP(Cl)$_2$ by iterative scans between –1.30 and +1.80 V/SCE; (b) polymer obtained from 5,15-ZnOEP(py)$_2^{2+}$ by iterative scans between –1.50 and +1.80 V/SCE and (c) polymer obtained from 5,15-ZnOEP(py)$_2^{2+}$ by iterative scans between 0 and +1.80 V/SCE.
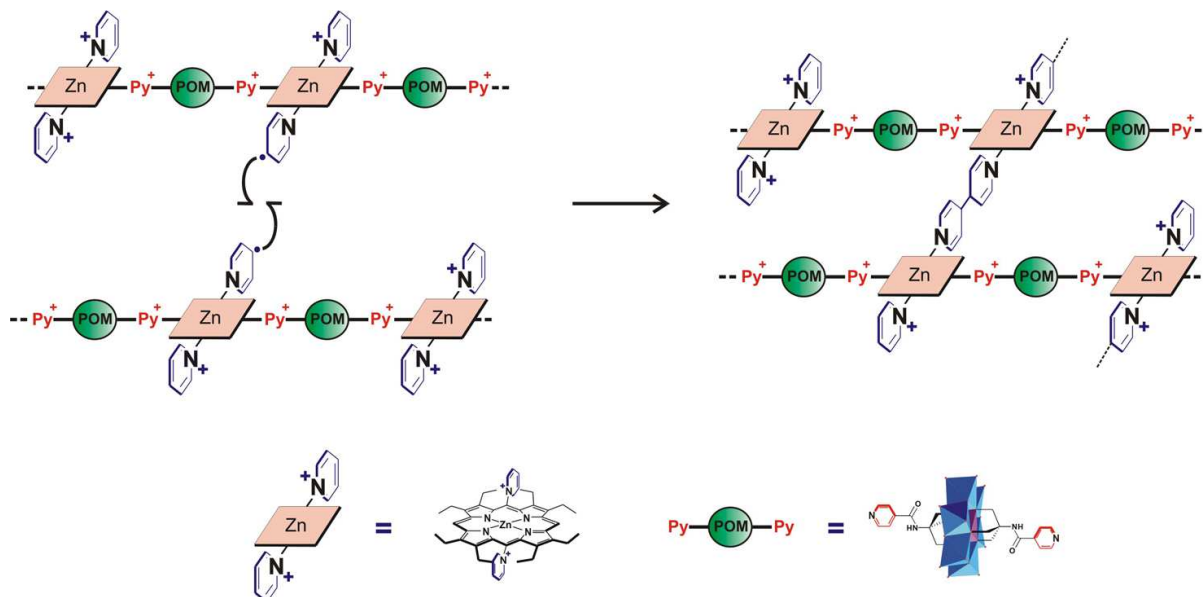

Fig. 20. Scheme of the coupling in 4-position of the electrogenerated pyridyl radicals leading to their oligomerization.

This agglomeration of the coils when 5,15-ZnOEP(py)$_2^{2+}$ is used can be explained by the chemical reactivity of the pyridyl radicals obtained during the cathodic scans by reduction of the pyridiniums used as protecting groups. Indeed, these electrogenerated pyridyl radicals can react each other to give oligomeric species resulting from the coupling at the 4-position of the radicals (Fig. 20). This coupling has already been described in several works (Brisach-Wittmeyer et al., 2005; Carelli et al., 1998, 2002; Karakostas et al. 2010; Schaming et

al., 2009). To check this explanation, the electropolymerization with 5,15-ZnOEP(py)$_2$$^{2+}$ has also been performed by iterative scans limited to the anodic part (cyclic voltammograms performed between 0 and +1.80 V/SCE) in order to avoid the reduction of the pyridinium substituents. As expected, the coils appear non-agglomerated in this case (Fig. 19.c).

6.2.4 Photocatalytic tests

As previously said, this porphyrin–POM copolymer has been prepared in order to use it as photocatalyst for the reduction of metal cations. For this purpose, we have chosen silver cations as a model system to perform photocatalytic tests (Schaming et al., 2010b).

To carry out this experiment, the copolymer has previously been removed from the electrode by dissolution in DMF, and then, a drop of the copolymer solution has been deposited on a slide of quartz and the solvent evaporated in air. Then, the covered slide has been plunged in an aqueous solution of Ag$_2$SO$_4$ (80 µM) containing 0.13 M of propan-2-ol used as sacrificial electron donor. Finally, the sample has been exposed during 8 hours to visible light. The reaction has been followed by UV-visible absorption spectroscopy (Fig. 21.a): during light irradiation, a very large plasmon band appeared progressively, suggesting the formation of silver aggregates. Transmission electron micrographs and electron diffraction patterns have confirmed this result: silver triangular nanosheets were principally obtained (Fig. 21.b and c). The mechanism explaining the reaction has been discussed in detail in our previous works (Schaming et al., 2010a, 2011c).
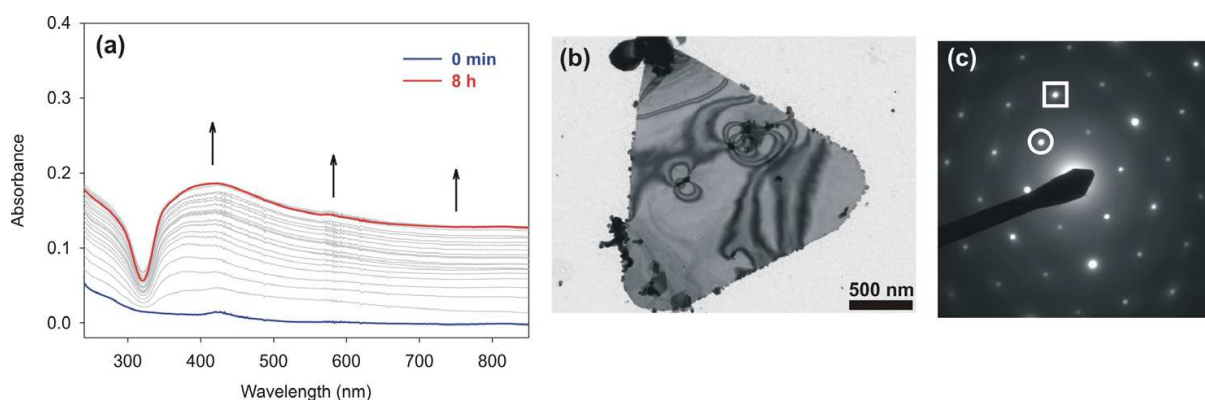

Fig. 21. (a) Change in the UV-visible absorption spectrum of a porphyrin–POM copolymer deposited on quartz in aerated aqueous solution containing 80 µM of Ag$_2$SO$_4$ and 0.13 M of propan-2-ol under visible illumination. (b) Transmission electron micrograph of a silver triangular nanosheet obtained. (c) Selected-area electron diffraction pattern of the previous silver nanostructure. The first spots (circled) correspond to the formally forbidden ⅓{422} reflections and the second spots (squared) correspond to the {220} reflections.

For this study, silver has been chosen as a model system for metal reduction, but this copolymer could be used in water depollution for reduction or recovery of valuable or toxic metals that could also be combined with degradation of organic pollutants (used instead of sacrificial donor) as already proposed (Troupis et al., 2006).

6.2.5 Electrostatic {porphyrin–POM} systems

It can be noticed that hybrid {porphyrin–POM} systems can be obtained for similar application purposes by plunging an ITO electrode coated with a cationic polymer of porphyrins, as described in the first parts of this chapter, into an aqueous solution of POMs. The aim of this process is to replace the counteranions of the polycationic polymers (PF$_6$$^-$ further to the

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electropolymerization) by POMs which are large polyanions. Thus, electrostatic interactions between the cationic porphyrin polymers and the anionic POMs can occur, leading to a hybrid supramolecular assembly. For instance, the dipping of an ITO electrode coated with a polymer obtained from 5,10-ZnOEP(bpy)$_2^{2+}$ in an aqueous solution of $SiW_{12}O_{40}^{4-}$ for 10 hours has been studied (Hao et al., 2008). Atomic force microscopy studies of the deposit show strong modifications to its morphology (Fig. 22). Indeed, the initial regular arrangement of the coils aggregated in the form of "peanuts" (Fig. 11.c) has disappeared and regular cloudy assemblies which are still oriented in the same direction are now observed. Such supramolecular assemblies are the consequence of an agglomeration of "peanuts" by the POMs.
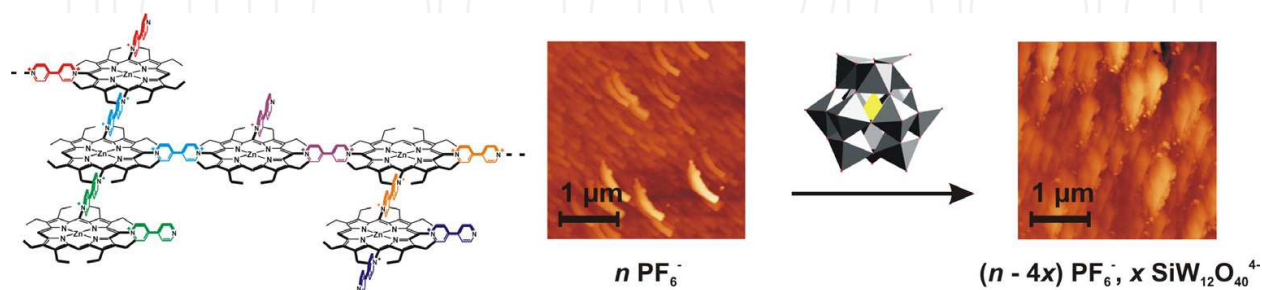

n PF$_6^-$ $(n - 4x)$ PF$_6^-$, x SiW$_{12}$O$_{40}^{4-}$

Fig. 22. Atomic force micrographs of an ITO electrode coated with the polymer obtained from 5,10-ZnOEP(bpy)$_2^{2+}$ after plunging for 10 hours in water (left) and in a solution of $SiW_{12}O_{40}^{4-}$ (1 mM) (right).

7. Conclusion

In this chapter, we have shown that electropolymerization of porphyrins can be easily performed by nucleophilic attacks of di-pyridyl compounds directly onto electrogenerated dications of octaethylporphyrins, by an ECEC-type mechanism.

The first tests have been performed with porphyrins substituted with bipyridinium(s). According to the degree of substitution of the monomer (which is linked to its charge), different morphologies of the polymers can be observed, which seem to be induced by the electric field imposed during the electropolymerization process.

We have further shown that it is also possible to use non-substituted β-octaethylporphyrins in the presence of free Lewis bases having two nucleophilic sites. This second way of electropolymerization allows to avoid the somewhat complicated synthesis of the monomeric substituted porphyrin, and consequently allows to modulate easily the nature of the bridging spacers between the macrocycles. Thus, original organic or inorganic compounds, with specific interesting properties, can be used, on condition that two pyridyl groups have beforehand been grafted. Consequently, this new easy way of electropolymerization of porphyrins appears as a promising approach to elaborate new functional materials, for example with catalytic properties if polyoxometalates are used as spacers. Other applications can be envisaged according to the spacer chosen.

Finally, it is interesting to note that as all the electropolymerization methods, it is easy to control the thickness of the polymers, according to the number of scans performed, which is also a great advantage compared to the classical chemical methods of polymerization.

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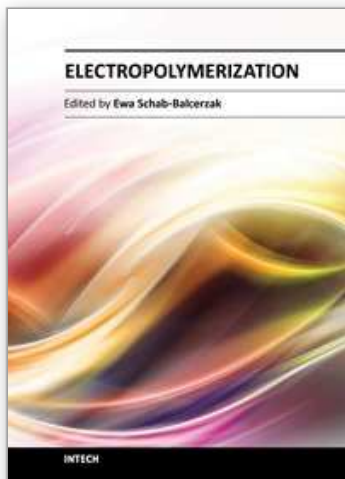
Electropolymerization

Edited by Dr. Ewa Schab-Balcerzak

In recent years, great focus has been placed upon polymer thin films. These polymer thin films are important in many technological applications, ranging from coatings and adhesives to organic electronic devices, including sensors and detectors. Electrochemical polymerization is preferable, especially if the polymeric product is intended for use as polymer thin films, because electrogeneration allows fine control over the film thickness, an important parameter for fabrication of devices. Moreover, it was demonstrated that it is possible to modify the material properties by parameter control of the electrodeposition process. Electrochemistry is an excellent tool, not only for synthesis, but also for characterization and application of various types of materials. This book provides a timely overview of a current state of knowledge regarding the use of electropolymerization for new materials preparation, including conducting polymers and various possibilities of applications.

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