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PAPER

Bis-porphyrin copolymers covalently linked by pyridinium spacers obtained by electropolymerization from β-octaethylporphyrins and pyridyl-substituted porphyrins†

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Five bis-porphyrin copolymers have been obtained by an electropolymerization process using zinc β-octaethylporphyrin (ZnOEP) type macrocycles and porphyrins functionalized by several pyridyl groups. This electropolymerization process is based on a nucleophilic attack of the pyridyl groups onto electrogenerated ZnOEP dications at their *meso*-positions. It is the first time that bis-porphyrin copolymers have been obtained. In this study, the copolymers have been characterized by electrochemistry, UV-visible absorption spectroscopy and atomic force microscopy. In particular, interactions between pyridinium spacers are thoroughly discussed.

Introduction

Porphyrins and porphyrin-containing materials are among the most-studied chromophores, 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. In particular, conducting porphyrin polymers are used in applications such as solar energy transformation cells, potentiometric or amperometric sensors, catalysts, biomedicine, electronic devices and photonics.[1–7]

Different routes allowing the formation of porphyrin polymers have already been described in the literature. Among them, the strategies most developed correspond to the formation of coordination and covalent polymers.

A first general method to obtain metalloporphyrin polymers is the use of bridging ligands which can coordinate the metal center. For instance, such coordination polymers have been obtained by coordination of nitrogenous ligands with ruthenium, osmium or iron porphyrins.[8,9]

Concerning covalent polymers, they can be principally obtained by a classical chemical way or by an electrochemical way. For example, several reports have exposed the possibility to achieve direct polymerization of porphyrins *via* a *meso–meso* coupling. Indeed, Osuka *et al.* have proposed a method based on the chemical oxidation of zinc diarylporphyrins using $Ag^{I}PF_6$ as oxidant.[10,11] Moreover, a similar *meso–meso* coupled polymer has also been recently obtained by electrooxidation of the magnesium porphine at a potential corresponding to the first oxidation of the macrocycle.[12] However, more currently, the formation of covalent polymers relies on the use of porphyrins with polymerizable substituents attached on the ring periphery. For instance, polymerization of amino, pyrrole or thiophene-substituted porphyrins has been allowed either by a classical chemical route[4,13] or by an electrochemical process.[2,13–19]

In this context, we have developed in our precedent works an original methodology for electropolymerization of porphyrins, based on the nucleophilic attacks of di-pyridyl compounds directly onto electrogenerated β-octaethylporphyrin (OEP) dications.[20,21] Indeed, compounds having two pendant pyridyl groups present two accessible nucleophilic sites which can both react with electrooxidized porphyrin rings in the *meso*-position. A detailed study has been performed using 4,4′-bipyridine as a spacer. This methodology has further been extended to the use of other pyridine-derived spacers, where the organic links between the two pyridyl groups have been changed according to their specific properties: rigid or not, long or short, with conjugated π bonds or successive σ bonds. This novel easy way of electropolymerization opens up also original synthesis routes for the elaboration of new functional materials. Indeed, for instance, it has been possible to obtain original hybrid organic–inorganic copolymers by using an inorganic compound (such as polyoxometalate) functionalized

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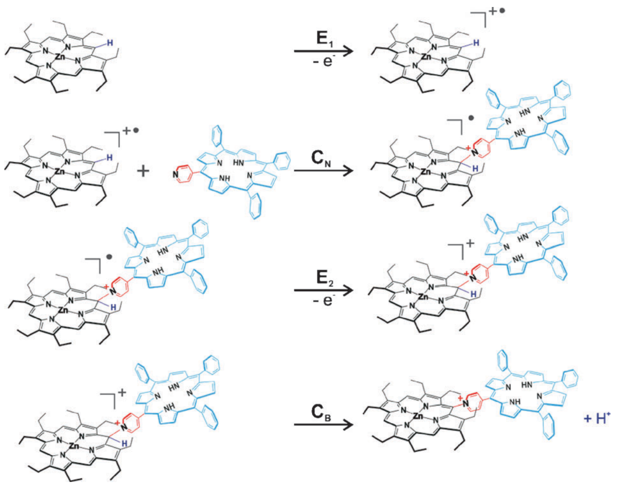
by two pendant pyridyl groups.[22] Such porphyrin–polyoxometalate copolymers have presented interesting photocatalytic properties.

In this paper, we show hereafter that this method of electropolymerization also allows to easily obtain copolymers of porphyrins containing two different types of macrocycles. Indeed, porphyrins substituted by at least two pendant pyridyl groups can be used as spacers to link a second type of macrocycle (for instance, OEP-type). To our knowledge, it is the first method of electropolymerization which allows formation of such bis-porphyrin copolymers. Moreover, for these copolymers, the bridging spacer between the macrocycles is shorter compared to spacers previously used, because only pyridinium groups bridge the porphyrins with another.

Results and discussion

Electropolymerization and electrochemical properties of the copolymers

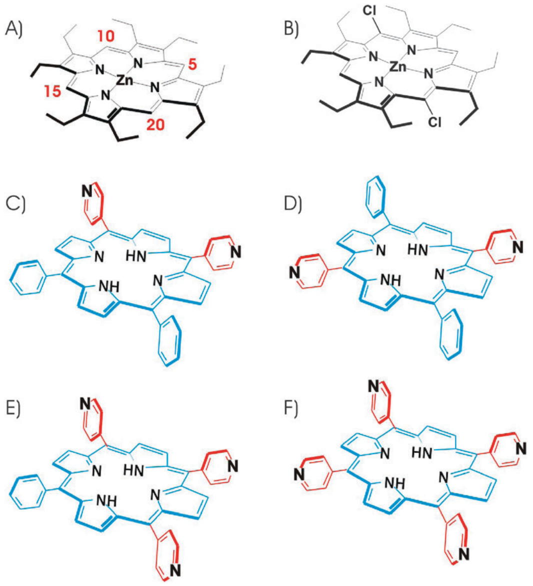
We have recently shown that the use of a porphyrin substituted by one pendant pyridyl group allows the formation of a dimer of porphyrins in the presence of electrooxidized zinc β-octaethylporphyrin (step E_1) *via* an $E_1C_NE_2C_B$ process (Scheme 1).[23] Indeed, the pyridyl group can attack in the *meso*-position of the electrooxidized ZnOEP (step C_N), leading first to the formation of an isoporphyrin. Then, a second step of oxidation (step E_2) allows the re-aromatization of the ZnOEP macrocycle *via* an acid–base reaction (step C_B), leading to the substitution of the pyridyl group onto the ZnOEP ring, *i.e.* to the formation of a dimer of porphyrins with pyridinium as spacer between the two macrocycles.



Scheme 1 Illustration of the $E_1C_NE_2C_B$ mechanism for ZnOEP with H_2PyPh_3P.

Thus, the same type of reaction should lead to the formation of oligomers and/or polymers of porphyrins if macrocycles substituted by two (or more) pendant pyridyl groups are used. Indeed, both pyridyl can attack different oxidized ZnOEP macrocycles. Moreover, several attacks can occur on one ZnOEP macrocycle, because the four *meso*-positions 5, 10, 15 and 20 are free (Scheme 2A).

For this study, we have first employed dipyridyl diphenylporphyrins ($H_2Py_2Ph_2P$) as dipyridyl-substituted macrocycles.



Scheme 2 Porphyrins used as monomers for the different copolymers formed: (A) ZnOEP, (B) $ZnOEP(Cl)_2$, (C) *cis*-$H_2Py_2Ph_2P$, (D) *trans*-$H_2Py_2Ph_2P$, (E) H_2Py_3PhP and (F) H_2Py_4P.

The two possible isomers, *i.e.* the 5,10-dipyridyl-15,20-diphenylporphyrin (*cis*-$H_2Py_2Ph_2P$, Schemes 2C and 3A) and the 5,15-dipyridyl-10,20-diphenylporphyrin (*trans*-$H_2Py_2Ph_2P$, Schemes 2D and 3B), have been compared. Fig. 1A and B show the voltammograms recorded during iterative scans performed between −0.9 and +1.6 V/SCE in the case of the use of *cis*-$H_2Py_2Ph_2P$ and *trans*-$H_2Py_2Ph_2P$, respectively, in the presence of ZnOEP (Scheme 2A).

The current increases progressively during these iterative scans, showing the formation of a conducting polymer coating the electrode. According to our previous studies, this polymerization can be described by a $E(EC_NEC_B)_nE$ mechanism (Scheme S1, ESI†).[20,21] The process is different to the mechanism described for the monosubstitution (Scheme 1). Indeed, the formation of the dication of the ZnOEP (two steps E) is needed to observe an electropolymerization. Thus, a pyridyl group of the $H_2Py_2Ph_2P$ macrocycle can react with $ZnOEP^{2+}$ in the *meso*-position to give an isoporphyrin (step C_N). For recall, an isoporphyrin corresponds to a porphyrin whose aromaticity is broken because of the simultaneous presence of two substituents (a pyridinium and a proton in our case) on the same *meso*-carbon. Afterwards, this isoporphyrin can be oxidized again (step E). Finally, the spare proton is lost, leading to the re-aromatization of the macrocycle (step C_B) and allowing the formation of a dimer of porphyrins (ZnOEP-Py^+-H_2Ph_2P-Py in this case).

Then, the free pyridyl group can react in a similar way with another oxidized ZnOEP macrocycle, and little by little, the copolymer can grow.

One can also underline that even if the $H_2Py_2Ph_2P$ rings are oxidized during the iterative scans, no substitution in β-positions of these macrocycles by pyridyl groups of other $H_2Py_2Ph_2P$ macrocycles could occur. Indeed, the kinetics of a nucleophilic substitution in the β-position is probably too slow compared to the kinetics of a substitution in the *meso*-position. A simple explanation can be offered since the charge density at β-positions

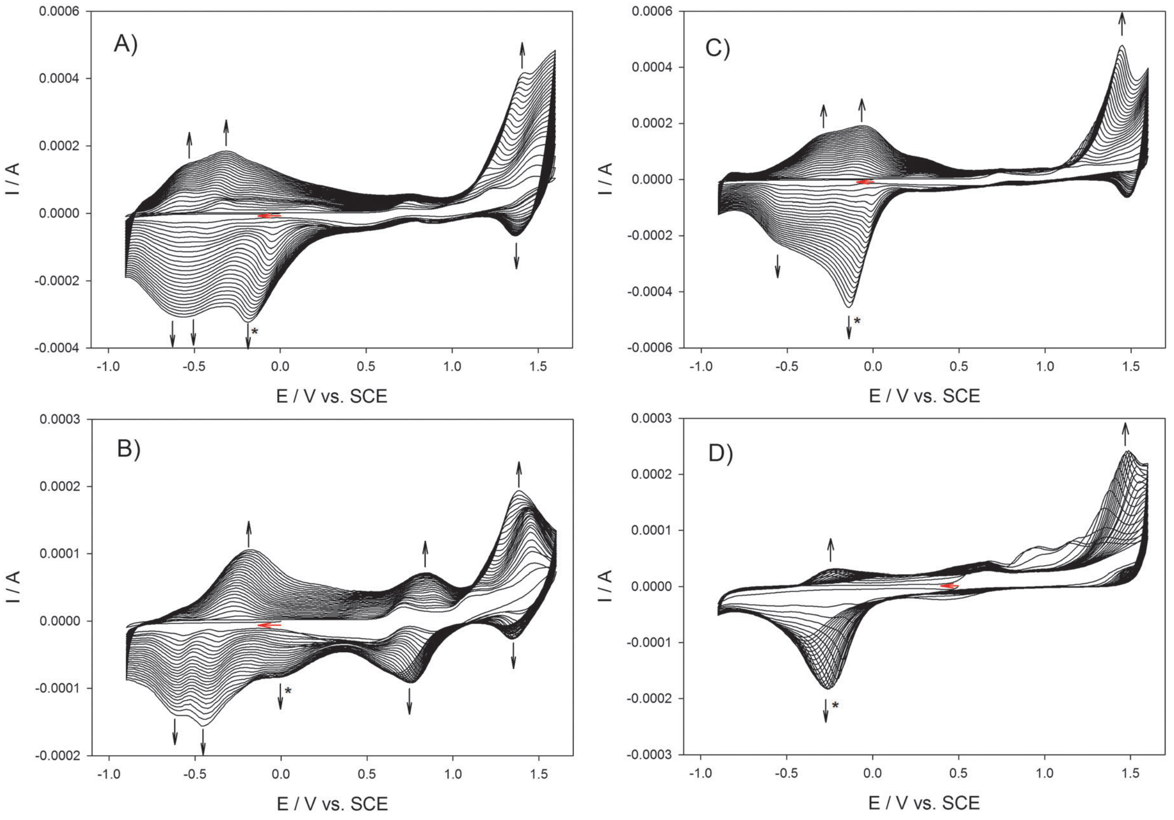


Fig. 1 Cyclic voltammograms recorded during the electropolymerization of (A) *cis*-$H_2Py_2Ph_2P$, (B) *trans*-$H_2Py_2Ph_2P$, (C) H_2Py_3PhP and (D) H_2Py_4P in the presence of ZnOEP in $CH_3CN/1,2\text{-}C_2H_4Cl_2$ (1 : 4) with 0.1 M NEt_4PF_6. Working electrode: ITO; S = 1 cm^2; scan rate: 0.1 V s^{-1}.

is much smaller than that at *meso*-positions.[24,25] Moreover, Rachlewicz and Latos-Grazynski *et al.* have shown that oxidized tetraphenylporphyrins react with pyridine to form *meso*-5-iso-tetraphenylporphyrins and β-pyridinium substituted porphyrins which suggested that the *meso*-isoporphyrin is an intermediate product of the reaction of β-substitution.[26] The zinc(II) iso-porphyrin intermediate was also described by Dolphin *et al.*[27] Thus, this reactivity shows that the pyridyl group is able to attack at both *meso*- and β-positions of the ring, but due to the charge density distribution, it prefers first the attack at the *meso*-position. Then, a second nucleophilic attack at the β-position (in concomitance with the release of the pyridinium group at the *meso*-position) leads to β-pyridinium substituted porphyrins.[28,29] Thus, in the case of electropolymerization in the presence of ZnOEP, a competitive attack at the *meso*-positions onto the ZnOEP and the $H_2Py_2Ph_2P$ macrocycles takes place. However, the nucleophilic attack at *meso*-positions is preferred onto ZnOEP macrocycles because of a severely restricted access to $H_2Py_2Ph_2P$ due to the presence of the phenyl groups, even more in the case of the formation of oligomers and polymers, rendering this nucleophilic attack less favorable. Moreover, the phenyl groups of the $H_2Py_2Ph_2P$ macrocycles being bad leaving groups, a second nucleophilic attack at the β-position must be accomplished in order to have finally the β-substitutions, which is probably impossible under our experimental conditions. Indeed, the rate of the iterative sweeps is too fast to let enough time for the β-attack and the β-substitutions. Thus, nucleophilic attacks at the substitutable *meso*-positions of ZnOEP would be preferred. Consequently, electropolymerization of $H_2Py_2Ph_2P$ itself is very difficult and maybe even impossible.

The cyclic voltammograms recorded during electropolymerization of both $H_2Py_2Ph_2P$ in the presence of ZnOEP show three waves in the cathodic part (well observed for instance in Fig. 1A), at least during the first sweeps (indeed, sometimes, the waves can merge each other when the number of scans increases). These three waves are always absent during the first scan, *i.e.* before the oxidation of the ZnOEP ring. The first peak (peak*), around 0.0 and −0.2 V/SCE, corresponds to the reduction of the isoporphyrin which is formed during the electropolymerization process.[21,30] The two other waves between −0.2 and −0.8 V/SCE are assigned to the reduction of the pyridinium spacers which are formed between each macrocycle within the polymeric chain.[20,21,30]

In order to have an electrochemical characterization of these copolymers, after 25 iterative scans, the coated electrodes have been removed from the electrochemical cell, washed with CH_3CN to remove the weakly adsorbed macrocycles and used as working electrodes in new electrolytic solutions containing only the solvent and the supporting electrolyte (Fig. 2A and B).

The shape of the waves is characteristic of a process where the species involved do not diffuse from and toward the electrode (non-diffusive species). The reduction potentials of the copolymers are listed in Table 1. As previously observed, three waves appear in the cathodic part. The first one, around 0.0 V/SCE, corresponds to the reduction of the isoporphyrin. The two other well-distinct waves, observed between −0.2 and

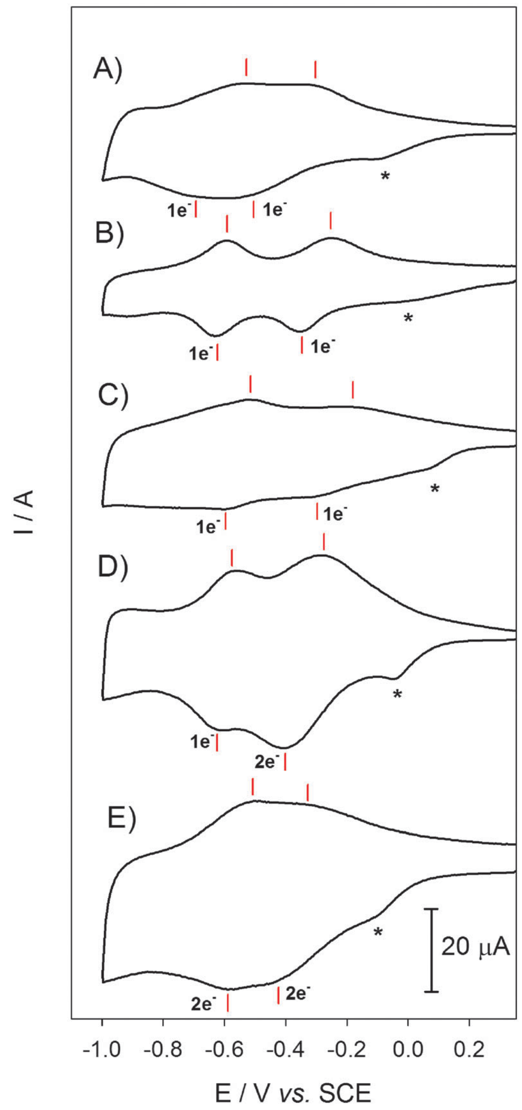


Fig. 2 Cyclic voltammograms of ITO electrodes modified with copolymers obtained after 25 iterative scans: (A) poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP, (B) poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP, (C) poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP$(Cl)_2$, (D) poly-H_2Py_3PhP-ZnOEP and (E) poly-H_2Py_4P-ZnOEP. Solvent: $CH_3CN/1,2\text{-}C_2H_4Cl_2$ (1 : 4) with 0.1 M NEt_4PF_6; scan rate: 0.1 V s^{-1}.

−0.7 V/SCE and attributed to the reduction of the pyridinium spacers, deserve more attention. Indeed, if all the pyridiniums are not reduced at the same potential while they seem to be chemically equivalent, that means that pyridiniums substituted onto the same macrocycles are in mutual interaction. These couplings can occur either between pyridiniums substituted onto the same ZnOEP rings, or between pyridiniums substituted onto the same H_2Ph_2P rings.

According to our previous works concerning the substitution of pyridiniums onto ZnOEP macrocycles, such a mutual interaction between two pyridiniums is observed in the case of *cis*-substitutions (substitutions in 5 and 10 *meso*-positions), leading well to two successive reduction steps instead of only one.[21,29,31] In contrast, when the two pyridinium groups are substituted in *trans*-positions (5 and 15 *meso*-positions), the reductions of both pyridiniums are simultaneous.

If we assume that in the case of our two copolymers the two waves in the cathodic part are due to couplings between pyridiniums onto the same ZnOEP rings, and noticing that these two waves have nearly the same intensity, it will be straightforward to conclude that only two substitutions occur on each ZnOEP macrocycle within the polymeric chain, and that these two substitutions should be performed in the *cis*-position (5 and 10 *meso*-positions).

In order to validate this first assumption concerning the *cis*-position substitutions onto the ZnOEP macrocycles occurring when *cis*-and *trans*-isomers of $H_2Py_2Ph_2P$ are used, a similar copolymer has also been prepared using the 5,15-dichloro-β-octaethylporphyrin (ZnOEP$(Cl)_2$, Scheme 2B; Fig. S3, ESI†) instead of ZnOEP. In this case, two of the four *meso*-positions of the macrocycle are "protected" by chloride groups (substituted in *trans*-positions onto the ZnOEP ring). Consequently, only a linear copolymer can be obtained,[32] where the pyridinium spacers within the polymeric chain are necessarily in *trans*-positions (Scheme 3C). Fig. 2C exhibits the cyclic voltammogram corresponding to this linear copolymer measured into a new electrolytic solution containing only the solvent and the supporting electrolyte. Two waves assigned to the reduction of the pyridinium spacers are again observed in this case. Only one should be expected in regard to our former work in the case of substitutions of pyridiniums in *trans*-positions on a ZnOEP ring. Indeed, a lack of any interactions between *trans*-pyridiniums must be observed leading to only one wave of two electrons for the reduction of the two pyridiniums. Consequently, it seems that the couplings observed between pyridiniums within these copolymers are not due to pyridiniums substituted in the *cis*-position onto the same ZnOEP macrocycles. Indeed, even if this type of interaction was widely observed in the case of pyridiniums-substituted ZnOEP (5,10-ZnOEP$(py)_2^{2+}$, 5,10-ZnOEP$(bipy)_2^{2+}$, 5,10,15,20-ZnOEP$(py)_4^{4+}$),[29,31,33] it is generally not observed in the case of oligomers[34] or polymers of porphyrins.[20,30] That can be tentatively explained by a very important change of the deformation of the ZnOEP rings when substitutions onto macrocycles are too numerous. As a consequence, the non-planarity of the ZnOEP macrocycle must be very different and especially less flexible when entrapped in the copolymers compared to the monomeric pyridinium-substituted macrocycle where the dynamic macrocycle inversion process between the non-planar conformations must be present and function of the temperature.

As a matter of fact, it seems that the presence of two successive waves of one electron for the reduction of the pyridiniums in the case of poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP$(Cl)_2$ shows an unexpected coupling between pyridiniums in regard to our previous work of monomers in solution. Consequently, the second hypothesis based on the presence of couplings occurring between pyridiniums substituted onto the same H_2Ph_2P rings seems more appropriate by supposing a lack of interaction with the ZnOEP rings. Thus, in this case, the two waves assigned to the successive one-electron reductions of the pyridinium spacers observed both for poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP and poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP copolymers (obtained from the *cis*- and the *trans*-$H_2Py_2Ph_2P$ macrocycles, respectively) indicate interactions existing both for substitutions in *cis*- and *trans*-positions onto the same H_2Ph_2P macrocycles.

Table 1 Electrochemical data of the six porphyrins used as monomers and of the five copolymers obtained

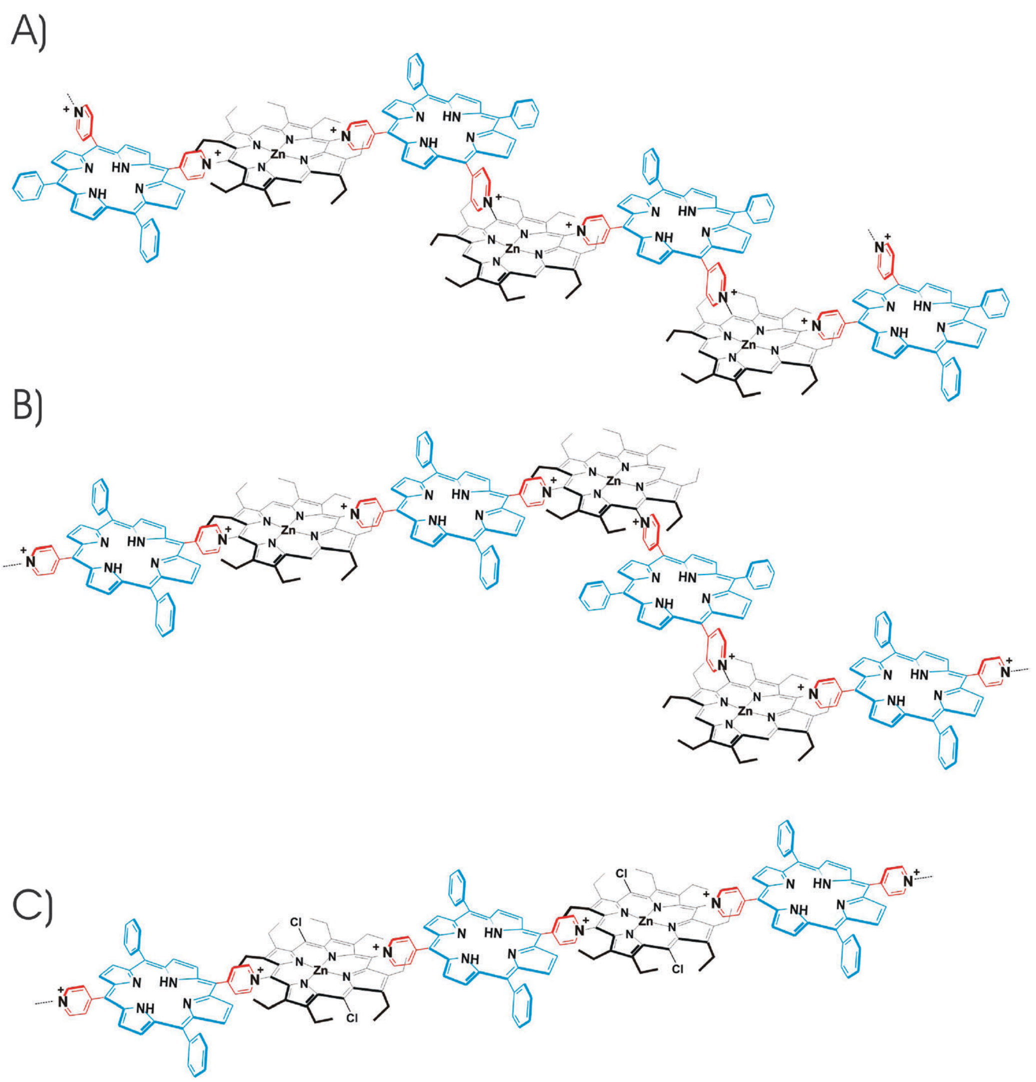
Compounds	Oxidation		Reduction	
Porphyrins	Dication	Radical cation	Radical anion	Dianion
ZnOEP^a	0.94	**0.68**	−1.60	
ZnOEP(Cl)$_2$^{a}	0.95	**0.73**	−1.41	
cis-$H_2Py_2Ph_2P^b$	1.46	*1.27*	−1.04	−1.37
trans-$H_2Py_2Ph_2P^b$	1.45	*1.26*	−1.04	−1.37
$H_2Py_3PhP^b$	1.56	*1.34*	−0.99	−1.33
$H_2Py_4P^c$	1.68	*1.38*	−0.98	−1.35
Copolymers	Radical cation $H_2Py_xPh_{(4-x)}P$ (x = 2, 3 or 4)	Radical cation ZnOEP	Isoporphyrin ZnOEP (peak*)	Py^+ spacers
Poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP^c	*1.48*	**1.30**	−0.11	−0.45 (1e$^-$) −0.58 (1e$^-$)
Poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP^c	*1.37*	**1.22**	0.00	−0.31 (1e$^-$) −0.62 (1e$^-$)
Poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP(Cl)$_2$^{c}	*1.44*	**1.16**	0.05	−0.27 (1e$^-$) −0.56 (1e$^-$)
Poly-H_2Py_3PhP-ZnOEP^c	*1.54*	**1.29**	−0.05	−0.34 (2e$^-$) −0.59 (1e$^-$)
Poly-H_2Py_4P-ZnOEP^c	*1.47*	**1.17**	−0.13	−0.39 (2e$^-$) −0.55 (2e$^-$)

All potentials in V *vs.* SCE were obtained from cyclic voltammetry in $CH_3CN/1,2\text{-}C_2H_4Cl_2$ (1 : 4) containing 0.1 mol L^{-1} NEt_4PF_6 at 100 mV s^{-1} (working electrode: ^{a} Pt electrode, ^{b} glassy carbon electrode and ^{c} ITO electrode). In brackets: number of electrons exchanged per $H_2Py_xPh_{4\text{-}x}P$ unit (x = 2, 3 or 4).

This aspect has been initially studied by Evans,[35] then by Savéant[36,37] and by Amatore[38,39] and more recently by Santi *et al.*[40] for monomeric systems in solution where conformational changes play a major role in these phenomena, as well the solvent reorganisation, the nature of the supporting electrolyte, the conjugation and of course electrostatic interactions (more especially in the case of polymers). It is therefore not surprising to observe different behaviours in the copolymers obtained compared to monomer species dissolved in solution. Thus, in the case of poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP(Cl)$_2$, of poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP and of poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP (symbolized $(Py^+\text{-}H_2Ph_2P\text{-}Py^+\text{-ZnOEP})_n$), the two successive one-electron reversible waves observed can be easily understood as an electrostatic effect reflecting the fact that it is more difficult to insert an electron into the pyridinium–ion radical system $((Py^+\text{-}H_2Py_2Ph_2P\text{-}Py^\bullet\text{-ZnOEP})_n)$ than it is to reduce the starting di-cationic $(Py^+\text{-}H_2Ph_2P\text{-}Py^+\text{-ZnOEP})_n$ species.

In order to modulate the steric hindrance of the copolymers, porphyrins bearing three and four pendant pyridyl groups have also been used, namely the 5,10,15-tripyridyl-20-phenylporphyrin (H_2Py_3PhP, Schemes 1E and S2A, ESI†) and the 5,10,15,20-tetrapyridylporphyrin (H_2Py_4P, Schemes 1F and S2B, ESI†). As previously observed, the evolution of the cyclic voltammograms characterizes the formation of polymers coating the electrodes (Fig. 1C and D). Fig. 2D and E exhibit the cyclic voltammograms obtained at the end of the electropolymerization of these two copolymers, after replacing the ITO electrodes into new electrolytic solutions containing only the solvent and the supporting electrolyte. In the case of the polymer obtained from the H_2Py_3PhP ring (Fig. 2D and Table 1), three waves are observed in the cathodic part, the first one around 0.0 V/SCE corresponds to the reduction of the isoporphyrin, and the other two, between −0.2 and −0.7 V/SCE, are assigned again to the reduction of the pyridinium spacers. Regarding the intensity of the two waves attributed to the pyridiniums, the first one (around −0.4 V/SCE) corresponds to the transfer of two electrons per H_2Py_3PhP while the second one (around −0.6 V/SCE) corresponds to the transfer of one electron per H_2Py_3PhP. Consequently, the voltammogram is consistent with substitutions of the three pendant pyridyl groups of the H_2Py_3PhP macrocycles. The apparent two-electron wave should be in fact two successive one-electron waves with a difference in potentials lower than 60 mV. Finally, in the case of the polymer obtained from the H_2Py_4P ring (Fig. 2E and Table 1), two successive two-electron waves (per H_2Py_4P) assigned to the reduction of the pyridinium spacers are observed.

The waves corresponding to the reduction of the isoporphyrins deserve also attention (peaks*). Indeed, regarding the five cyclic voltammograms recorded during electropolymerization of the five copolymers (Fig. 1; Fig. S3, ESI†), an increase in the intensity of this peak is observed from the use of *trans*-$H_2Py_2Ph_2P$ to the use of *cis*-$H_2Py_2Ph_2P$, and then for H_2Py_3PhP and H_2Py_4P. One can also note that in this last case, the isoporphyrin peak is so important that it completely masks the pyridinium reduction waves after several scans. One can tentatively connect this increase of the intensity of this wave to the increase of the steric hindrance of the copolymers obtained with each porphyrin. Indeed, the steric hindrance of the copolymers naturally increases when the number of pendant pyridyl groups onto the macrocycles increases. And more the number of pendant pyridyl groups is high, more isoporphyrins can be formed. Nevertheless, this increase of the number of substitutions with the number of pyridyl groups



Scheme 3 Tentative representation of copolymers: (A) poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP, (B) poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP and (C) poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP$(Cl)_2$.

leads to an increase of the deformation of the macrocycles within the copolymers, which should lead to a more difficult rearomatization of the rings, *i.e.* an accumulation of isoporphyrins near the electrode. For the cyclic voltammograms recorded at the end of the electropolymerization after replacing the ITO electrodes into new electrolytic solutions (Fig. 2), the isoporphyrin reduction peaks remain but decrease in intensity, due to a poor stability of the isoporphyrins, for instance to further reaction leading finally to the nucleophilic substitution.

After electropolymerisation, even after several weeks, the wave assigned to the isoporphyrin reduction does not completely disappear but a decrease of the intensity of the peak current has been observed showing a good stability of such isoporphyrins inside the copolymer compared to the isoporphyrin monomer.

Finally, after this description of the cathodic behavior, one needs to discuss the anodic part, corresponding to the oxidation waves of the macrocycles. During iterative scans, these oxidation signals progressively shift anodically as the coating of the electrode progresses (Fig. 1). This is due to the electron-withdrawing character of the pyridinium spacers onto the macrocycles. Indeed, the number of positively charged pyridiniums within the copolymers increases with the number of cycles, leading progressively to an increase in the difficulty to oxidize the macrocycles. As a matter of fact, at the end of the electropolymerization, when the ITO electrodes are used as working electrodes in new electrolytic solutions, the potentials of the first oxidation waves of each macrocycle within the macrocycle are significantly shifted compared to the oxidation waves of these same free porphyrins (Table 1).

UV-visible spectroscopic characterization and AFM morphology

The copolymers have also been characterized by UV-visible absorption spectroscopy (Table 2). A typical spectrum recorded on a coated ITO electrode is depicted in Fig. 3 (see also Fig. S2, ESI†), and is compared to the spectra of both monomers. The Soret band of the copolymers is split, because of the presence of two different kinds of macrocycles within the polymeric chain. Moreover, each Soret band is larger and

Table 2 Spectroscopic data of the six porphyrins used as monomers and of the five copolymers obtained

Compounds	Soret bands/ nm	Q bands/nm
Porphyrins		
ZnOEP	402	531; 568
ZnOEP(Cl)$_2$	402	531; 568
cis-$H_2Py_2Ph_2P$	417	514; 548; 593; 646
trans-$H_2Py_2Ph_2P$	417	514; 548; 585; 643
H_2Py_3PhP	417	511; 548; 582; 647
H_2Py_4P	417	513; 546; 588; 644
Copolymers		
Poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP	429; 464	603; 675
Poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP	435; 456	597; 686
Poly-*trans*-$H_2Py_2Ph_2P$-ZnOEP(Cl)$_2$	436; 449	597; 687
Poly-H_2Py_3PhP-ZnOEP	431; 468	601; 673
Poly-H_2Py_4P-ZnOEP	431; 458	591; 665

Spectra of porphyrin monomers have been measured in solution in 1,2-$C_2H_4Cl_2$ while spectra of copolymers have been measured directly onto optically transparent ITO electrodes.

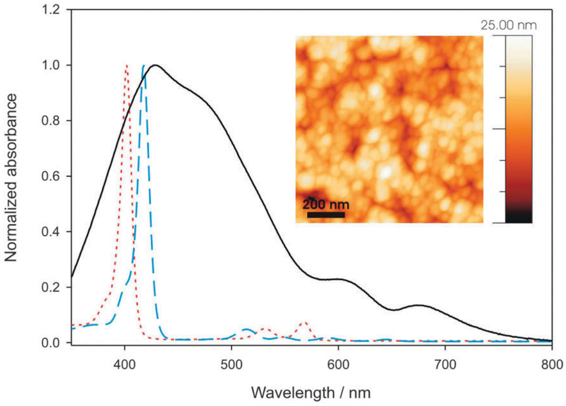


Fig. 3 Normalized UV-visible absorption spectra of ZnOEP in 1,2-$C_2H_4Cl_2$ (red dotted line), of *cis*-$H_2Py_2Ph_2P$ in 1,2-$C_2H_4Cl_2$ (blue dashed line) and of a modified ITO electrode with poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP (black full line). Inset: atomic force micrograph of poly-*cis*-$H_2Py_2Ph_2P$-ZnOEP.

red-shifted compared to the one of the corresponding monomer. This evolution can be interpreted by the exciton-coupling theory involving intra- and inter-molecular interactions between the porphyrin subunits within the polymer.[20,21,30] These two changes compared to the free porphyrins can also be explained by a greater deformation of the macrocycles within the polymers due to the many substitutions onto porphyrin rings.[41] Moreover, the red-shift of the Soret band compared to the corresponding monomer results also from the electron-withdrawing effect of the pyridinium groups on the macrocycles.[20,21,28]

The morphology of the copolymers coated onto ITO electrodes has also been scrutinized by atomic force microscopy (AFM). Whatever the porphyrins used, the deposited copolymers appear in the form of tightly packed coils with an average diameter of *ca.* 60–100 nm (Fig. 3; Fig. S4, ESI†). The rms roughness does not change a lot with the steric hindrance of the copolymers, since the values (calculated from an area of 1.0 μm^2) are between 3.4 and 3.7 nm according to the porphyrins used. Only for the linear copolymer obtained from ZnOEP(Cl)$_2$ with *trans*-$H_2Py_2Ph_2P$ the rms value is lower (equal to 2.4 nm).

Conclusions

In summary, we have successfully obtained five copolymers by electropolymerisation of ZnOEP-type macrocycles and porphyrins functionalized by two, three or four pendant pyridyl groups. The electropolymerization process is based on the now well-known nucleophilic attack of the pyridyl groups onto electrogenerated ZnOEP dications at their *meso*-positions. To our knowledge, we have developed a simple method which allows the formation of copolymers having two different kinds of macrocycles perfectly alternated. Moreover, these copolymers possess short spacers between macrocycles, namely pyridinium spacers. Electrochemical studies of these copolymers have allowed us to show that couplings between pyridiniums occur only when they are substituted onto same $H_2Ph_{(4-x)}P$ rings (x = 2, 3 or 4), but not when they are substituted onto same ZnOEP macrocycles. Spectroscopic measurements and AFM morphologies have also been performed to obtain a better characterization of these copolymers.

Further development of this polymerization process is the next step in the development of new polymers with design properties.

Experimental section

Chemicals

All solvents were of reagent grade quality and used without further purification.

The zinc-β-octaethylporphyrin (ZnOEP) and the 5,10,15,20-tetrapyridylporphyrin (H_2Py_4P) were purchased from Sigma-Aldrich.

UV-visible spectroscopic measurements

UV-visible spectra were recorded with a Hewlett-Packard HP8453 spectrophotometer.

Atomic force microscopy (AFM)

AFM was performed directly on the surface of an ITO electrode using a Dimension 3100 (Veeco) in the tapping mode under ambient conditions. Silicon cantilevers (Veeco probes) with a spring constant of 300 N m^{-1} and a resonance frequency in the range of 120–139 kHz were used. The scanning rate was 1.0 Hz.

Syntheses

Porphyrins with pendant pyridyl groups (*cis*-$H_2Py_2Ph_2P$, *trans*-$H_2Py_2Ph_2P$ and H_2Py_3PhP). These porphyrins were prepared and purified according to a published procedure.[42] A mixed solution of benzaldehyde (3.05 mL, 30 mmol), 4-pyridinecarbaldehyde (2.83 mL, 30 mmol) and pyrrole (4.2 mL, 60 mmol) was refluxed (130 °C) in propionic acid during 1 h. The reaction mixture was then cooled and allowed to stand overnight. After that, the reaction solution was concentrated to about 50 mL and then acetone (500 mL) was added with stirring. The crystalline products of the porphyrin mixture were obtained after filtration. This crude product, a mixture of six porphyrins, was dissolved in CH_2Cl_2 and loaded onto a column of silica gel. The six porphyrins were separated by a dichloromethane/methanol solvent system consisting initially of 100% CH_2Cl_2, and gradually ending with 90% CH_2Cl_2/10% CH_3OH. After separation, the desired products include *cis*-$H_2Py_2Ph_2P$ (yield of 9.7%), *trans*-$H_2Py_2Ph_2P$ (yield of 1.1%) and H_2Py_3PhP (yield of 4.3%).

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C):

cis-$H_2Py_2Ph_2P$: δ = 9.06 (d, 4H, 3,5-Py), 8.87 (m, 8H, β-H), 8.23 (d, 4H, 2,6-Ph), 8.18 (d, 4H, 2,6-Py), 7.81 (m, 6H, 3,4,5-Ph), −2.80 (s, 2H, NH).

trans-$H_2Py_2Ph_2P$: δ = 9.05 (d, 4H, 3,5-Py), 8.87 (m, 8H, β-H), 8.21 (d, 4H, 2,6-Ph), 8.18 (d, 4H, 2,6-Py), 7.79 (m, 6H, 3,4,5-Ph), −2.82 (s, 2H, NH).

H_2Py_3PhP: δ = 9.07 (d, 6H, 3,5-Py), 8.86 (m, 8H, β-H), 8.22 (d, 2H, 2,6-Ph), 8.17 (d, 6H, 2,6-Py), 7.81 (m, 3H, 3,4,5-Ph), −2.86 (s, 2H, NH).

ZnOEP(Cl)$_2$. The synthesis was performed according to a published method.[43] β-Octaethylporphyrin H_2OEP (300 mg, 0.561 mmol) was suspended in 500 mL of dichloromethane. *N*-Chlorosuccinimide (150 mg, 1.12 mmol) and azobisisobutyronitrile (AIBN, 30 mg, 0.18 mmol) were added and the mixture was heated to reflux for 24 h. After evaporation of the solvent, the residue was chromatographed on SiO_2 with cyclohexane/dichloromethane (7 : 3). 42 mg (0.070 mmol, 12%) of 5,15-dichloro-β-octaethylporphyrin ($H_2OEP(Cl)_2$) were obtained. Then to perform metallation, $H_2OEP(Cl)_2$ (35 mg, 0.058 mmol) was heated in 25 mL of chloroform with a large excess (10 eq.) of zinc(II) acetate for 2 h. The mixture was filtered hot and the solid was washed with chloroform until the washings were colorless. The combined filtrates were reduced under vacuum to about 5 mL and then exposed to methanol vapors. After 24 h, a purple solid was isolated (10 mg, 0.015 mmol, 26%).

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 10.01 (s, 2H, *meso*-H), 4.13 (m, 16H, CH_2), 2.12 (m, 24H, CH_3).

Electropolymerizations. Electropolymerizations were carried out with a three-electrode system using a PARSTAT 2273 potentiostat. One-side indium tin oxide electrodes (ITO, Sigma-Aldrich, 8–12 Ω per square) were used as working electrodes. A platinum wire was used as an auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). It was electrically connected to the solution by a junction bridge filled with CH_3CN containing 0.1 M of tetraethylammonium hexafluorophosphate (NEt_4PF_6).

The electropolymerizations were performed under an argon atmosphere in a 0.1 M solution of NEt_4PF_6 in CH_3CN/1,2-$C_2H_4Cl_2$ (1 : 4) containing 0.75 mM of pyridyl-substituted porphyrins (*cis*-$H_2Py_2Ph_2P$, *trans*-$H_2Py_2Ph_2P$, H_2Py_3PhP or H_2Py_4P) and 0.25 mM of ZnOEP. Cyclic scans (0.1 V s^{-1}) of the working electrode were applied between −0.9 and +1.6 V/SCE.

For each polymer, 25 iterative scans were carried out. After electropolymerizations, the working electrodes were washed in CH_3CN to remove traces of the conducting salt present on the deposited films.

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