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Electrochemical behavior of the tetracationic porphyrins $(py)ZnOEP(py)_4^{4+}4PF_6^-$ and $ZnOEP(py)_4^{4+}4Cl^-$

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ABSTRACT

Electro-oxidation of β-octaethylporphyrinato zinc(II) (ZnOEP) in the presence of an excess of pyridine yields the water soluble salt [*N*-pyridyl-Zn-5,10,15,20-tetrakis (*N*-pyridinium)-2,3,7,8,12,13,17,18-octa-ethyl-porphyrin]$^{4+}$ $4PF_6^-$ ($(py)ZnOEP(py)_4^{4+}4PF_6^-$). Its water solubility can be strikingly increased by replacing the counter anions PF_6^- by Cl^- yielding the $ZnOEP(py)_4^{4+}4Cl^-$ porphyrin without axial pyridine coordinated on the zinc. The electrochemical properties of $ZnOEP(py)_4^{4+}4Cl^-$ and $(py)ZnOEP(py)_4^{4+}4PF_6^-$ were investigated in CH_3CN by cyclic voltammetry and spectroelectrochemistry. Reduction takes place first at the pyridinium sites in four well separated one-electron steps due to mutual interactions between the four substituents, followed by the reduction of the porphyrin ring occurring at a potential close to the unsubstituted parent porphyrin ZnOEP. The third and the fourth reduction steps led to the formation of coated electrodes. The morphology of the deposits was scrutinized by AFM and appeared in the form of tightly packed coils indicative of polymers formation. UV–visible absorption spectra of the films showed a significant broadening associated with a splitting of the Soret band characteristic of important excitonic interactions between the porphyrin subunits in the polymers.

1. Introduction

Numerous "water-soluble" porphyrins have been studied with respect to their physicochemical and redox properties in both aqueous and nonaqueous media [1]. These compounds have also received considerable attention due to their possible applications in medicine. For example, 5,10,15,20-tetrakis-(1-methyl-4-pyridyl) porphyrins (TMpyP) with specific metal ions have been used in nuclear medicine [2], tested as tumor and liver contrast agents in mice using magnetic resonance imaging techniques [3], examined as mimics for superoxide dismutase [4,5], and demonstrated to act against the human immunodeficiency virus [6] as well as mad-cow disease [7]. More recently, the TMpyPs have been examined for the purpose of developing DNA-specific photosensitizers for photodynamic virus inactivation [8].

The porphyrin functionalisation was necessary to get the required properties and was often obtained by the addition of appropriate substituents on the porphyrin macrocycle. In turn, these multiple peripheral substitutions on porphyrins have been shown to induce significant conformational distortions of the porphyrin skeleton that minimize steric interactions between the substituents [9,10]. Therefore, the macrocyclic deformations could drastically affect the optical, redox, magnetic properties as well as radical and excited-state properties of the nonplanar porphyrins [9,10].

The reactions of electrogenerated porphyrin π-cation radicals and dications with nucleophiles to yield *meso* or β-substitutions are now well established and have been used to attach substituents via nitrogen, phosphorous and sulfur atoms at the *meso* or β positions of porphyrins [11–22]. Previous works [19,23] have demonstrated that the exhaustive oxidative electrolysis of ZnOEP in the presence of pyridine or bipyridine afford tetracationic porphyrins in which the four *meso* protons of ZnOEP are replaced by four pyridinium or bipyridinium groups linked via their nitrogens atoms. Even more recently, the corresponding free-base porphyrin $H_2OEP(py)_4^{4+}$, and its Fe and Mn complexes, were synthesized [24,25]. The latter are new biomimetic hydroxylation catalysts that exhibit good solubility in both polar aprotic solvents and water.

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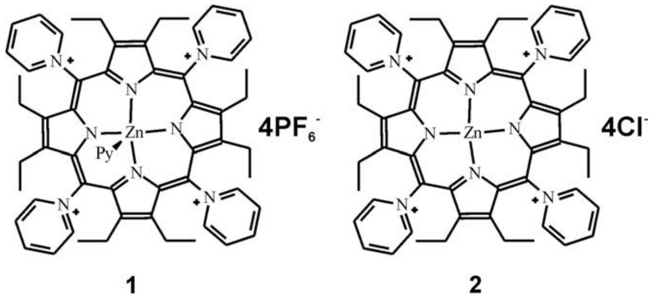

Fig. 1. Porphyrins investigated in this study.

This kind of dodeca-substituted porphyrins was the first representative of a new class of dodeca-substituted nonplanar metalloporphyrins bearing four positive charges less than 5 Å from the metal center. The porphyrin skeleton adopts a severely nonplanar saddle conformation in the solid state that minimizes steric hindrance between the 12 peripheral substituents as previously demonstrated by the crystallographic data of the [*N*-pyridyl-Zn-5,10,15,20-tetrakis (*N*-pyridinium)-2,3,7,8,12,13,17,18-octaethyl-porphyrin]$^{4+}$ 4PF$_6^-$, (abbreviated (py)ZnOEP(py)$_4^{4+}$4PF$_6^-$, 1, Fig. 1) where an axial pyridine coordinated on the metal is observed [23].

Although this porphyrin (py)ZnOEP(py)$_4^{4+}$4PF$_6^-$ is soluble both in polar protic and aprotic solvents as H_2O and CH_3CN, its weak solubility in water limits its interest in aqueous media. This solubility can be strikingly increased by replacing counter anions PF$_6^-$ by halides (Cl$^-$ for example) obtained just by passing (py)ZnOEP(py)$_4^{4+}$4PF$_6^-$ (**1**) on a Cl$^-$ exchange ion column. During chromatography, the axial pyridine on Zn is lost leading to ZnOEP(py)$_4^{4+}$4Cl$^-$ (**2**, Fig. 1).

The study of the redox pattern of water soluble porphyrins in nonaqueous media allows to benefit from comparable conditions to correlate their redox properties to these of the main parent porphyrins which are known only in aprotic media due to their insolubility in water.

A direct comparison of electrochemical properties obtained in protic and in aprotic media can be risky.

As only the crystallographic structure of **1** has been resolved, and due to the fact that the redox behavior of porphyrins is structure dependent, we carried out the electrochemical and spectroelectrochemical investigations of (py)ZnOEP(py)$_4^{4+}$4PF$_6^-$ (**1**) and the non-coordinated parent ZnOEP(py)$_4^{4+}$4Cl$^-$ (**2**) in CH_3CN. These behaviors were compared with this of the monosubstituted moiety ZnOEP(py)$^+$PF$_6^-$ (**3**) [17] in the same experimental conditions.

2. Results and discussion

2.1. ^{1}H NMR spectroscopy

The ^{1}H NMR spectrum in CD_3CN solution for ZnOEP(py)$_4^{4+}$4Cl$^-$ (**2**, Fig. 2) showed that the four *meso* protons of ZnOEP were missing and replaced by pyridinium substituents whose protons appeared downfield as one doublet (8H), one triplet (4H) and one double doublet (8H) which clearly identified the ortho, para and meta protons, respectively. The β-ethyl groups appeared as a triplet (terminals methyls) and as a broad multiplet (methylene) in the 0.60–2.05 ppm range (not shown). The broad methylene peaks were indicative of a dynamic macrocycle inversion process, i.e. fast interconversion (on the NMR timescale) between nonplanar saddle conformations, a process that has been observed in several saddle-shaped porphyrins as a function of the temperature [26,27]. The (py)ZnOEP(py)$_4^{4+}$4PF$_6^-$ porphyrin (**1**) presented a ^{1}H NMR similar spectrum with three additional signals which appeared downfield as one triplet (1H), one double doublet (2H) and one doublet (2H) in the 4.46–6.93 ppm range. These additional signals corresponded to the para, meta and ortho protons of a single axially to Zn ligated pyridine, respectively. By comparison with the ^{1}H NMR spectrum of the pyridine, the upfield shift of the ortho protons of the pyridiniums was consistent with an axially ligated pyridine to the Zn.

2.2. UV–visible absorption spectra

The absorption UV–visible spectra of the two tetracationic porphyrins consisted in two absorption bands corresponding to two π–π* transitions. According to the admitted notation, these bands are called Q and B corresponding to S_1 and S_2 electronic states [28,29].

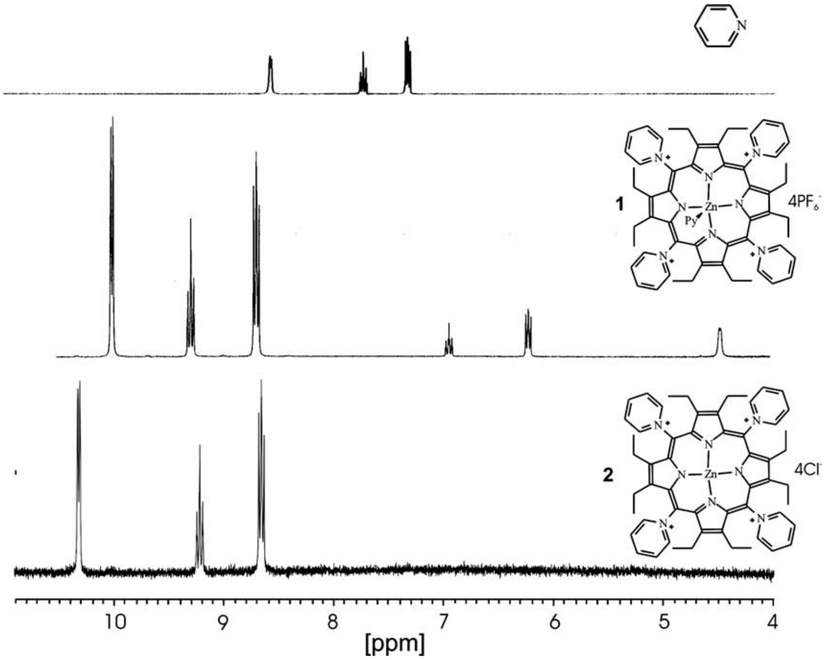

Fig. 2. ^{1}H NMR of py, (py)ZnOEP(py)$_4^{4+}$4PF$_6^-$ (**1**) and ZnOEP(py)$_4^{4+}$4Cl$^-$ (**2**) (300 MHz, CD_3CN) in the 10.5–4 ppm range.