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Photophysical, electro- and spectroelectro-chemical properties of the nonplanar porphyrin [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$] in aqueous media

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ABSTRACT

The photophysical and electrochemical properties of the tetracationic zinc 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(*N*-pyridiniumyl) porphyrin chloride (ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$) were studied in aqueous solutions. The steady state and time-resolved absorption and emission measurements indicate that the porphyrin skeleton adopts a severely nonplanar conformation which minimizes steric crowding between the 12 peripheral substituents. The absorption spectrum of [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$] in water exhibits significant red shifts of the visible Q and Soret bands as well as considerable broadening and decrease in intensity of the latter compared to the spectrum recorded for the planar [ZnTMPyP^{4+},4Cl$^-$] porphyrin. The $S_2 \rightarrow S_1$ internal conversion is faster than the experimental resolution (<90 fs) while the S_1 excited state has a lifetime of 170 ps. The electrochemical properties of [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$] were investigated in water at pH 6.5 and 3.0 by cyclic and differential pulse voltammetry as well as spectroelectrochemistry. Reductions take place initially at the pyridinium sites with four successive one-electron steps at pH 6.5 or a one-electron step followed by a three-electron process at pH 3.0. Both oxidation and reduction processes undergone by the porphyrin are irreversible.

1. Introduction

Porphyrins and their derivatives constitute a major class of chemical compounds due to their various optical, physicochemical and redox properties. Naturally occurring porphyrins play essential roles in photosynthesis, cellular respiration and biological electron transfer reactions [1]. Consequently, much attention has been devoted to these compounds with respect to their potential biological and medical applications such as DNA cleavage catalysts [2,3] or photosensitizers in photodynamic therapy [4–9]. Interactions between porphyrin derivatives and DNA have also been the subject of several works [10–16]. But, only a few planar *meso*-substituted water soluble porphyrins, such as 5,10,15,20-tetra(*N*-methyl-4-pyridyl)porphyrins (TMPyP^{4+}), have been investigated.

Studies of the crystal structures of protein complexes formed by porphyrinic chromophores and prosthetic groups have revealed skeletal distortions of the porphyrin macrocycle [17–19]. These findings have consequently stimulated efforts devoted to synthesis of nonplanar model porphyrins, for instance by substituting bulky groups at the peripheral positions of the macrocycle and/or changing the central metal [20,21]. Indeed, it has been shown that the conformational distortion of the skeleton minimizes the steric interactions between its substituents. Most of the dodecasubstituted porphyrins which have been synthesized, exhibit nonplanar, highly distorted structures [22]. That was the case for the first reported dodecasubstituted tetracationic metalloporphyrins that were derived from β-octabromo-*meso*-tetra(*N*-methyl-4-pyridiniumyl)porphyrin [23]. Even if the origin of the changes is controversial [24–26], it is known that macrocyclic deformations can profoundly affect the optical, redox, magnetic, radical and excited-state properties of the porphyrins [27–33].

Substituted metalloporphyrins bearing multiple charges should be of particular interest because they would combine solubility in water and possible interactions with various biological targets such as proteins and nucleic acids. While there are numerous studies in non-aqueous media for conformationally perturbed porphyrins, similar studies in water are rather scarce. The dodecasubstituted and tetracationic zinc porphyrin [(Py)ZnOEP(Py)$_4$$^{4+}$,4PF$_6$$^-$] with four pyridinium groups bound at the *meso* position through their nitrogen atom and one axially ligated pyridine, was the first representative of a new class of nonplanar metalloporphyrins bearing four positive charges at a distance shorter than 5 Å from the metal

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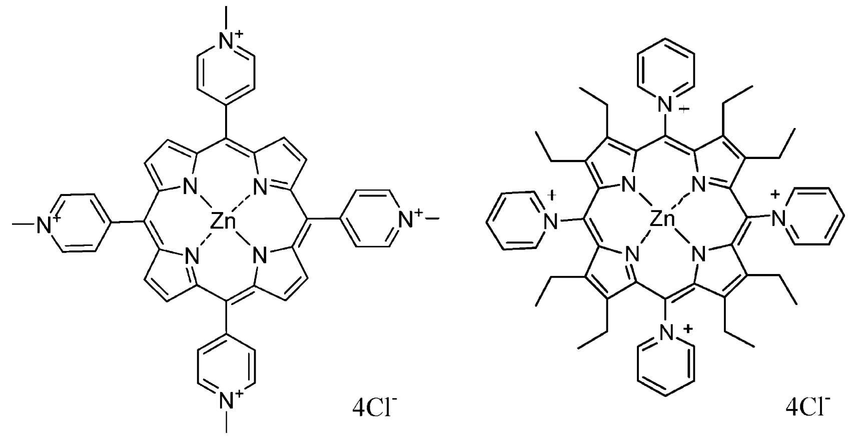

Fig. 1. Simplified structures of the [ZnTMPyP^{4+},4Cl$^-$] (left) and [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$] (right) porphyrins.

centre [34]. The structure has been resolved in the solid state by crystallography and corresponds to a saddle conformation of the cationic macrocycle with the pyrrole rings (and their alkyl substituents) displaced up and down alternately [34]. By passing this porphyrin through a Cl$^-$ exchange resin column, the counterion is exchanged, the axial pyridine is removed and the water soluble derivative, [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$] is obtained (Fig. 1) [35].

The present study deals with the photophysical and redox properties of this distorted porphyrin and their relations with the conformation of the macrocycle. In this context, the behavior of [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$] is compared to that of the planar tetracationic porphyrin [ZnTMPyP^{4+},4Cl$^-$].

2. Experimental

2.1. Materials

ZnOEP (Zn-2,3,7,8,12,13,17,18-octaethyl porphyrin), [ZnTMPyP^{4+},4Cl$^-$] (zinc 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin chloride) and pyridine compounds were of reagent grade quality, purchased from Sigma Aldrich and used without further purification.

The zinc 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(*N*-pyridiniumyl)porphyrin chloride, [ZnOEP(Py)$_4$$^{4+}$,4Cl$^-$], was synthesized following previous reports [35].

H_2SO_4 solutions, solid Na_2SO_4 and NaOH were commercial products from Prolabo.

Pure water was obtained by passing through a Milli-RO$_4$ unit and subsequently through a Millipore Q water purification set.

2.2. Photophysical measurements

All photophysical measurements were carried out in water at natural pH at room temperature (22 ± 2 °C).

Steady-state optical absorption spectra were recorded with a PerkinElmer Lambda 9 spectrophotometer. Steady-state luminescence emission spectra were obtained using a Spex fluorolog 1681 spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier which was cooled to the temperature of −20 °C. The fluorescence spectra were corrected for the detector spectral sensitivity.

Time-resolved fluorescence measurements were carried out using a time-correlated single photon counting set-up. The source was a Ti:sapphire laser (MIRA 900F) pumped by a Nd:YVO$_4$ laser (VERDI). The repetition rate was reduced to 3.8 MHz and the second harmonic (420 nm, vertically polarized) was generated in a BBO crystal and used to excite the samples. The emission was selected via a polarizer, set at the magic angle (54.7°) with respect to the excitation electric vector. A monochromator was used for wavelength selection and the signals were collected by an optical spectrometric multichannel analyzer.

Laser flash photolysis was performed using third harmonic pulses (355 nm, 3 ns FWHM 10 mJ/pulse) from a Nd:YAG laser (BMI). Detection of the transient species was carried out by an optical absorption set-up, consisting of a pulsed Xe arc lamp, monochromator and photomultiplier. Samples were argon-bubbled aqueous solutions contained in 1 cm path cell.

Femtosecond transient absorption pump–probe experiments were performed with a Ti:sapphire amplified laser system (Spectra Physics) delivering 100 fs pulses at 790 nm, with an energy of 1 mJ at a repetition rate of 1 kHz. The laser beam was splitted into two parts. The main part is used to produce the pump beam at 395 nm by frequency doubling in a BBO crystal. The pump pulses were then attenuated to 10 μJ and focused to a 0.5 mm beam on the sample. After travelling along an optical delay line, the small fraction of the Ti:sapphire output was used for white light continuum generation in a 3 mm sapphire crystal. This white light beam was divided before the cell and used in the one hand as the probe beam and in the other hand as a reference beam (unaffected by the pump). The pump and probe beams overlapped in a fused silica sample cell with 1 mm path, and their polarizations were set at the magic angle. The detection system consisted of an imaging polychromator and a CCD camera (1340 × 400 Princeton Instruments). Measurements were performed in aerated solutions. The spectra were corrected for the group velocity dispersion (GVD).

2.3. Electrochemical and spectroelectrochemical measurements

All electrochemical measurements were carried out under argon at 20 °C on a glassy carbon disk electrode (d = 3 mm). Voltammetric data were obtained with a standard three-electrode system using a PARSTAT 2273 potentiostat. 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 water containing the supporting electrolyte. The electrolyte was made up from 0.5 M Na_2SO_4 aqueous solution, and its pH was precisely adjusted to 3.0 by addition of 0.5 M H_2SO_4 aqueous solution and to pH 6.5 by addition of NaOH. The solutions were deaerated thoroughly for at least 30 min by bubbling argon (Ar–U from Air Liquide) and kept under argon atmosphere during the whole experiment.

For the spectroelectrochemical studies, a standard three-electrode system was used with a Bruker EI 30 M potentiostat and high-impedance millivoltmeter (Minisis 6000, Tacussel), in H_2O