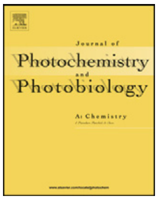
Journal of Photochemistry and Photobiology A: Chemistry 226 (2011) 23–35

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Formation, photophysical and photochemical properties of water-soluble bismuth(III) porphyrins: The role of the charge and structure

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ARTICLE INFO

Article history:
Received 29 May 2011
Received in revised form 19 August 2011
Accepted 8 October 2011
Available online 14 October 2011

Keywords:
Water-soluble porphyrin
Out-of-plane
Bismuth(III) ion
Primary photochemistry
Intermediate
S_1- and S_2-fluorescence

ABSTRACT

Bismuth(III) ion forms kinetically labile complexes with the 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin anion (H_2TSPP^{4-}) and the 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin cation (H_2TMPyP^{4+}), the formation constants of which are $3.54 \times 10^4\,M^{-1}$ and $1.62 \times 10^3\,M^{-1}$, respectively (at pH = 6). In these complexes, the metal center, due to its large ionic radius (103 pm), is located out of the ligand plane, distorting it. Accordingly, the absorption and fluorescence spectra of these coordination compounds display special properties characteristic of the so-called sitting-atop (SAT) or out-of-plane (OOP) porphyrin complexes. The shifts of the absorption bands upon metalation indicate that the structural distortion results in stronger perturbation on the S_2- than on the S_1-states of the porphyrin ligand. Metalation significantly decreases the lifetime and the quantum yield of the fluorescence from the S_1 excited state. The relatively rare S_2-fluorescence can also be detected for these metalloporphyrins. Quantum chemical calculations (DFT and TDDFT) confirm the considerable OOP displacement of the Bi(III) center (88 pm) and the typical tendencies of the band-shifts. Differing from the normal (in-plane) metalloporphyrins, excitation of these bismuth(III) porphyrins leads to an irreversible ligand-to-metal charge transfer (LMCT) followed by the opening of the porphyrin ring, which is also typical of SAT complexes. The quantum yields of this photoinduced redox reaction are significantly higher for the anionic than for the cationic complex, due to the stronger Lewis-basicity of H_2TSPP^{4-}. In the mechanism of the reaction between these free-base porphyrins and bismuth(III) ions formation of a longer-lived intermediate was observed. In the case of the cationic porphyrin also the photochemistry of this intermediate could be studied; deviating from the photoinduced behavior of the final product metalloporphyrins, excitation of this intermediate results in predominantly the dissociation to the initial porphyrin ligand and metal ion, indicating a relatively weak coordination bond and significantly distorted structure.

1. Introduction

Metalloporphyrins play key roles in several biochemical processes, such as photosynthesis and oxygen transport as well as in various redox reactions [1–8]. Within this important group of compounds the so-called out-of-plane (OOP) or sitting-atop (SAT) metalloporphyrins are characterized by special properties [9–12] originating from the non-planar structure caused by, first of all, the size of the metal center. In these complexes, the ionic radius (>80–90 pm) of the metal center is too large to fit into the cavity of the ligand, hence it is located above the porphyrin plane, distorting it. The symmetry of this structure is lower (generally C_{4v}–C_1) than that of both the free-base porphyrin (D_{2h}) and the regular, coplanar metalloporphyrins (D_{4h}), in which the metal center fits into the ligand cavity. The rate of formation of in-plane (or normal) metalloporphyrins is much slower than that of the OOP complexes because of the rigidity of porphyrins. Larger metal ions such as Pb^{2+}, Hg^{2+}, or Cd^{2+}, however, can catalyse the formation of normal metalloporphyrins via generation of OOP complex intermediates [13–18]. In these species the distortion caused by the out-of-plane location of the larger metal center makes two diagonal pyrrolic nitrogens more accessible to another metal ion, even with smaller ionic radius, on the other side of the porphyrin ligand [19].

Deviating from the normal (coplanar) metalloporphyrins, the SAT complexes, on account of their distorted structure and kinetic lability, display special photochemical properties, such as photoinduced charge transfer from the porphyrin ligand to the metal center, leading to irreversible ring opening of the ligand and dissociation on excitation at both the Soret- and the Q-bands [20]. The absorption and emission features of these complexes also significantly differ from those of the in-plane metalloporphyrins.

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doi:10.1016/j.jphotochem.2011.10.011

The photoinduced behavior of normal metalloporphyrins have been thoroughly studied for several decades, while the investigation of OOP complexes started in this respect only in the past 8–10 years. The size of bismuth(III) with an ionic radius of 103 pm [21] is favorable for the formation of OOP metalloporphyrins. Accordingly, several studies have been published regarding such complexes of bismuth(III) with various hydrophobic porphyrins. The 1:1 complexes with simple porphyrin ligands (such as octaethyl or tetratolyl porphyrins) proved to be kinetically labile [22–29], similarly to the corresponding dimers in which the monomers are connected with two axially coordinated halogen bridges [25]. Thus, for medical applications in radio-immunotherapy, Boitrel and coworkers prepared special porphyrin derivatives functionalized with pendant arms (pickets) terminated with various groups of oxygen donor atoms [26,30–33] or with a strap with a hanging carboxylate group [34–36] in order to hinder the demetalization of these metalloporphyrins. The main Soret-band of the hydrophobic bismuth(III) porphyrins display a strong red shift compared to that of the corresponding free base. Its wavelength is in the range of 457–479 nm, depending on the substituents of the porphyrin ring and the axial ligands. The out-of-plane displacement of the metal center in the crystal structure was found to be 107–131 pm, the larger distances in this range belong to complexes with various axial ligands [24–26,30,31,36]. These values are in accordance with those determined for bismuth(III) phthalocyanines (112–115 pm [37], 149 pm [38]).

These types of metalloporphyrins displaying such a large red shift were called hyperporphyrins by Gouterman [24], especially if the metal ion is a *p*-field element then *p*-type hyperporphyrins. Gouterman's definition was applied for the complexes the electronic spectrum of which in the visible region could not be described by his 4 MO-model [39]. Since specially substituted free-base porphyrins (such as protonated meso-(dimethylaminophenyl)porphyrins) display similar spectral phenomena, his interpretation had to be modified [40]. Eventually, the request for the re-interpretation of hyperporphyrins was born on the basis of the highly distorted structure of these porphyrins showing strong red shifts [41].

Probably due to the difficulty caused by the strong inclination of Bi^{3+} to hydrolyse, the only water-soluble bismuth(III) porphyrin has been prepared so far with 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin; the complex displayed a 465-nm Soret-band [42], which also suggests a significant OOP displacement. In spite of the numerous papers on bismuth(III) porphyrins, photochemical features of these complexes have not been investigated yet, neither in organic nor in aqueous systems. Only a hydrophobic tetrapyrrole complex of bismuth(III), with the porphyrin-like triphenyl corrole, was studied quite recently in structural and photochemical points of view [43]. Its irradiation led to the oxidation of the metal center.

On the basis of the precedents in this topic, the aim of our work, in the frame of a systematic investigation of the photophysics and photochemistry of water-soluble, sitting-atop metalloporphyrins, was to study the formation and mainly the photoinduced behavior of the bismuth(III) complexes with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin, an anionic and a cationic ligand (Fig. 1). The effects of the charge and the molecular structure on the formation, photophysical and photochemical properties were also examined in this work.

2. Experimental

2.1. Reagents and solutions

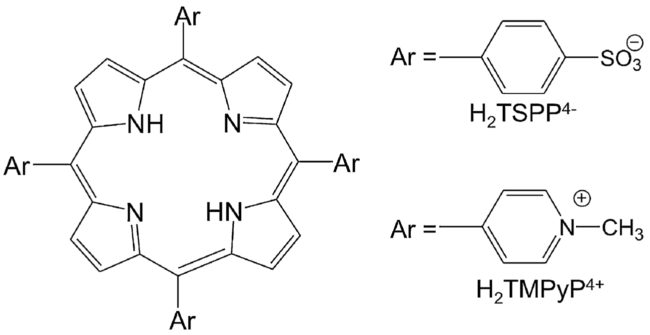

Fig. 1. Structures of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TSPP^{4-}) and 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin (H_2TMPyP^{4+}).

Analytical grade tetrasodium 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($Na_4H_2TSPP{\cdot}12H_2O$), 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin tetra(p-toluenesulfonate) (H_2TMPyP tetratosylate salt) and $Bi(NO_3)_3{\cdot}5H_2O$ (Sigma–Aldrich) were used for the experiments. The solvent was double-distilled water purified with Millipore Milli-Q system. Oxygen-free experiments were carried out by argon-bubbling and the Schlenk technique prior to the irradiation. The solutions containing metalloporphyrin were prepared well (at least 1 day) before the photophysical and photochemical experiments so that the onset of complex equilibration was ensured. The actual concentrations of the porphyrin stock solutions prepared were checked spectrophotometrically, using the molar absorptions of the reagents at characteristic wavelengths. The pH of each solution was adjusted to 6 by application of acetate buffer, also keeping the ionic strength at constant value of 1 M. It is worth mentioning that the acetate buffer was utilized also to avoid hydrolysis of Bi(III) ions. Too low a pH could not be applied because H_2TSPP^{4-} is protonated at pH = 5 ($pK_3 = 4.99$, $pK_4 = 4.76$ [44]). Since bismuth(III) ions are strongly prone to hydrolysis, a rather high concentration of buffer was used (1 M).

2.2. Instruments and procedures

The absorption spectra were recorded and the photometric titrations were monitored using a Specord S-100 and a Specord S-600 diode array spectrophotometer. For the measurement of fluorescence spectra a Perkin ELMER LS 50-B and a Horiba JobinYvon Fluoromax-4 spectrofluorimeter were applied. The latter equipment supplemented with a time-correlated single-photon counting (TCSPC) accessory was utilized for determination of fluorescence lifetimes, too. Rhodamine-B and $Ru(bpy)_3Cl_2$ were used as references for correction of the detector sensitivity and for determination of the fluorescence quantum yields [45,46]. Each compound studied was excited at the wavelength of its absorption maximum. Luminescence spectra were corrected for detector sensitivity. For the elimination of the potential reabsorption effects in the detection of luminescence low concentration and a holder for solid samples were applied. In this case, the emitted light beam arrives from the surface of the cell to the detector. Moreover, because of the small Stokes-shifts and the disturbing effect of the (Rayleigh and) Raman scattering, the spectrum analyses were carefully carried out by fitting Gaussian and Lorentzian curves in MS Excel.

For continuous irradiations an AMKO LTI photolysis equipment (containing a 200-W Xe–Hg-lamp and a monochromator) was applied [47]. Incident light intensity was determined with a thermopile calibrated by ferrioxalate actinometry [48,49]. Quartz cuvettes of 1 and 5 cm pathlength were utilized as reaction vessels. During the irradiations the reaction mixtures were continuously homogenized by magnetic stirring. All measurements were carried out at room-temperature. The experimental results were processed and evaluated by MS Excel programs on PCs.