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Review

Spectroscopic and photochemical properties of water-soluble metalloporphyrins of distorted structure

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ABSTRACT

The location of the metal center in the porphyrin complexes strongly depends on its size, charge and spin multiplicity. Metal ions can form normal (in-plane) metalloporphyrins, or several of them, being too large to fit into the coordination cavity of the porphyrin ring, are located above the ligand plane, resulting in out-of-plane (OOP) complexes. The distorted structure of the latter type induces special photophysical and photochemical features that are characteristic of all OOP complexes. Efficient LMCT processes can take place upon excitation of these compounds. In this paper we review the results of recent studies on water-soluble (1:1) porphyrin complexes of several metal ions to reveal how the size (and partly the oxidation state) of the metal center influences their structure and photoinduced behavior. The effects of the pre-distortion (via bromination) and the charge of the porphyrin ligand on the structure and photoreactivity of these complexes are also discussed. While the porphyrin complex of Ag^{2+} (r_{ion} = 94 pm) formed in the reaction of the Ag^+ ion and the $TSPP^{6-}$ ligand (H_2TSPP^{4-} = 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin anion) displays OOP features, the corresponding complex also of open-shell Au^{3+} (r_{ion} = 85 pm) is unambiguously of planar structure, and does not show any fluorescence and photoredox degradation. In the case of the anionic complex of Cd^{2+} (r_{ion} = 95 pm), octabromination of the $TSPP^{6-}$ ligand results in significant red-shifts in the absorption and emission spectra, dramatically diminishes the fluorescence quantum yield and lifetime, and turns the photodegradation into a very oxygen-sensitive reaction. The axial coordination of HO^- ligand further increases the distortion and photoreactivity. The efficiency for

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the photoinduced LMCT reaction of the cationic complex of Bi^{3+} (r_{ion} = 103 pm) formed with the $TMPyP^{2+}$ ligand (H_2TMPyP^{4+} = 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin cation) is significantly lower than that for anionic $BiTSPP^{3-}$, due to the weaker Lewis-basicity of the positively charged porphyrin. DFT calculations of the geometrical structures show good correlation with the observed photophysical and photochemical properties. Deviating from the inner-sphere LMCT reaction of OOP complexes, the cationic ligand (such as $TMPyP^{2+}$ and $TAPP^{2+}$ (H_2TAPP^{4+} = 5,10,15,20-tetrakis(4-trimethylammonium phenyl)porphyrin cation)) is favorable for the outer-sphere photoinduced reduction of the metal center in the in-plane manganese(III) porphyrins because the anionic porphyrin ligands of higher Lewis-basicity stabilize the +3 oxidation state. The cationic porphyrin ligands enhance the formation of manganese(II) complexes with OOP characteristics, and can be utilized in photocatalytic systems applicable for water splitting.

1. Introduction

Metalloporphyrins play important roles in numerous biochemical processes, such as photosynthesis, charge- and oxygen transport as well as in various redox reactions [1–8]. Within this significant group of compounds, besides the generally photochemically less reactive normal (in-plane) complexes, there is a class characterized by peculiar features [9–12] due to the strain in the ligand frame caused by the size of the metal center. In these complexes the ionic radius (>80–90 pm) of the metal center is too large to coplanarly fit into the cavity of the ligand. Thus, it is located above the porphyrin plane, causing out-of-plane distortion (these are called out-of-plane (OOP) or sitting-atop (SAT) metalloporphyrins), or, if the metal ion remains in the center of the ligand cavity, the latter is stretched and suffers in-plane distortion. In the following we shall refer to both kinds of complexes with a strained porphyrin ring as out-of-plane or OOP complexes irrespectively whether the distortion of the porphyrin frame is planar or nonplanar.

The rate of formation of the normal metalloporphyrins is much lower than that of the OOP complexes because of the rigidity of the porphyrin ligands. However, metal ions of larger radius such as Pb^{2+}, Hg^{2+}, or Cd^{2+} can catalyze the formation of in-plane metalloporphyrins via generation of OOP complex intermediates [13–18]. In these species, due to the distortion, two diagonal pyrrolic nitrogen atoms become more accessible to another metal ion, even with smaller ionic radius, on the other side of the porphyrin ligand [19].

Metalloporphyrins of distorted structure play important roles in some natural biological processes, such as enzyme functions (e.g., high-spin Fe^{2+} is located out of the ligand plane in hemoglobin, bacteriochlorophyll is distorted promoting faster electron transfer) [20] or biosynthesis of normal (in-plane) metalloporphyrins where sitting-atop intermediates are formed [21].

Deviating from the coplanar complexes, OOP metalloporphyrins, on account of their distorted structure and kinetic lability, display special photochemical features. For example, they undergo 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 [22]. The absorption and emission properties of these compounds also significantly differ from those of the normal metalloporphyrins.

In this contribution, we review the results of recent studies on water-soluble (1:1) porphyrin complexes of several metal ions to demonstrate how the size (and partly the oxidation state) of the metal center affect their structure and photoinduced behavior. Metalloporphyrins with relatively large metal center such as Ag^{2+} (r_{ion} = 94 pm), Cd^{2+} (r_{ion} = 95 pm) and Bi^{3+} (r_{ion} = 103 pm) displaying OOP peculiarities will be compared with the in-plane porphyrins of Au^{3+} (r_{ion} = 85 pm) and Mn^{3+} (r_{ion} = 58 pm), and the border-line case of Mn^{2+} (r_{ion} = 83 pm). The effects of the pre-distortion and the charge of the porphyrin ligand on the structure and photoreactivity of the OOP complexes will also be discussed. Fig. 1 shows the structures of the anionic and cationic porphyrins applied in these studies. The results of DFT calculations on the geometrical structures of some metalloporphyrins in this work will also be summarized. Besides, the photoredox properties of manganese porphyrins of opposite charges will be compared, exploiting the different oxidation states of the metal center for realization of photocatalytic cycles.

2. Spectroscopic, structural and photoinduced properties of metalloporphyrins

2.1. General spectroscopic and photochemical features of metalloporphyrins

Prior to the discussion of the properties of the individual complexes, it is expedient to compare the general spectroscopic and photochemical features of the typical normal and out-of-plane metalloporphyrins with those of the corresponding free-base porphyrin. Fig. 2 displays the most characteristic ranges of both the absorption and the emission spectra of $Hg(II)TSPP^{4-}$ (as an OOP complex), $Pd(II)TSPP^{4-}$ (as a normal metalloporphyrin), and H_2TSPP^{4-} (as the corresponding free base). The Soret- or B-bands assigned to the $S_0 \rightarrow S_2$ transitions can be found in the shorter-wavelength range (380–440-nm), while the longer-wavelength range (500–700-nm) contains the Q-bands assigned to the $S_0 \rightarrow S_1$ transitions. The position of both the Soret- and the Q-bands of the typical in-plane metalloporphyrin $Pd(II)TSPP^{4-}$ are blue-shifted compared with those of the free-base porphyrin, while $Hg(II)TSPP^{4-}$, one of the first examples of OOP complexes, displays red-shifted bands [22–24]. As a consequence of the split of the S_1-state in the free-base porphyrin originating from the presence of protons on two pyrrolic nitrogen atoms, the shift of Q-bands must be calculated with respect to the average energy of the $Q_x(0,0)$ and $Q_y(0,0)$ bands of the free-base porphyrin. The fluorescence bands in the 550–800-nm range of the emission spectra can be assigned as $S_1 \rightarrow S_0$ transitions (the individual bands correspond to the (0,0), (0,1) and (0,2) transitions with respect to vibrational states). The fluorescence bands of both types of metalloporphyrins are blue-shifted and less intense compared with those of the free-base porphyrin. The hypsochromic effect in the fluorescence is in contrast with the red-shift in the absorption. Notably, this blue shift–red shift anomaly is virtual, because the emission derives not from the hypothetical average level, but from the energetically lower S_{1x}-state (populated in $Q_x(0,0)$ absorption).

Excitation of porphyrin complexes of out-of-plane structure, at both Soret and Q bands, leads to irreversible LMCT reaction resulting in the oxidation of the ligand and reduction of the metal center [23–28]. The reduced metal ion of increased radius and originally located above the ligand plane is easily ejected from the oxidized porphyrin ring, which is subsequently cleaved to form bilinones (Scheme 1). A parallel dissociation of the kinetically labile complex (without charge transfers) can generally occur in this photolysis.