A heme-like, water-soluble iron(II) porphyrin: thermal and photoinduced properties, evidence for sitting-atop structure

Róbert Huszánk and Ottó Horváth*

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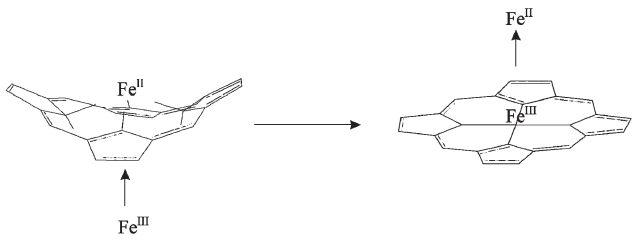
Water-soluble ferrous porphyrin (Fe^{II}TPPS) was prepared by complexation reaction of free base porphyrin (H_2TPPS) with iron(II) ions in the presence of iron(III)-trapping acetate buffer; the catalytic and photoinduced properties of this air-stable complex proved unambiguously its sitting-atop structure.

It is well known that heme proteins play an essential role for living organisms in oxygen transport and storage (hemoglobin, myoglobin) and in electron transfer processes (cytochrome c, cytochrome oxidase). Modelling of hemoglobin and myoglobin has been tried for many years by preparation of oxygen carriers which are able to function in aqueous media under physiological conditions. However, all synthetic, almost exclusively hydrophobic iron(II) porphyrin complexes previously reported in the literature were very unstable in air and rapidly oxidized to ferric porphyrin.[1] While both thermal and photoinduced properties of iron(III) porphyrins were thoroughly investigated,[2–4] only a few studies were carried out with the corresponding iron(II) complexes, especially with the water-soluble derivatives.[5,6] Our report on iron(II)-tetrakis(4-sulfonatophenyl)porphyrin (Fe(II)TPPS) reveals typical characteristics of these complexes, proved to be of sitting-atop (SAT) structure.

Preparation of this simple ferrous porphyrin has been found to be rather difficult. In the complexation reaction of free base porphyrin and any kind of iron(II) salt, ferric porphyrin was the product in all cases so far published, even if the solutions were very dilute and carefully deoxygenated. Thus, in the latter cases, iron(III) ions could not be the result of oxidation by dissolved O_2. Surprisingly, no complexation between ferric ions and free base porphyrins has been observed yet (within at least a one-week reaction period). These phenomena suggest that a very effective substitution reaction occurs between the ferrous porphyrin and the trace amount of iron(III) ions, which always exist in iron(II) solutions (Scheme 1). This kind of catalytic behavior was observed for some metal ions which are too large to be at the core of the porphyrin ring such as Hg(II), Cd(II), Pb(II), and Cu(I).[7] This effect is based on the formation of kinetically labile SAT complexes. As the iron(II) porphyrin is formed in the first step, two new coordination positions arise on the other side of the porphyrin plane (on two diagonally situated nitrogen atoms) and become accessible for another metal ion, iron(III) in our case.† Following the coordination of iron(III), it excludes the iron(II) ion bound more weakly on the other side of the porphyrin, and occupies the very centre of the ligand. Scheme 1 is a simplified summary of this latter stage in the catalytic process of the formation of iron(III) porphyrin. The complex formed in this way is a kinetically inert regular (non-SAT) metalloporphyrin, hence, this substitution is irreversible. However, in the presence of reagents which can capture the iron(III) traces, for example acetate, ferrous porphyrin can be prepared. On the basis of this experience, Fe(II)TPPS was prepared in argon-saturated aqueous solution containing 0.3 M acetate, 1.5×10^{-4} M iron(II), and 3×10^{-6} M porphyrin at pH 6. This compound proved to be kinetically labile, its formation constant was measured by a spectrophotometric method in the range of the Soret band ($K = 7.0 \pm 0.5 \times 10^4$ M^{-1}), using two days for the equilibration.



Scheme 1

After the complex had been formed, the solution was saturated with air. The ferrous species proved to be stable, no conversion to the ferric form has been observed even over weeks. The reason for this is that, in contrast to organic media where the complexes are neutral, the dimerization process of Fe^{II}TPPS through an oxygen molecule (*i.e.*, a peroxo bridge) is not favorable in – especially diluted – aqueous solution, because of the highly negative charge of the complex.

The absorption spectra of both the free ligand and the metalloporphyrins consist of two groups of bands, the more intensive B or Soret band ($S_0 \rightarrow S_2$) and the Q bands ($S_0 \rightarrow S_1$). The ferric porphyrin's B(0,0) band is at 393 nm, the more intensive Q(1,0) band is at 528 nm, so these bands are blue-shifted compared to the corresponding ones of the free base porphyrin ($\lambda_B = 412$ nm, Fig. 1 A). This regular paramagnetic metalloporphyrin complex does not luminesce at room temperature. The ferrous porphyrin displays a very intensive B(0,0) absorption band at 421 nm and a weak B(1,0) at 400 nm, the Q(0,0) and its vibrational overtone Q(1,0) bands are at 597 and 556 nm. The positions of these absorption bands agree well with those observed earlier,[5] in preparing Fe(II)TPPS by *in situ* reduction of Fe(III)TPPS. Just oppositely to the ferric form, these bands are red-shifted compared to those of the free ligand. The absorption spectrum of Fe(II)TPPS is very similar to that of the deoxyhemoglobin[9] where the central ion lies 0.4 Å above the porphyrin plane.[10] Deviating from the corresponding iron(III) complex, the ferrous porphyrin shows

*otto@vegic.sol.vein.hu

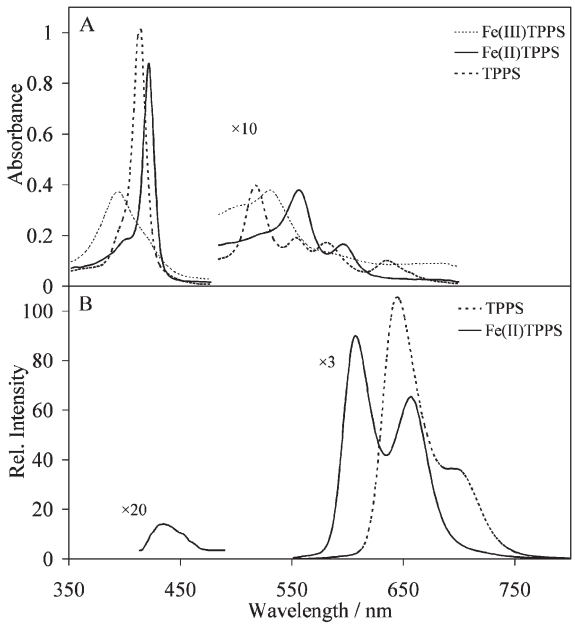


Fig. 1 The ground-state absorption and fluorescence spectra of H_2TPPS, Fe^{II}TPPS and Fe^{III}TPPS in water (λ_{exc} = 390 nm for the Soret and 421 nm for the Q fluorescence).

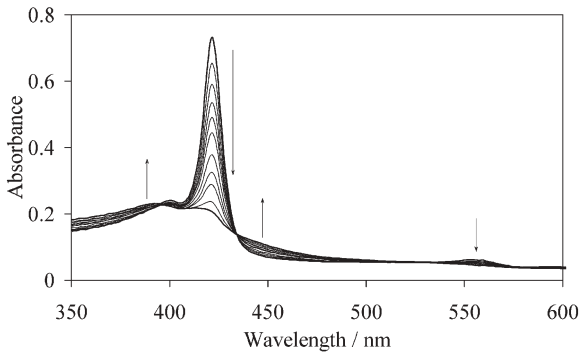
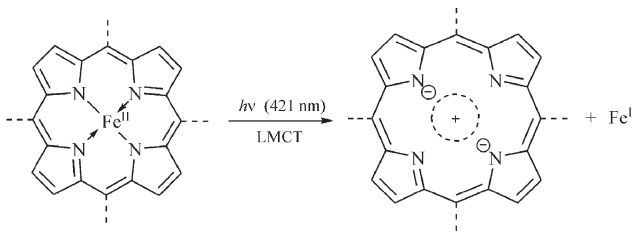


Fig. 2 Degradation of Fe(II)TPPS and formation of bile type derivatives upon irradiation at 421 nm.



Scheme 2

characteristic emissions. The intensive fluorescence bands at 608 and 656 nm can be assigned to the Q(0,0) and Q(0,1) transitions, respectively (Fig. 1 B). The quantum yields of this fluorescence were 0.0095 and 0.0070 for the Q- and Soret-band excitation, respectively. A weak emission was also observed at 433 nm upon excitation at 390 nm. This band may be assigned to the B(0,1) $S_0 \leftarrow S_2$ transition on the basis of recent transient (femtosecond) spectroscopic studies on hydrophobic porphyrins.[11] The Q emission bands of Fe(II)TPPS are blue-shifted compared to the corresponding ones of the free base porphyrin. All these spectroscopic features confirm the SAT structure of our iron(II) complex because the unambiguous sitting-atop Hg(II) and Tl(I) porphyrins have exactly the same type of absorption and emission spectra (the corresponding peaks are at similar wavelengths).[12] It means that there is only a minor perturbation by the electrons of the central metal ion and the optical properties are determined essentially by the porphyrin ring's p electrons and the distortion of the plane, affecting the energy levels of the delocalized π and π^* frontier orbitals. So, this kind of absorption and emission properties represents a typical SAT-complex behaviour. According to recent *ab initio* calculations,[13] iron(II) porphyrins have sitting-atop structure only in the case of a high-spin configuration of the metal center. This result agrees well with the situation in the deoxyhemoglobin.

Photolysis of this iron(II) porphyrin at both the Soret and the Q bands resulted in the degradation of the complex itself (Fig. 2), accompanied by the formation of ring-opened tetrapyrrole derivatives (bile type pigments) as indicated by the new bands at 390 and 450 nm.[14] The quantum yields for the degradation were 7.8×10^{-4} and 9.2×10^{-4} with Soret- and Q-band excitation, respectively. Addition of electron scavenger (nitrate) did not change the efficiency of the photodegradation of the iron(II) complex, indicating that no electron ejection occurs upon irradiation at these wavelengths. These phenomena suggest that the photochemistry of this complex, similarly to other SAT metalloporphyrins, is characterized by a porphyrin ligand to metal charge transfer reaction. In contrast, irradiation of the analogous iron(III) porphyrin, under the same conditions, caused no permanent chemical change in the system, even if a similar LMCT reaction may take place in the primary photochemical step. The reason for this is that the regular metalloporphyrins can be reversibly oxidized or reduced,[15] because the formed π cation is very stable and the electron can be transferred back to the porphyrin ligand. But, in the case of SAT porphyrins, after the LMCT reaction has occurred, the reduced central ion leaves the ring – as kinetic lability is also increased by the enlarged size of the metal center, the electron cannot be transferred back, thus an irreversible redox process takes place, involving subsequent ring-opening steps. Scheme 2 demonstrates the key step of this photoinduced reaction. For the sake of simplicity, the ionic substituents are designated just by dashed lines.

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Róbert Huszánk and Ottó Horváth*
University of Veszprém, Department of General and Inorganic Chemistry, H-8200 Veszprém, P.O. Box 158, Hungary.
E-mail: otto@vegic.sol.vein.hu; Fax: 3- 88-427-915; Tel: 3- 88-427-915

Notes and references

† In the free base porphyrins, two nitrogen atoms are out of plane because of the steric effect of the hydrogen atoms attached to them. So the conjugation of the non-bonding electron pairs on these nitrogen atoms is hindered and a less symmetric 18-atom pathway delocalisation is favoured.[8] In the case of most SAT type porphyrins, the conjugation pathway is the same because of the deforming effect of the central ion. Thus, these

nitrogen atoms have another coordination bonding position on the other side of the porphyrin plane.

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