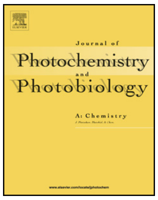
Journal of Photochemistry and Photobiology A: Chemistry 328 (2016) 233–239

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



# Photophysical and photochemical properties of manganese complexes with cationic porphyrin ligands: Effects of alkyl substituents and micellar environment☆

Melinda A. Fodor[a], Ottó Horváth[a,*], Lajos Fodor[a], Katarina Vazdar[b], Günter Grampp[c], Alexander Wankmüller[c]

[a] Department of General and Inorganic Chemistry, Institute of Chemistry, University of Pannonia, P.O. Box 158, 8201 Veszprém, Hungary
[b] Division of Physical Chemistry, Ruđer Bošković Institute, P.O.B. 180, HR-10002 Zagreb, Croatia
[c] Institute of Physical and Theoretical Chemistry, Graz University of Technology, 8010 Graz, Stremayrgasse 9, Austria, Austria

## ARTICLE INFO

*Article history:*
Received 29 January 2016
Received in revised form 7 June 2016
Accepted 12 June 2016
Available online 15 June 2016

*Keywords:*
Cationic manganese(III) porphyrins
Amphiphilic
Micellar
Fluorescence
Photocatalysis
Triplet state

## ABSTRACT

Although Mn(III) porphyrins were considered earlier to be very weakly emissive, the fluorescence displayed by Mn(III) complexes with the cationic $TMPyP^{2+}$ ligand ($H_2TMPyP^{4+}$ = 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin) as well as with its other alkyl (such as hexyl and dodecyl) derivatives proved to be strong enough for a comparative study. Elongation of the alkyl substituent increased both the quantum yield and the lifetime of the emission for the Mn(III) porphyrins, while resulted in an opposite effect for the corresponding free bases in homogeneous solutions. The presence of cationic micelles, however, reversed this tendency regarding the emission lifetime of the complexes. These cationic metalloporphyrins were applied in a photocatalytic system involving triethanolamine (TEOA) as a sacrificial electron donor and methylviologen ($MV^{2+}$) as an acceptor. In the first step of the catalytic process outer-sphere photoinduced reduction of the metal center took place via quenching of the triplet excited state of these metalloporphyrins by TEOA. The corresponding manganese(II) porphyrins formed in this way were also photoactive; they forwarded an electron to $MV^{2+}$ upon irradiation, regenerating the starting complex. Elongation of the alkyl substituents increased the quantum yield of the formation of methylviologen radical ($MV^{\bullet+}$) in this system, but considerably decreased the durability of the photocatalyst. Anionic micelles totally hindered the photoinduced generation of Mn(II) porphyrins, while cationic micellar environment appreciably increased the efficiency of the accumulation of $MV^{\bullet+}$.

## 1. Introduction

Metalloporphyrins represent a very important group of compounds playing key roles in nature, due to their special spectral, coordination and redox features. Their favorable photoinduced properties can also be utilized in various photocatalytic procedures [1]. Water-soluble derivatives can be applied in environmentally benign aqueous systems. Kinetically inert in-plane metalloporphyrins, in which the metal center is coplanarly located in the cavity of the ligand, may offer promising possibilities for realization of photocatalytic systems based on outer-sphere electron transfer [2]. Within the normal or in-plane metalloporphyrins, the so-called hyper porphyrins are especially interesting from this viewpoint, due to their distorted structure, which may increase the (photo)redox reactivity of these complexes. The Mn(III) ion of 58 pm ionic radius [3] is rather small compared to the size of the cavity in the ligand center. Thus, it promotes the contraction of the porphyrin ring, distorting it, forming typical hyper porphyrin complexes. According to the generally accepted concept, earlier the highly distorted complexes with Mn(III) or Co(III) metal center were considered not to display appreciable fluorescence at room temperature [4]. However, in recent studies characteristic emission spectra were observed in the case of Co(III)$TMPyP^{5+}$ [5] and manganese(III) complexes with 5-[4-(5-carboxy-1-butoxy)-phenyl-10,15,20-tris(1-methylpyridinium-4-yl)porphyrin [6], 5,10,15,20-tetraphenylporphyrin, and 5,10,15,20-tetra(3-hydroxyphenyl)porphyrin [7].

---

☆ Dedicated to the memory of Professor Ivan Habuš.
* Corresponding author.

*E-mail addresses:* amfor89@gmail.com (M.A. Fodor), otto@mk.uni-pannon.hu (O. Horváth), lajos@vegic.uni-pannon.hu (L. Fodor), katarina.vazdar@irb.hr (K. Vazdar), grampp@tugraz.at (G. Grampp), a.wankmueller@tugraz.at (A. Wankmüller).

http://dx.doi.org/10.1016/j.jphotochem.2016.06.011
1010-6030/

Photoredox reactions of water-soluble manganese(III) porphyrins, sometimes along with the corresponding cobalt(III) complexes, were investigated in several respects. Photocatalytic oxidation of sulfide to sulfate in a wastewater was studied with Co(III)TMPyP$^{5+}$, Mn(III)TMPyP$^{5+}$, and Fe(III)TMPyP$^{5+}$ ($H_2$TMPyP$^{4+}$ = 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin) [8]. Manganese(III) porphyrins, both cationic Mn(III)TMPyP$^{5+}$and anionic Mn(III)TSPP$^{3-}$, ($H_2$TSPP$^{4-}$ = 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin), were applied for photocatalytic oxygenation of various bicyclic organic compounds, utilizing visible light [9–11]. Mn(III)TMPyP$^{5+}$proved to be successful also in photoinduced oxidation of polynucleotides [12]. Cationic manganese(III) porphyrins were efficient photocatalysts in the systems containing suitable electron donors (such as EDTA and TEOA) and methylviologen (MV$^{2+}$) as an appropriate electron acceptor [1,13,14]. However, the mechanism of the catalytic processes has not been completely elucidated. Thus, the aim of our work was to study the photophysical (especially fluorescence) and photochemical (mostly photocatalytic) properties of Mn(III)TMPyP$^{5+}$ as well as its corresponding hexyl and dodecyl derivative, in order to investigate the effect of the length of alkyl chain. Besides, connecting to the hydrophobic/hydrophilic interactions, the influence of the micellar environment on the photoinduced behaviors was also studied.

## 2. Experimental

### 2.1. Materials

The compounds used in our experiments were of reagent grade. Amphiphilic porphyrin ligands ($H_2$THPyP$^{4+}$ = 5,10,15,20-tetrakis(1-hexylpyridinium-4-yl)porphyrin and $H_2$TDPyP$^{4+}$ = 5,10,15,20-tetrakis(1-dodecylpyridinium-4-yl)porphyrin) were synthesized according to a literature method [15]. $H_2$TMPyP$^{4+}$ was purchased from Sigma-Aldrich. For preparation of the manganese(III) porphyrins and for the photoinduced experiments with them, water purified in a Millipore/Milli-Q system was applied as solvent. Stock solutions of manganese(III) porphyrins were prepared by in situ generation by the reaction between the corresponding free base and manganese(II) sulfate (in 4 folds excess at the porphyrin concentration of $3 \times 10^{-4}$ M) under aerated conditions. The reaction is rather slow at room temperature (at least one week), thus it was accelerated by addition of $HgCl_2$ in a very low concentration ($10^{-6}$ M). Catalytic effect of mercury(II) with a large ionic radius (102 pm [3]) is based on the formation of an out-of-plane intermediate Hg(II) porphyrin [16]. The distortion of this species makes two diagonal pyrrolic nitrogens more accessible to another metal ion, even with smaller ionic radius, on the other side of the porphyrin ligand [17]. The behavior of the final product (manganese(III) porphyrin) was not affected by the presence of Hg(II) in the samples prepared by 50–100 times dilution from the stock solution. Control experiments were carried out with commercially available pure Mn(III)TMPyP$^{5+}$ (from Frontier Scientific), and no deviation was observed from the behavior of the corresponding home-made metalloporphyrin. Borate buffer was applied to adjust pH to 8.3. In the case of dodecyl substituted porphyrin, the solvent was 1:1 ethanol: water mixture.

### 2.2. Analytical procedures

The absorption spectra were recorded by using a Specord S-600 diode array spectrophotometer. For the measurement of fluorescence a Fluoromax-4 (Horiba JobinYvon) spectrofluorimeter was applied. It was supplemented with a time-correlated single-photon counting accessory for determination of fluorescence lifetimes, too. $Ru(bpy)_3Cl_2$ [18] was used as a reference for determination of the fluorescence quantum yields. The emission quantum yield of this complex is 0.042 at 20–25 °C. It displays a strong absorption in the 400–480-nm range, covering the Soret-bands of the free-base porphyrins and their manganese(III) complexes. Considering the relatively long emission lifetime of $Ru(bpy)_3^{2+}$, its solution was carefully argon-saturated by 40-min bubbling. Transient absorption measurements were carried out on a laser kinetic equipment described elsewhere [19]. All analytical measurements were realized at room temperature.

### 2.3. Photolyses

Photochemical experiments were carried out with 3.5-cm$^3$ argon-saturated solutions in 1-cm cells at room temperature. During the irradiations the reaction mixtures were continuously homogenized by magnetic stirring. For illumination a LED light of 430–490-nm emission with a 457-nm maximum intensity was utilized. Incident light intensity was determined by ferrioxalate actinometry [20,21].The experimental results were processed and evaluated by MS Excel programs on PCs.

## 3. Results and discussion

### 3.1. Photophysical properties

#### 3.1.1. Absorption spectra

Absorption spectra of porphyrins, both free bases and metalloporphyrins, display two types of bands. The Q-bands, assigned to the $S_0 \rightarrow S_1$ transitions, can be found in the longer-wavelength range (500–700-nm), while the more intense Soret- or B-bands with one order of magnitude higher molar absorbances, assigned to the $S_0 \rightarrow S_2$ transitions, appear in the shorter-wavelength range (380–480-nm). Generally, the Soret-bands of the normal (in-plane) metalloporphyrins display characteristic blue-shift compared to that of the corresponding free base, while the out-of-plane (OOP) complexes, in which the metal center, due to its large size, is located above the plane of the porphyrin ligand, distorting it, display red-shifted bands [22–25]. Deviating from the general tendency, however, in the case of the in-plane porphyrin complexes of Mn(III), this band is red-shifted [1,6,7]. This phenomenon is well demonstrated by the spectra of $H_2$THXPyP$^{4+}$, Mn(III)THXPyP$^{5+}$ and Mn(II)THXPyP$^{5+}$ as shown in Fig. 1 and by the data of Table 1. A similar behavior can be observed for the Q-bands. In the free-base porphyrins the presence of protons on two (diagonally situated) pyrrolic nitrogens results in a split of the $S_1$-state. Hence, 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.

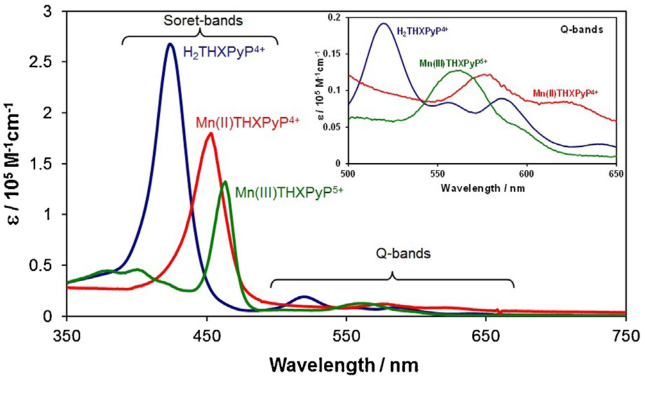


**Fig. 1.** Molar absorption spectra of Mn(III) and Mn(II) complexes formed with $H_2$THXPyP$^{4+}$, compared to that of the free base.