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Photophysical and photocatalytic behavior of cobalt(III) 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin

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Abstract

Although kinetically inert cationic Co(III)TMPyP⁵⁺ (H₂TMPyP⁴⁺ = 5,10,15,20-tetrakis(methylpyridinium-4-yl)porphyrin) was considered earlier to be very weakly emissive, both the spectrum and the lifetime of its fluorescence could be determined. Besides, this complex proved to be favorable for outer-sphere photoinduced reduction of the metal center in the presence of triethanolamine (TEOA) as electron donor quenching the triplet excited state of this metalloporphyrin. The corresponding cobalt(II) porphyrin formed in this way was also photoactive; it forwarded an electron to a suitable acceptor (e.g., methylviologen) upon irradiation, regenerating the starting complex. Hence, this system may be a candidate for hydrogen generation from water by utilization of visible light.

Keywords: cobalt(III) porphyrin, water-soluble, fluorescence, photocatalysis, triplet state

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Metalloporphyrins play important roles in nature, due to their special spectral, coordination and redox features. Their advantageous photoinduced properties can also be exploited in various photocatalytic procedures [1]. Water-soluble derivatives can be utilized in environmentally benign systems not containing organic solvents. Kinetically inert in-plane metalloporphyrins, in which the metal center coplanarly fits into the cavity of the ligand, may offer promising possibilities for realization of photocatalytic systems based on outer-sphere electron transfer [2]. The so-called hyper-porphyrins can be especially interesting in this respect, due to their distorted structure, which may increase the (photo)redox reactivity of these complexes. From water-soluble metalloporphyrins of this type, photoredox reactions of manganese(III) complexes were thoroughly studied [1, 3, 4], while scarce attention was paid to the corresponding cobalt(III) porphyrins in this respect.

Photocatalytic oxidation of the sulfide content of a wastewater to sulfate was studied with Co(III)TMPyP⁵⁺, Mn(III)TMPyP⁵⁺, and Fe(III)TMPyP⁵⁺ (H₂TMPyP⁴⁺ = 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin) [5]. Upon irradiation in the range of the Soret-bands, the cobalt(III) complex proved to be the most efficient, but the results have not been interpreted. This metalloporphyrin can also connect to the chain of DNA and oxidatively split it in the presence of suitable electron acceptors [6]. Since cationic manganese(III) porphyrins proved to be efficient photocatalysts in the presence of appropriate electron donors (such as EDTA and TEOA) and methylviologen as electron acceptor [1, 3, 7], cationic cobalt(III) porphyrins, the other characteristic representatives of water-soluble hyper-porphyrins, are also worth investigating in this respect. Hence, in this work, some photophysical and photochemical properties of Co(III)TMPyP⁵⁺ were studied, also confirming its photocatalytic behavior, which may be utilized in water-splitting by solar radiation.

The compounds used for our experiments were of reagent grade. Water purified in a Millipore/Milli-Q system was applied as solvent. Stock solutions of Co(III)TMPyP⁵⁺ were prepared by in situ generation by the reaction between the corresponding free base and cobalt(II) sulfate (in 4× excess at the porphyrin concentration of 3×10⁻⁴ M) under aerated conditions. Since the reaction is rather slow at r.t. (at least one week), it was accelerated by addition of HgCl₂ in a very low concentration (10⁻⁶ M). Catalytic effect of Hg(II) with a large ionic radius (102 pm [8]) is based on the formation of an out-of-plane intermediate Hg(II)-porphyrin [9]. In this species, due to the distortion, two diagonal pyrrolic nitrogens become more accessible to another metal ion, even with smaller ionic radius, on the other side of the porphyrin ligand [10]. The behavior of the final product (Co(III) porphyrin) was not affected by the presence of Hg(II) in the samples prepared by 50-100 times dilution from the stock solution. Borate buffer was applied to adjust pH to 8.3.

Absorption and emission spectra were recorded by using a Specord S-600 diode array spectrophotometer and a Fluoromax-4 (Horiba JobinYvon) spectrofluorimeter, respectively. The latter equipment supplemented with a time-correlated single-photon counting accessory was applied for determination of fluorescence lifetimes too. Ru(bpy)₃Cl₂ [11] was utilized as a reference for determination of the fluorescence quantum yields. Transient absorption measurements were carried out on a laser kinetic equipment describe elsewhere [12]. Photochemical experiments were carried out with 3.5-cm³ argon-saturated solutions in 1-cm cells at r.t., continuously homogenized by magnetic stirring. For illumination a LED light of 415-465-nm emission with a 440-nm maximum intensity was utilized. Incident light intensity was determined by ferrioxalate actinometry [13].

The Co(III) ion of 55 pm ionic radius [8] is small enough to fit into the cavity of the porphyrin ligands, forming unambiguously in-plane complexes [14]. The metalloporphyrins of the significantly larger Co(II) ion (*r*_{ion} = 75 pm) display spectral properties and photochemical behavior deviating from those of the Co(III) complexes. Absorption spectra of porphyrins, both free bases and metalloporphyrins, are featured by two characteristic types of

bands. The very intense Soret- or B-bands assigned to the $S_0 \rightarrow S_2$ transitions can be found in the shorter-wavelength range (380-470-nm), while the Q-bands with one order of magnitude lower molar absorbances, assigned to the $S_0 \rightarrow S_1$ transitions, appear in the longer-wavelength range (500-700-nm). The Soret-band of the normal (in-plane) metalloporphyrins generally display characteristic blue-shift compared to that of the corresponding free base [14, 15]. However, deviating from the general tendency, in the case of the in-plane porphyrin complexes of Mn(III) and Co(III), this band is red-shifted [16]. This phenomenon is well demonstrated by the Soret-bands of H_2TMPyP^{4+} and $Co(III)TMPyP^{5+}$ at 421 and 434 nm, respectively [17]. Such metalloporphyrins, the spectra of which cannot be interpreted by the 4 MO theory of Gouterman, are classified as hyper-porphyrins [18]. This unusual phenomenon can be explained by the very strong interaction between the π orbital of the porphyrin ring and the d orbital of the metal center [3]. Additionally, a structural distortion can also strengthen this effect; the radius of the low-spin Co^{3+} ion is so small (55 pm) that the porphyrin ring contracts, resulting in a ruffled distortion [19]. The Soret-band of the corresponding cobalt(II) porphyrin (at 429 nm [20]) is also red-shifted compared to that of the free base, however, it is blue-shifted in the relation of the (more distorted) cobalt(III) hyper-porphyrin. This phenomenon can be accounted for the larger radius of the Co^{2+} ion, similarly to the case of manganese (II/III) complexes studied earlier [1, 14].

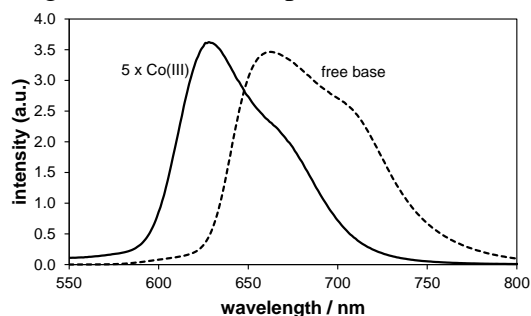


Fig. 1. Emission spectra of $Co(III)TMPyP^{5+}$ (solid line) and H_2TMPyP^{4+} (dashed line) obtained by excitation at the Soret-bands ($c = 5 \times 10^{-6}$ M).

The fluorescence bands in the 550-800-nm range of the emission spectra of porphyrins, both free bases and metalloporphyrins, 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) [14]. The fluorescence bands of metalloporphyrins (of any type) are blue-shifted and less intense, compared to those of the corresponding free-base porphyrin. This phenomenon is also manifested in the emission spectra of $Co(III)TMPyP^{5+}$ and the corresponding free base (Fig. 1). The bands assigned to the (0,2) transition are not perceptible in this case. Generally, the highly distorted porphyrin complexes with diamagnetic metal center do not display appreciable fluorescence at room temperature [18]. Accordingly, earlier, Mn(III) and Co(III) porphyrins were not found to be fluorescent at all [17]. However, due to our rather sensitive equipment, the emission of this cobalt(III) porphyrin could be measured with an appropriate resolution. In accordance with the expectations, the fluorescence bands of the complex (obtained upon Soret-band excitation) are blue-shifted compared to those of the free base, especially in the case of the longer-wavelength band. Notably, the same spectrum was obtained at Q-band excitation (at 548 nm), too, indicating that it is the result of the same transition ($S_1 \rightarrow S_0$).

The intensity of the emission of the cobalt(III) porphyrin is one order of magnitude lower than that of the free base. The radiation quantum yields measured at Soret-band excitation confirm this observation. Φ_{fl} for $Co(III)TMPyP^{5+}$ is only 1.37×10^{-3} , while for H_2TMPyP^{4+} Φ_{fl}

was determined to be 0.0295 in aqueous solution [21] and 0.059 in methanol [22]. The much weaker fluorescence of the Co(III) complex may be accounted for the in-plane position of the open-shell metal center, resulting in an electronic effect (strong interaction between the orbitals of the ligand and the metal), and the ruffled distortion as a steric effect.

The fluorescence decay of the first excited singlet state of this Co(III) porphyrin could be described by a biexponential function. This observation fully agreed with that regarding the emission lifetime of the corresponding free base [22]. In that case the τ_1 and τ_2 values were 4.17 ns (0.43) and 10.05 ns (0.57) (the amplitudes, i.e., the pre-exponential ratios are given in parentheses) in aqueous system. The corresponding data for Co(III)TMPyP⁵⁺ are 0.75 ns (0.42) and 1.83 ns (0.58), in accordance with the much lower fluorescence quantum yield of the complex, indicating an inner quenching effect of the metal center, due to the above mentioned reasons.

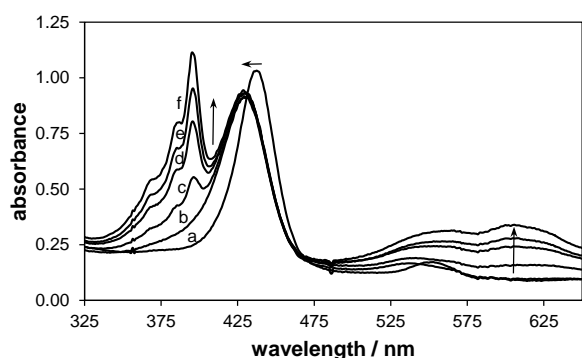


Fig. 2. Spectral change in the system initially containing 8.3×10^{-6} M Co(III)TMPyP⁵⁺, 5×10^{-4} M TEOA and 2×10^{-3} M MV²⁺ during the irradiation at 0 s (a), 50 s (b), 100 s (c), 150 s (d), 200 s (e) and 300 s (f) ($\lambda_{ir} = 440$ nm, $l = 1$ cm).

Similarly to cationic manganese(III) porphyrins [1, 7], Co(III)TMPyP⁵⁺ has also been proved to be suitable for realization of a photoredox catalytic cycle in the presence of TEOA and MV²⁺ as electron donor and acceptor, respectively. As Fig. 2 indicates, at appropriate concentrations, photocatalytic generation of MV^{•+} can be achieved with this photocatalyst for a relatively long period of irradiation.

The first step in the catalytic process is the photoinduced reduction of the cobalt(III) complex with TEOA (Eq. 1), indicated by the change in the position and intensity of the Soret band. Then the corresponding cobalt(II) porphyrin formed is photochemically oxidized with MV²⁺ (Eq. 2) as shown by the appearance of the characteristic bands of MV^{•+} at 398 and 605 nm [23].



As Fig. 2 shows, practically the whole amount of the starting cobalt(III) complex was converted to the corresponding Co(II) species in the initial period of irradiation. The latter (reduced form) persisted till the end of the 240-min illumination. Besides, the catalyst proved to be relatively stable; less than 15% was degraded during this period. The nearly 100% conversion of the cobalt(III) catalyst before MV^{•+} appeared suggested that ground-state reduced form (Co(II)TMPyP⁴⁺) does not react with MV²⁺. This assumption was confirmed by an independent experiment, where MV²⁺ was added to the system (in the dark, under anaerobic conditions) only after the photoreductive generation of the cobalt(II) species. No

formation of $MV^{\bullet+}$ was observed. This is not surprising because the ground-state anionic cobalt(II) porphyrin, $Co(II)TSP^{4-}$ ($H_2TPPS^{4-} = 5,10,15,20$ -tetrakis(4-sulfonatophenyl)porphyrin), which is more reductive due to the negative charge, does not react either with MV^{2+} [24]. Hence, excitation of the reduced catalyst ($Co(II)TMPyP^{4+}$) is also needed for the electron transfer toward the methylviologen, as indicated in Eq. 2. The overall quantum yield for the formation of $MV^{\bullet+}$ was determined from the initial rate of the accumulation of this radical. Its value ($\Phi = 0.026$) may be acceptable for application of this system for hydrogen generation from water, using a suitable co-catalyst.

Since the singlet excited state of $Co(III)TMPyP^{5+}$ is too short-lived (<1.9 ns) to be efficiently quenched by TEOA, its triplet state is expected to play role in the first redox step (Eq. 1). Accordingly, a long-lived ($\tau = 102$ μs) transient was detected upon excitation at 540 nm (Fig. 3), which can be assigned to the triplet state of this cobalt(III) porphyrin. It was efficiently quenched with TEOA ($k_q = 4.7 \times 10^6$ $M^{-1}s^{-1}$), confirming our suggestion. A similar situation is reasonable for the reaction between MV^{2+} and the excited state of the $Co(II)TMPyP^{4+}$ complex formed.

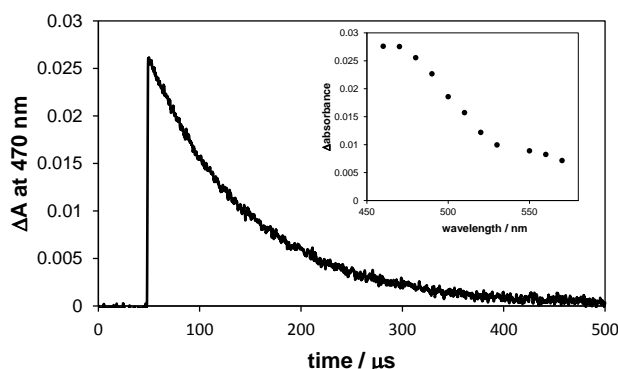


Fig. 3. Transient absorption decay at 470 nm after a 540-nm laser pulse. Inset: the spectrum of the transient absorption right after the pulse.

These results well demonstrate that $Co(III)TMPyP^{4+}$ is a potential photosensitizer for solar energy utilization by water-splitting, besides it displays a characteristic fluorescence despite being a diamagnetic metalloporphyrin.

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