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

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Abstract

Kinetically inert cationic Ni(II)TMPyP^{4+} (H$_2$TMPyP^{4+} = 5,10,15,20-tetrakis(methylpyridinium-4-yl)porphyrin) displayed a characteristic fluorescence (τ = 1.2-1.4 ns, $\Phi = 2.0\times10^{-3}$), which was quenched with triethanolamine (TEOA) in a static way. This complex proved to be an efficient photocatalyst in the system containing TEOA and methylviologen (MV^{2+}) as electron donor and acceptor, respectively. Interestingly, however, deviating from the behavior of the analogous Co(III) and Mn(III) complexes in such a system, TEOA did not dinamically quench the triplet excited state of Ni(II)TMPyP^{4+} (τ = 6.31 μs), hence no reduction of the metal center occured upon irradition. Instead, in the presence of this electron donor (at 1×10^{-3}M) the excited-state lifetime dramatically increased (to τ = 36.6 μs), indicating the formation of a Ni(II)TMPyP^{4+}-TEOA associate. This longer-lived triplet was efficiently quenched by MV^{2+} ($k_q = 9.9\times10^6$ M^{-1}s^{-1}), leading to the formation of MV$^{\bullet+}$. The overall quantum yield of this one-step photoassisted electron transfer is considerably high (Φ = 0.011-0.013 at Soret-band irradiation). Hence, this system, combined with a suitable co-catalyst, may be applicable for visible light-driven hydrogen generation from water.

Keywords: nickel(II) porphyrin, water-soluble, fluorescence, photocatalysis, triplet state, static and dynamic quenching

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Several metal complexes of porphyrins and their derivatives are key compounds in natural systems as exemplified by chlorophylls, hemoglobin and various cytochromes [1, 2] due to their favorable spectral, coordination, and redox features. Their peculiar photoinduced behavior can also be used in various artificial photocatalytic systems [3]. Water-soluble metallporphyrins are promising for utilization in environmentally friendly procedures. Kinetically inert in-plain metalloporphyrins, in which the metal center coplanarly fits into the cavity of the ligand, were successfully applied in photocatalytic systems based on outer-sphere electron transfer [4, 5]. This type of metalloporphyrins can be formed with the ions of the iron group, such as Fe(III), Co(III), and Ni(II). However, while the photoredox chemistry of iron(III) and cobalt(III) porphyrins was thoroughly studied in the past 2-3 decades [6,7, 8, 9, 10], the corresponding nickel(II) complexes were hardly examined in this respect [11, 12]. Since the complexes of iron(III), cobalt(III) as well as manganese(III) with the cationic 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin (H_2TMPyP^{4+}) proved to be promising in various photocatalytic systems [3, 7, 8, 13, 14, 15, 16, 17], in this work some photophysical and photochemical properties of $Ni(II)TMPyP^{4+}$ were studied in order to examin the potential applicability of this metalloporphyrin in utilization of solar radiation in the visible range.

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 $Ni(II)TMPyP^{4+}$ were prepared by in situ generation by the reaction between the corresponding free base and nickel(II) sulfate (in 5 fold excess at the porphyrin concentration of 3×10^{-5} M) under aerated conditions. Since the reaction is extremely slow at r.t., it was accelerated by addition of $HgCl_2$ in a very low concentration (10^{-6} M) and an elevated temperature (70^{o}C). Even under these conditions, the total conversion took ca. 10 days. The catalytic effect of Hg(II) with a large ionic radius (102 pm [18]) is based on the formation of an out-of-plane intermediate Hg(II)-porphyrin [19]. 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 [20]. The behavior of the final product (Ni(II) 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 8.4.

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. $Ru(bpy)_3Cl_2$ [21] was utilized as a reference for determination of the fluorescence quantum yields. Transient absorption measurements were carried out on a laser kinetic equipment described elsewhere [22]. Photochemical experiments were carried out with 3.5-cm^3 argon-saturated solutions in 1-cm cells at r.t., continuously homogenized by magnetic stirring. For Soret-band illumination a LED light of with a 443-nm maximum intensity was utilized. Incident light intensity was determined by ferrioxalate actinometry [23].

The Ni(II) ion of 63 pm radius [18] is small enough to fit into the cavity of the porphyrin ligands, forming unambiguously in-plane complexes [24]. 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 [24, 25]. Interestingly, the spectrum of the water-soluble nickel(II) porphyrins (such as $Ni(II)TMPyP^{4+}$) in aqueous solutions represents a border-line case.

As Fig 1 shows, it displays a double Soret-band due to its two spin states in equilibrium [26]. The low-spin metal center is characterized with a square planar coordination sphere, while the high-spin one with an octahedral one. The Soret-band of the latter species appears at 449 nm, while that of the low-spin complex can be found at 420 nm (very close to the Soret-band of the free-base ligand). Due to this band slightly redshifted compared to that of the free base, Ni(II) porphyrins were categorized as hypso type [4, 27].

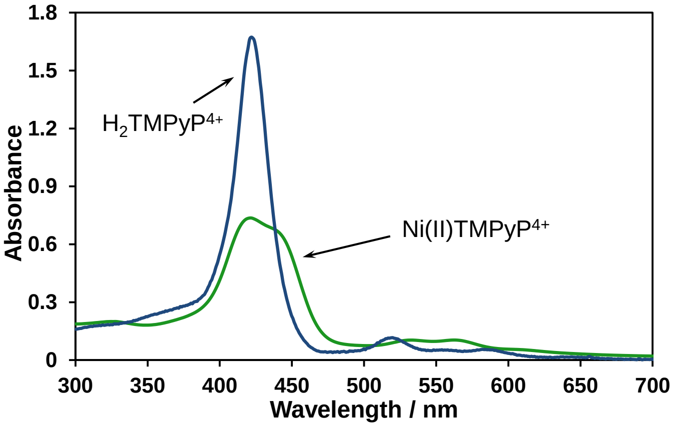

Fig. 1. Absorption spectra of $Ni(II)TMPyP^{4+}$ and the free base (H_2TMPyP^{4+}) in aqueous solution ($c = 1\times10^{-5}$ M, $\ell = 1$ cm).

The emission spectrum displayed by $Ni(II)TMPyP^{4+}$ upon Soret-band excitation (Fig 2) is very similar to those of the corresponding cationic Co(III) and Mn(III) metalloporphyrins [7, 17]. The fluorescence bands in the 550-800-nm range of the fluorescence spectra of porphyrins, both metalloporphyrins and free bases, 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 latter one is generally not perceptible) [19]. Due to the strong metal-ligand interaction, the emission bands of metalloporphyrins are less intense and blue-shifted compared to those of the corresponding free-base porphyrin as in the case of $Ni(II)TMPyP^{4+}$, too (Fig 2).

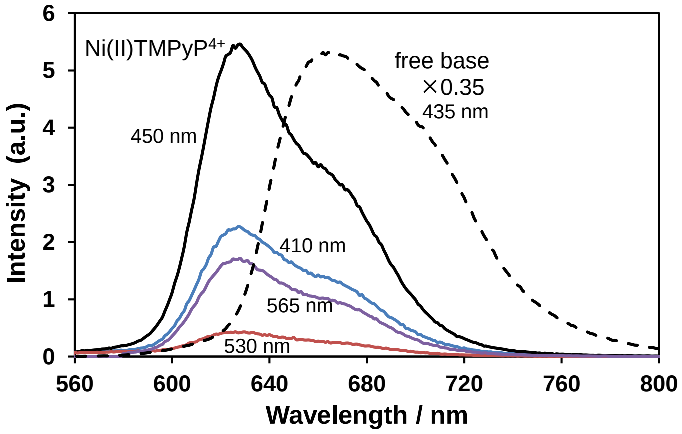

Fig. 2. Emission spectra of $Ni(II)TMPyP^{4+}$ (solid lines) and H_2TMPyP^{4+} (dashed line) obtained by excitation at the Soret-bands ($c = 5\times10^{-6}$ M). The corresponding excitation wavelength is given at each spectrum.

No excitation-wavelength-dependence was observed for the shape and the position of the emission spectrum, neither in the Soret- nor in the Q-range. This phenomenon indicates that the excited state from which the fluorescence originated was the same in each case (S_1), besides, it did not depend on which ground state (low-spin or high-spin) was excited. Nevertheless, the fluorescence lifetimes for these two spin states slightly deviated: 1.36 ns for the square planar and 1.19 ns for the octahedral complex. The fluorescence quantum yield at Soret-band excitation ($\Phi_{fl} = 2.0\times10^{-3}$) is in the same order of magnitude as that observed earlier for Co(III)TMPyP^{5+} (9.9×10^{-4} [7]). The higher value may be attributed to the larger ionic radius of Ni(II) (63 vs. 55 pm [18]) causing a smaller distortion (shrinkage) of the porphyrin ring. This fluorescence efficiency, however, is one order of magnitude lower than that of the corresponding free base ($\Phi_{fl} = 0.0203$ in aqueous solution [28]), in accordance with the significantly longer emission lifetime of H$_2$TMPyP^{4+} (τ_{fl} = 5.2-6.0 ns [28, 29]). The reason for this substantial decrease may be the strong interaction between the orbitals of the ligand and the open-shell metal center of in-plane position (electronic effect) and the distortion of the porphyrin ring (steric effect). Since triethanolamine (TEOA) was applied as an electron donor for photocatalytic redox system with Ni(II)TMPyP^{4+} (see later), its influence on the fluorescence was also measured. It did not perceptively affect the emission lifetime, but considerably decreased the quantum yield; by about 25% upon addition of 0.05 M TEOA.

Similarly to the corresponding manganese(III) and cobalt(III) porphyrins [7, 15, 17], a photocatalytic system was realized with Ni(II)TMPyP^{4+} too in presence of TEOA and MV^{2+} as electron donor and acceptor, respectively, in argon-saturated aqueous solutions at room temperature (Fig. 3). In the previous cases, the formation of stable Mn(II) and Co(II) porphyrins were observed, which forwarded an electron to methyl viologen in the second photochemical step. In the nickel(II) porphyrin system, however, no change in the spectrum of the photocatalyst accompanied the photoinduced accumulation of MV$^{\bullet+}$ (Fig 5). The quantum yield for the formation of this product at Soret-band excitation moderately depended on the pH (Φ = 0.011 at pH 8.4 and 0.013 at pH 10). These values are of the same order of magnitude as those observed with the corresponding Co(III) and Mn(III) porphyrins ((Φ = 0.026 and 0.015, respectively). Notably, even H$_2$TMPyP^{4+} can act as a photocatalyst in this system, although with a much lower efficiency. Also Q-band irradiation of Ni(II)TMPyP^{4+} resulted in the accumulation of MV$^{\bullet+}$ in this photocatalytic system, but no quantum yield measurements were carried out because of the strong inner filter effect of this product.

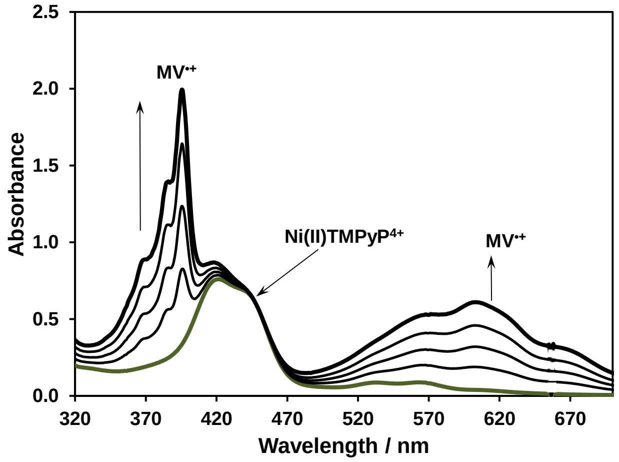

Fig. 3. Spectral change of the solution initially containing 1.0×10^{-5} M Ni(II)TMPyP^{4+}, 5×10^{-4} M TEOA and 2×10^{-3} M MV^{2+} during the Soret-band irradiation at 0, 48, 144, 276 and 720 s (ℓ = 1 cm).

In the case of Ni(II)TMPyP^{4+}, formation of the highly instable Ni(I) porphyrin (or reduced nickel porphyrin) may be a key step of the mechanism. Such a reduced complex can only be generated via triplet excited state quenched by TEOA, similarly to the corresponding cobalt(III) and manganese(III) porphyrins. The formation of triplet excited state of the Ni(II)TMPyP^{4+} photocatalyst was proved by time-resolved laser flash photolysis experiments (Fig 4). However, it could not be quenched by the electron donor applied in these systems, moreover, its lifetime (6.31 μs) increased to 31.6 μs upon addition of 1.0×10^{-3} M TEOA.

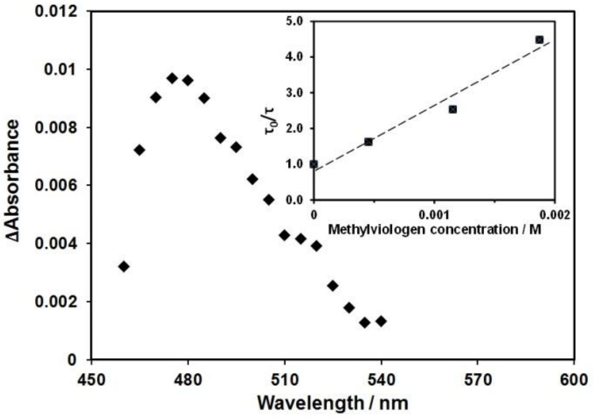

Fig. 4. Transient spectrum of triplet excited state of Ni(II)TMPyP^{4+} recorded 510 ns after a 355-nm laser pulse of 5 ns duration. Inset: quenching of triplet Ni(II)TMPyP^{4+} with MV^{2+} in the presence of 1.0×10^{-3} M TEOA ($\ell = 1$ cm).

This phenomenon suggests the formation of an associate between the electron donor and the ground-state complex, and the excited triplet state of this species is much longer than that of the nickel(II) porphyrin alone. This is in accordance with the static quenching of the fluorescence. Additionally, the triplet state of this associate was efficiently quenched by MV^{2+}, with a rate constant of $k_q = 9.9\times10^6$ s^{-1}M^{-1} (Fig 4, inset). A similar, even if much slighter effect of TEOA was observed with the free-base ligand, too; its triplet-state lifetime increased by 5% upon addition of 1.0×10^{-3} M, and by 50% in the presence of 1.0×10^{-2} M TEOA. This observation indicates that the electron donor does not coordinate axially to the metal center. Instead, it is connected to the ligand. This conclusion was confirmed by the change of the absorption spectrum of Ni(II)TMPyP^{4+} upon addition of TEOA; the ratio of the Soret-bands was shifted toward the shorter-wavelength one belonging to the square planar structure, while an axial coordination would have increased the octahedral one. Besides, similarly to the corresponding nickel(II) porphyrin, the triplet excited state of the free base in the presence of 1.0×10^{-3} M TEOA could also be quenched by MV^{2+}, with a rate constant of $k_q = 1.03\times10^7$ s^{-1}M^{-1}. It is in accordance with the photocatalytic generation of MV$^{\bullet+}$ by H$_2$TMPyP^{4+}, even if with much lower efficiency.

The observations above clearly indicate that, deviating from the corresponding Mn(III) and Co(III) system, in the case of the nickel(II) porphyrin (and the free base as well) the electron transfer from TEOA to MV^{2+} takes place directly in one step, due to the ground-state association of the electron donor and the photocatalyst (Eqs. 1, 2).

$$\mathrm{Ni(II)TMPyP^{4+} + TEOA \leftrightarrow Ni(II)TMPyP^{4+}{—}TEOA} \qquad (1)$$

$$\mathrm{Ni(II)TMPyP^{4+}{—}TEOA + MV^{2+} + h\nu \rightarrow Ni(II)TMPyP^{4+} + MV^{\bullet+} + TEOA_{ox}} \qquad (2)$$

Accordingly, the photocatalyst in this system functions as a special sensitizer, which immediately transmits its excitation energy to the electron donor, promoting the direct charge transfer towards the acceptor.

These results well demonstrate that Ni(II)TMPyP^{4+} may be applicable for solar energy utilization in the visible range by photocatalytic hydrogen generation, in the presence of a suitable co-catalyst.

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