# Photocatalytic application of water-soluble metalloporphyrins: an experimental and theoretical study

final report
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## Abstract

Comprehensive structural, kinetic, photophysical and –chemical study of both labile out-of-plane and kinetically inert in-plane metalloporphyrins was accomplished.

DFT calculations established that – in accordance with the expectations due to the lanthanide contraction – the stability constants of lanthanide(III) complexes with 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, for both 1:1 and 3:2 (metal:ligand) compositions, decrease upon increasing ionic radius of the metal center, because of the increasing out-of-plane distance of Ln(III). For the same reason, the efficiency of their photolysis causing predominantly irreversible redox (MLCT) reaction increases, due to the favored charge separation. The structure of the 3:2 bisporphyrin complexes was concluded from photophysical results.

Photocatalytic cycles were realized by application of kinetically inert Mn(III), Co(III) and Ni(II) complexes with cationic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, which generated methylviologen radical cations in the presence of triethanolamine electrondonor. These radicals are applicable for hydrogen evolution from water. The cycle of the Mn(III) and Co(III) complexes was shown to significantly differ from that of the Ni(II) porphyrin; the previous ones transfer the electron to the acceptor in two steps, while the latter species in a single one. Both anionic and (amphiphilic) cationic Mn(III) porphyrins were applied for oxygenation and oxidative degradation of organic compounds.

## 1. Introduction

Metalloporphyrins display special spectral and coordination features. Their advantageous photoinduced properties can also be exploited in various photocatalytic procedures. Water-soluble derivatives can be utilized in environmentally benign systems not containing organic solvents.

Kinetically inert in-plain 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. Metal ions can be located out of the ligand plane too, resulting in kinetically labile out-of-plane (OOP or sitting-atop=SAT) complexes with dome-distorted structure, displaying typical photophysical and photochemical properties. Besides, the OOP position promotes the formation of bis- or oligoporphyrins. Lanthanide(III) complexes can be typical examples of metallo-oligoporphyrins [2, 22, 38], in which the π-π interaction depends on the distance between the macrocycles, strongly influenced by the size of the metal center. Therefore, lanthanide(III) ions are good candidates for fine tuning of the out-of-plane distances, due to the lanthanide contraction.

The aim of our work was to study the photophysical and photochemical properties of various water-soluble metalloporphyrins, both kinetically inert in-plane and the labile sitting-atop (SAT) or out-of-plane (OOP) complexes, in order to explore their potential applicability in visible light-driven photocatalytic systems. Such systems may utilize solar radiation for hydrogen production from water (via reduction) or oxidize organic parent molecules for preparative purpose (oxygenation) as well as decompose pollutants (mineralization).

## 2. Formation and photoinduced behavior of SAT (sitting-atop or out-of-plane (OOP)) complexes

Formation and primary photochemical features of complexes of a water-soluble, anionic porphyrin, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin anion ($H_2TSPP^{4-}$) with numerous lanthanide(III) ions (Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), and Er(III)) were studied in this part of our work. Connecting to the formation kinetics and analysis of the photoinduced behaviors, the composition and complex equilibria of these metalloporphyrins were also investigated.

Their formation has been compared to those of other SAT complexes such as Cd(II), Bi(III) and Ag(I,II) porphyrins [1, 3, 18, 23, 37, 40].

### *2.1. Formation kinetics and complex equilibria*

Porphyrins are peculiar in the respect of complexation because they are planar, cyclic, rigid, aromatic, tetradentate, as well as protonated ligands; therefore, the formation of metalloporphyrins is a special ligand-controlled reaction. As a consequence of the coordination cavity's limited size, the metal ions, depending on their radius, can occupy an in-plane (IP) or an out-of-plane (OOP or SAT=sitting-atop) position.

The formation of kinetically labile SAT metalloporphyrins in aqueous solution (or in other polar solvents) is an equilibrium reaction, owing to the higher activity and mobility of metal ions than in nonpolar solvents. This process can be characterized by the apparent stability constant ($\beta'_{x:y}$ in Eqs. 1-2), which includes the proton concentration, determined mainly in buffered solutions. $H_2TSPP^{4-}$ {anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, also abbreviated as $H_2P^{4-}$ in our work} is the most widely used water-soluble porphyrin, besides its negative charge enhances the coordination of positively charged metal ions.

$$\mathrm{x\,M^{z+} + y\,H_2TSPP^{4-} \Leftrightarrow M_x(TSPP)_y{}^{xz-6y} + 2y\,H^+} \qquad (1)$$

$$\beta'_{x:y} = \frac{\beta_{x:y}}{[H^+]^{2y}} = \frac{[M_x(TSPP)_y{}^{xz-6y}]}{[M^{z+}]^x[H_2TSPP^{4-}]^y} \qquad (2)$$

Due to the out-of-plane position, a larger metal ion can simultaneously coordinate to the cavity of two macrocycles, and, reversely, two metal ions can connect to one ligand, resulting in the formation of so-called sandwich complexes with various compositions. In these complexes, the strength of $\pi$-$\pi$ interaction depends on the distance between the macrocycles, which is strongly influenced by the size of the metal center. Therefore, lanthanide(III) ions offer good opportunities to examine this dependence due to the fine tuning of the out-of-plane distances, utilizing the well-known lanthanide contraction. This expectation has been confirmed by the results of our quantum chemical calculations as shown below (not published yet).

Modeling of the changes of molecular geometry of porphyrin complexes of $M^{3+}$ ions has been performed using density functional theory. In the model calculations the ligand was restricted to the bare unsubstituted porphyrin ring. The DFT calculations applied the B3LYP functional combination. The SDD basis set and pseudopotential combination was used for the metal ion and the 6/31G** set for the C, N and H atoms. It is worth noting that numerous calculations were performed using the CRENBL basis/pseudopotential set, in some cases combined with the 6-31G** set for the ligand, but in many cases serious convergence problems were observed. Even when the Kohn-Sham calculations converged, the results displayed erratic behavior. This prevented us from collecting a meaningful data set using this basis set.

In the geometry optimization, $C_{4v}$ symmetry was enforced for the $MP^+$ ion. The optimization yielded dome distorted complexes. None of vibrational frequencies was imaginary, indicating that the structures are genuine minima. In several cases, especially with the open-shell ions, the geometry optimizations starting from different initial conditions produced two different minima with significantly different energies both of which having the same geometric symmetry which differed only in the degree of out-of-plane distortion. This indicates that the Kohn-Sham iteration does not always converge to the lowest energy wave function of the ion. The molecular state for the two minima was of different symmetry. In such cases, the lower-energy structure was used.

The analysis molecular geometries focused on the magnitude of OOP distortion. This was characterized by the distance of the metal ion from the plane of the four N atoms. This distance was found to be significant, at least 0.75 Å (this value being observed for Lu). Fig. 1 shows the correlation of the OOP distance as a function of the Shannon ionic radius of the metal ion. Very good correlation can be seen: the “smaller” the ion the less it protrudes from the porphyrin ring.

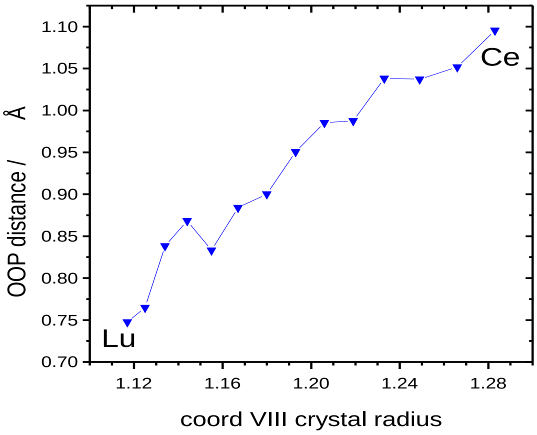


**Fig. 1.** The OOP distance of the metal ion in the series of $MP^+$ ions as a function of Shannon ionic radii as obtained in B3LYP/SDD+6-31G** calculations.

The insertion of lanthanide(III) ions into the cavity of porphyrins is a very slow process in water or also in other O-donor solvents as a consequence of the Pearson-type hard character of metal ions. The other reason for the simultaneous metal control in these typical ligand-controlled reactions is that the lanthanide ions may compose oligomer forms through the counter-anion or hydroxide bridges in aqueous solution [36], the pre-dissociation step of which is required for the formation of porphyrin complexes, too. From the study of the reaction rate of porphyrin’s metalation at different concentration of lanthanide(III) ions, we were able to indirectly estimate the degree of this oligomerization, as well as the stability constants of these oligomers [6, 19]. Furthermore, if the counter-anion in the applied metal salts is strongly bound, e.g. the bidentate O-donor acetate, then it can enhance the coordination of the first porphyrin ligand due to its trans effect, but it can hinder the connection of a further porphyrin because it remains on the metal center in axial position. Additionally, lanthanide ions connect rather to the peripheral substituent of porphyrins if it possesses similarly hard O-donor atom (e.g. carboxy-or sulfonatophenyl), than to the pyrrolic nitrogens under kinetic control, resulting in the formation of the free-base ligands’ tail-to-tail oligomer (Fig. 2) [6].

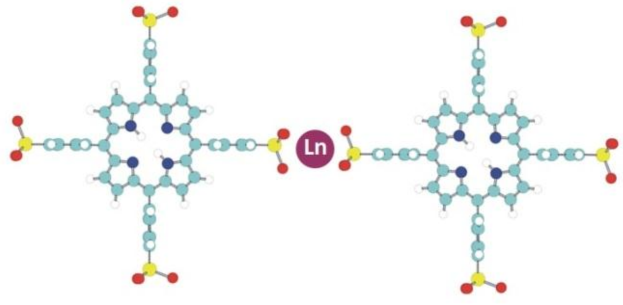


**Fig. 2.** Structure of the anionic porphyrin's tail-to-tail dimer, connected by a lanthanide(III) ion [6].

Only under thermodynamic control, at higher temperature (~60 $^{o}$C), can coordinate the metal ion also, or rather, to the four pyrroles; resulting in the formation of metalloporphyrins of various compositions (e.g., 1:1 or 3:2 M:P ratio). After the discovery of the possible coordination bonds between lanthanide ions and sulfonato substituents, the formation of lanthanide bisporphyrins, in the absence of acetate, was imagined as a tail-to-tail dimerization of two metallo-monoporphyrin complexes through a metal bridge, similarly to the free-base porphyrins (Figs. 2 and 3) [6, 17, 19], and deviating from the head-to-head connection as in the case of sandwich complexes. This assumption was confirmed by the large similarities between the absorption spectra as well as the singlet-1 fluorescence spectra of these lanthanide(III)-mono- and bisporphyrin complexes. These spectral similarities and comparable fluorescence quantum yields (see later) may only originate from very weak π–π interactions between the macrocycles [6, 30, 31].

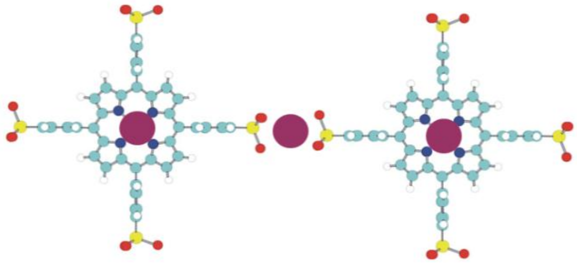


**Fig. 3.** Representation of $Ln_3P_2^{3-}$ lanthanide porphyrins [30, 31].

Fig. 4 well demonstrates that the formation constants (we determined by spectrophotometric method) for the complexes of $H_2TSPP^{4-}$ with lanthanide(III) ions studied display strong correlations with the size of the metal center [31].

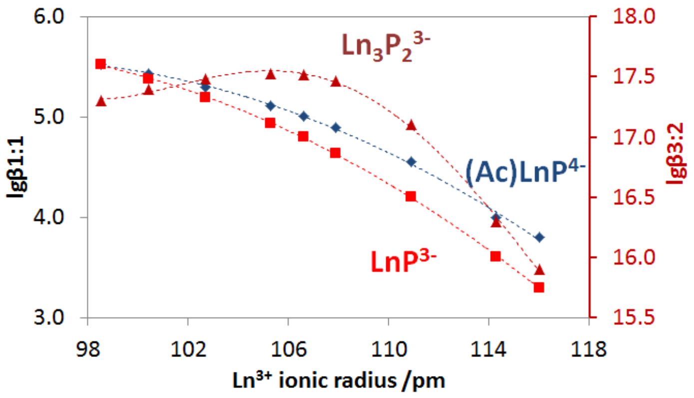


**Fig. 4.** Equilibrial trends for lanthanide(III) porphyrins [31].

It clearly shows that, due to the lanthanide contraction, the out-of-plane distance and domedness decrease resulting in the strengthening of coordinative bonds. In the second half of the lanthanide series, the stability constants of bisporphyrins start to slightly decrease, and neither those of the monoporphyrins increase as strongly as in the first half. The required periods of time to reach the equilibrium are longer, too. Both phenomena may originate from the harder type of late lanthanides, what can cause the higher stability of the aqua complexes, together with the hindrance of the coordination to the cavity, but mainly to the peripheral sulfonato groups of the porphyrin.

We also studied the effect of the temperature on the formation reaction rate and that of different (axially coordinating, and non-coordinating) counter-anions, besides, determined the activation parameters (Fig. 5) [6].

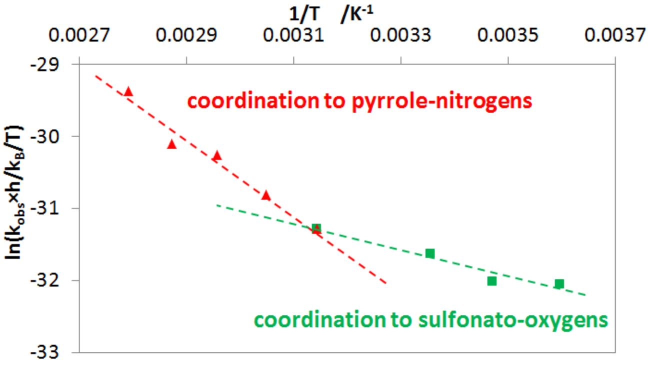


**Fig. 5.** Temperature dependence (using Eyring-Polányi equation) of the rate constant of reaction between 1.0×10$^{-6}$ M $H_2P^{4-}$ and 1.2×10$^{-2}$ M $Sm^{3+}$ in the presence of 1 M $NaClO_4$ (pH≈6) [6].

Fig. 5 unambiguously displays that only under thermodynamic control, i.e. at higher temperatures, can coordinate the metal ion also, or rather, to the four pyrrolic nitrogens; resulting in the formation of typical metalloporphyrin complexes.

From kinetic aspect, the presence of axial ligand(s) in the coordination sphere of the metal ion can accelerate the exchange reaction of the solvent molecules on the opposite site of the metal center. Thus, a coordinated hydroxide ion can cause a ~11-fold increase of the formation rate as well as the apparent stability constant as was demonstrated by the Cd(II)TSPP$^{4-}$[1]. If the out-of-plane distance of the metal center is fairly large, as in the case of bismuth(III), a ruffled-like deformation of the periphery may superpose on the highly dome-distorted structure, resulting in the appearance of two types of complexes, mainly in aqueous solution [3]. This phenomenon may be attributed to the appreciable coordination ability or the polarizing effect of water molecules, which can promote the complex to overcome the kinetic energy barrier toward the more stable structure, in which the metal center is located closer to the ligand plane, resulting in the decrease of distortion.

It was observed that the coordination of acetato or chloro ligands accelerated the insertion of the metal ion into the porphyrin's cavity, and promoted the stabilization of the complex formed. Further investigation indicated that these effects are the consequence of the ligandum's negative charge, increasing the (ionic strength-dependent) activity of the metal ion, decreasing its charge. This interpretation has been confirmed by application of various alcohols (e.g., ethanol and ethylene glycol) as neutral axial ligands [25, 33].

### *2.2. Photophysics and photochemistry of SAT complexes*

Due to their dome-distorted structure, thermodynamic instability, kinetic lability, SAT complexes show typical photophysical features, and photochemical reactivity.

### *2.2.1. Photophysics*

The characteristic photophysical data we determined for the lanthanide(III) complexes studied in this work are summarized in Table 1, along with those regarding the free-base ligand [31]. The bisporphyrins display a blueshifted and less intense singlet-1 fluorescence, related to the free-base porphyrin [23, 32]. While the lifetimes for mono- and bisporphyrin complexes are almost equal (~2 ns), only the fluoresence quantum yield decreases slightly because the formation of bisporphyrin results only in the deceleration of radiative decay, as a consequence of a special type of aggregation, probably through the peripheral, sulfonato substituents (tail-to-tail dimerization) without strong $\pi$-$\pi$ interactions between the macrocycles. These results clearly indicate that the structure of the lanthanide(III) bisporphyrins significantly deviates from that of the corresponding SAT complexes of main-group metal ions such as Bi(III) and Hg(II) [27].

**Table 1.** Photophysical parameters* of lanthanide(III) porphyrins [30, 31].

| **Ln$^{3+}$** | **H$_2$TSPP$^{4-}$** | **La** | **Ce** | **Nd** | **Sm** | **Eu** | **Gd** | **Dy** | **Er** | **Yb** |
|---|---|---|---|---|---|---|---|---|---|---|
| **ionic radius +3 /(8)$^a$ pm** | | 116 | 114.3 | 110.9 | 107.9 | 106.6 | 105.3 | 102.7 | 100.4 | 98.5 |
| **LnP$^{3-}$ (Ac)** | | | | | | | | | | |
| **$\phi(S_1)^b$ /$10^{-2}$** | 7.53 (6.24 Qy) | 2.74 | 3.1 | 3.93 | 4.39 | 4.47 | 4.15 | 3.43 | 3.51 | 3.60 |
| **$\phi(S_1\text{-}B)^c$ /$10^{-2}$** | 5.62 | 1.62 | 2.06 | 3.05 | 3.03 | 2.86 | 2.91 | 2.33 | 2.51 | 2.73 |
| **$\phi(IC)^d$** | 0.746 (0.828 Qy) | 0.591 | 0.664 | 0.776 | 0.689 | 0.640 | 0.702 | 0.681 | 0.714 | 0.758 |
| **$\tau(S_1)^e$ /ns** | 10.03 | 2 | 1.97 | 1.94 | 1.93 | 1.94 | 1.93 | 2.01 | 1.96 | 1.97 |
| **$k_r(S_1)^f$ /$10^6$ s$^{-1}$** | 7.51 | 14 | 15.7 | 20.2 | 22.8 | 23.1 | 21.5 | 17.0 | 17.9 | 18.3 |
| **$k_{nr}(S_1)^g$ /$10^7$ s$^{-1}$** | 9.22 | 48 | 49.2 | 49.4 | 49.6 | 49.2 | 49.7 | 48.0 | 49.3 | 49.0 |
| **Ln$_3$P$_2^{3-}$** | | | | | | | | | | |
| **$\phi(S_1)$ /$10^{-2}$** | | 1.03 | 1.42 | 2.59 | 3.09 | 2.88 | 2.37 | 2.08 | 2.26 | 2.39 |
| **$\phi(S_1\text{-}B)$ /$10^{-2}$** | | 0.671 | 0.948 | 1.71 | 2.20 | 1.92 | 1.73 | 1.56 | 1.78 | 1.99 |
| **$\phi(IC)$** | | 0.65 | 0.666 | 0.662 | 0.713 | 0.667 | 0.727 | 0.747 | 0.790 | 0.833 |
| **$\tau(S_1)$ /ns** | | 2 | 2.00 | 1.99 | 1.94 | 1.95 | 1.94 | 2.02 | 1.96 | 1.96 |
| **$k_r(S_1)$ /$10^6$ s$^{-1}$** | | 5 | 7.12 | 13.0 | 16.0 | 14.8 | 12.3 | 10.3 | 14.6 | 12.2 |
| **$k_{nr}(S_1)$ /$10^7$ s$^{-1}$** | | 49 | 49.3 | 48.8 | 50.0 | 49.8 | 50.4 | 48.4 | 49.7 | 49.8 |

*Designations: $^a$ for M$^{3+}$ metal center with coordination number 8; S$_1$-fluorescence quantum yield for $^b$ Q-band excitation, $^c$ Soret-band excitation; $^d$ quantum yield for S$_2$-S$_1$internal conversion; $^e$ emission lifetime; $^f$ radiative rate constant; $^g$ non-radiative rate constant.

The trends in fluorescence quantum yield of lanthanide(III) porphyrins are explicated on the basis of electronic and steric factors. The electronic factor is the increasing number of unpaired electrons together with the atomic number up to the half-filled subshell ($Gd^{3+}$), what enhances the strong interaction with π-electron system, may strengthen the spin-forbidden decays and cause a decrease in the fluorescence quantum yield. The steric factor is the lanthanide contraction, namely the radii of 3+ lanthanide ions decrease with the increasing atomic number, what reduces the out-of-pane (OOP) distance as well as the dome distortion of their porphyrin complexes, increasing the fluorescence quantum yields [31].

### *2.2.2. Photochemistry*

The photolysis of lanthanide(III) monoporphyrins existing in acetate buffer resulted mainly in the photoredox degradation of the complex, while the photoinduced dissociation of the metal ion (without charge transfers) took only a minor part (0-15 %) from the total photochemical reactions. The overall quantum yield of the photochemical processes was two orders of magnitude higher than that of the free-base or the in-plane metalloporphyrins as a consequence of the increased irreversibility of the photoinduced charge transfer from the ligand to the metal center in out-of-plane position. In the solution containing chloride or perchlorate, the lanthanide(III) mono- and bisporphyrins are simultaneously excited, moreover free-base ligand also remains in the equilibrium because of the lower stability constants. On the basis of the evaulation method based on the distribution of porphyrin-forms' concentration, it turned out that beside the photoredox degradations, the equilibrium between the complexes are varied by excitation, i.e. the significant parts of the overall photochemical quantum yields originate from the photoinduced transformation of complexes into each other in this photostationary state; the light accelerates these reactions by orders of magnitude, which were very slow in dark at room temperature [5, 13, 16, 26, 31, 39]. Table 2 summarizes the overall quantum yields determined for the individual complexes, along with the contributions (in %) of the simultaneous photoinduced reactions to these overall quantum yields. As the overall quantum yield data indicate (mostly determined by the irreversible photoredox reaction), due to the consequence of the lanthanide contraction, the out-of-plane distance in the lanthanide porphyrins decreases (as confirmed by our DFT calculations), which results in the decrease of the photochemical quantum yield values (after a small increase) because of the less effective photoinduced charge separation after the ligand-to-metal charge transfer [31].

**Table 1.** The quantum yield values determined for the investigated lanthanide(III) porphyrins for Soret-band irradiations ($NaClO_4$ = 0.01 M, c ($Ln^{3+}$) = $1.0\times10^{-3}$ M and c ($H_2P^{4-}$) = $1.0\times10^{-6}$ M) [31].

| Ln(III) | ionic radius $M^{3+}$ | Φ (LnP)/ $10^{-4}$ | redox % | diss. % | transf. % | Φ ($Ln_3P_2$) $10^{-4}$ | redox % | diss. % | transf. % |
|---|---|---|---|---|---|---|---|---|---|
| La | 116 | 7.6 | 86 | 10 | 4 | 15.1 | 78 | 12 | 10 |
| Ce | 114.3 | 12.8 | 82 | 0 | 18 | 11.2 | 74 | 11 | 15 |
| Nd | 110.9 | 8.1 | 88 | 12 | 0 | 22.5 | 86 | 12 | 2 |
| Sm | 107.9 | 5.2 | 83 | 12 | 5 | 16.4 | 76 | 12 | 12 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Eu | 106.6 | 5.0 | 90 | 3 | 7 | 6.9 | 90 | 5 | 5 |
| Gd | 105.3 | 5.9 | 72 | 15 | 13 | 5.6 | 99 | 1 | 0 |
| Dy | 102.7 | 7.5 | 68 | 13 | 19 | 2.9 | 100 | 0 | 0 |
| Er | 100.4 | 8.2 | 86 | 10 | 4 | 2.7 | 78 | 12 | 10 |
| Yb | 98.5 | 5.1 | 82 | 0 | 18 | 2.6 | 74 | 11 | 15 |

During a deeper investigation of the photochemical mechanism, photolyses were carried out at different ionic strengths. In the solutions containing perchlorate, the overall photochemical quantum yields linearly increased together with the $NaClO_4$ concentration as a consequence of the enhanced possibility of the photoinduced charge separation.

During the steady-state photolyses, irradiation wavelength-dependence was observed regarding intermediate and end-products formed from anionic lanthanide(III) porphyrins. At higher-energy Soret-band irradiations, a labile intermediate was observed at each case, which can be assigned to a radical. This disappeared in the dark, forming an open-chain tetrapyrrol derivative as it was observed for the correspondig complexes of main-group metals [14-16, 24, 30, 31, 35, 39]. Interestingly, in the case of the samarium(III) porphyrins, the ring-opening oxidation reaction continues in the dark. This phenomenon indicates that the Sm(II) ion formed in the primary photochemical reaction is relatively stable, due to its electron configuration approaching the half-filled 4f subshell, and can catalyze further redox reactions of the oxidized porphyrin ligand. Upon irradiation of all the studied Ln(III) porphyrins at the Q-bands (at lower energies), deviating, however, from the main-group metalloporphyrins [37], a stable colored end-product was formed, which can be assigned as a complex between open-chain dioxo-tetrapyrrols and the actual lanthanide(III) ion [14, 30, 31].

## 3. Preparation and photoinduced behavior of cationic in-plane metalloporphyrins

### *3.1. Preparation of cationic Mn(III), Co(III) and Ni(II) porphyrins*

Firstly in this topic, we prepared the Mn(III) and Co(III) complexes (of 1:1 composition) with amphiphilic derivatives of cationic $TMPyP^{2+}$ ($H_2TMPyP^{4+}$ = 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin) with hexyl or dodecyl groups as the substitutions for the methyl groups. The free-base porphyrins were synthesized by our Croatian colleagues, Prof. Ivan Habuš† and Dr. Katarina Vazdar. Thus, it could be studied how the length of the hydrocarbon chain affect the photoinduced behavior of these manganese and cobalt complexes both in homogeneous aqueous solutions and in cationic as well as anionic micellar systems. The structural change significantly influenced the photoredox reactions and the stability of these complexes in catalyses [29, 30].

On the basis of our experiences gained with cationic porphyrins of Mn(III) and Co(III), the preparation of the analogous nickel(II) complex with $TMPyP^{2+}$. However, its formation rate was very low at room temperature, compared to the previous cases. Thus, it was accelerated by addition of Hg(II) catalyst in a very low concentration ($10^{-6}$ M) and an elevated temperature

(70$^o$C). Besides, the addition sequence of the reactants was crucial, too. Even under optimum conditions, the total conversion took ca. 10 days [20, 24, 34].

### *3.2. Photophysics and photochemistry of cationic Mn(III), Co(III) and Ni(II) porphyrins*

#### *3.2.1. Photophysics*

In the case of most of the in-plane metalloporphyrins the size of the metal center corresponds to that of the ligand cavity, thus it is located in the porphyrin plane and does not distort it. However, if the ionic radius ($r_i$) of the central metal is significantly smaller than the core of the porphyrin, i.e. $r_i$ < 70 pm, it shrinks the ligand and, hence, causes its distortion. This structural change, compared to the normal in-plane metalloporphyrins, considerably modifies the visible absorption spectrum of these complexes, especially in the range of the Soret-bands. While the Soret-bands of most of the in-plane metalloporphyrins display blue shifts compared to those of the corresponding free bases, due to electronic interactions between the ligand and the metal center, the distorted ones exhibit red shifts in this respect. These are classified as hyper-porphyrins. The porphyrin complexes of manganese(III) ($r_i$ =58 pm, low-spin) and cobalt(III) ($r_i$ = 55 pm, low-spin) belong to this group [8].

The methyl, hexyl and dodecyl substituted amphiphilic porphyrin complexes did not show any differences in their absorption spectra. However, the Soret-band of the free-base porphyrins display a slight red-shift if the length of the hydrocarbon chain of the porphyrin grows. The Soret-bands of Mn(III) and Mn(II) porphyrins are red-shifted compared to that of the free-base porphyrin. The Soret-bands of the manganese(II) species has a blue-shift compared to the manganese(III) porphyrin. The spectra of the corresponding cobalt porphyrins display similar effects [29, 30].

Both Mn(III)TMPyP$^{5+}$ and Co(III)TMPyP$^{5+}$ display a characteristic fluorescence in the 600-750-nm range, which is more than an order of magnitude weaker than that exhibited by the corresponding free base. The shorter emission lifetimes of these complexes are also in accordance with this tendency caused by both electronic and steric interactions between the metal center and the ligand in these hyper-porphyrins [4, 29, 30].

Elongation of the alkyl chain on the pyridinium substituent (from methyl to hexyl or dodecyl) in the case of the cationic manganese(III) porphyrins resulted in a significant (about an order of magnitude) increase in the fluorescence quantum yield, while for the corresponding free bases just a moderate decrease within the same order magnitude was observed. In the solution of a cationic surfactant (cetyltrimethyl ammonium) providing a micelle:Mn(III)-porphyrin ratio > 1, the fluorescence lifetime decreased upon increasing the length of the alkyl chain. This tendency, which is just the opposite of the change observed in the homogeneous aqueous system, was attributed to the increasing hydrophobic interaction between the alkyl chains of the surfactant in the micelles and those of the substituents on the porphyrins [29, 30]. Notably, in the case of the Mn(III) porphyrins a significant excitation wavelength-dependence of the emission spectra was observed (along with a strong solvent-dependence). This phenomenon indicates a dual luminescence originating from two different excited states [10, 11].

Ni(II)TMPyP$^{4+}$ displayed a double Soret-band due to its two spin states in equilibrium. 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 red-shifted compared to that of the free base, Ni(II) porphyrins were categorized as hypso type. Upon addition of a strong axial ligand such as ammonia the high-spin isomer become predominant, while propanol promoted the formation of the low-spin species. Interestingly, triethanolamine (TEOA), which was applied as electron donor for the photocatalytic system based on this Ni(II) porphyrin, did not coordinate axially to the metal center, but associated to porphyrin, resulted in the formation of the low-spin square isomer [34]. Notably, the equilibrium between the two isomers could also be shifted toward the formation of square planar species by an intense irradiation at the Soret-bands, removing the coordinated aqua ligands [20, 21].

The emission spectrum displayed by Ni(II)TMPyP$^{4+}$ upon Soret-band excitation was very similar to those of the corresponding cationic Co(III) and Mn(III) metalloporphyrins. Due to the strong metal-ligand interaction, the emission bands of metalloporphyrins are less intense , blue-shifted and shorter-lived, compared to those of the corresponding free-base porphyrin as in the case of Ni(II)TMPyP$^{4+}$, too. However, 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 indicated 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 [20, 34].

### *3.2.2. Photochemistry, photocatalysis*

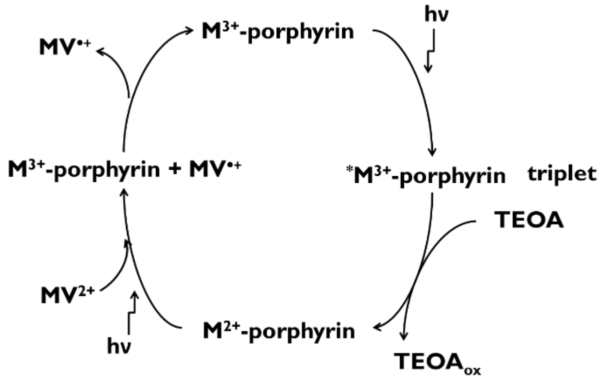
The modification of the previously realized photocatalytic system involving Mn(III)TMPyP$^{5+}$ catalyst, triethanolamine (TEOA) electron donor, and methyl viologen (MV$^{2+}$) electron was studied. Our purpose was to increase the efficiency and stability of the photocatalytic system by using cobalt(III) as metal center, and by lengthening of the hydocarbon chain on the substituent. The methyl substituted cobalt(III) porphyrin proved to be the most suitable catalyst for a reductive photocatalytic system [4, 30]. On the other hand, the longer alkyl chain and the presence of cationic detergent increased the stability of the catalyst in the case of the manganese(III) porphyrins [29]. Time-resolved transient absorption measurements of the reductive quenching between the triplet-state of Mn(III)TMPyP$^{5+}$ and TEOA were carried out by our ERA-Chemistry partners (Prof. G. Grampp and his colleagues) in Graz. The results confirmed that this reaction is one of the key steps in this photocatalytic system. Continuing our investigation of the photocatalytic behavior of Mn(III)TMPyP$^{5+}$ and Co(III)TMPyP$^{5+}$ in the presence of triethanolamine (TEOA) electron donor and methyl viologen (MV$^{2+}$) electron acceptor, the accumulation of the MV$^{\bullet+}$ product was spectrophotometrically followed at second time-scale for quantum yield (Φ) determination. The processes proved to be rather efficient (Φ= 1.5-2.5%) [4, 29, 30]. Similarly to the manganese(III) porphyrin, the triplet transient absorption, lifetime, and quenching rate constant with TEOA were also determined in the case of Co(III)TMPyP$^{5+}$, in cooperation with our ERA-Chemistry partners in Graz. The values obtained were comparable with those of the Mn(III)TMPyP$^{5+}$ system.

We have proven that in these photocatalytic systems both the reduction of the metal center of the catalyst (with a sacrificial electron donor) and the oxidation of its reduced form (with an appropriate acceptor) needed photoexcitation. Thus, the two steps can be described by the following general equations.

$$\mathrm{M(III)TMPyP^{5+} + TEOA + h\nu \rightarrow M(II)TMPyP^{4+} + TEOA_{ox}} \quad (3)$$

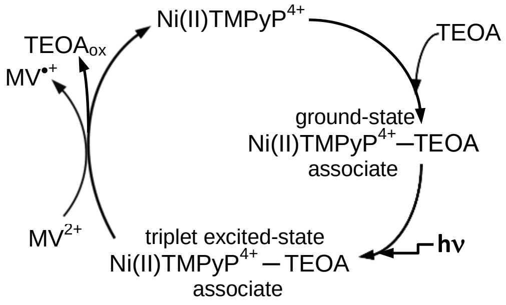
$$\mathrm{M(II)TMPyP^{4+} + MV^{2+} + h\nu \rightarrow M(III)TMPyP^{5+} + MV^{\bullet+}} \quad (4)$$

The corresponding photocatalytic cycle is summarized in Scheme 1 [30]. Due to the appreciable quantum yields for the formation of MV$^{\bullet+}$ at Soret-ban irradiation, these systems may be applicable for hydrogen generation from water.



**Scheme 1.** Photocatalytic cycle based on cationic manganese(III) or cobalt(III) porphyrins [30].

We also studied the photocatalytic behavior of Ni(II)TMPyP$^{4+}$ in the analogous sytem. In this case, however, deviating from the previous catalytic systems, no stable reduced metalloporphyrin was observed, although MV$^{\bullet+}$ radical cations were efficiently generated. Firstly, we suggested the formation of an instable nickel(I) porphyrin, which forwarded electron to methyl viologen in a thermal reaction [21]. Later on, further laser flash photolysis experiments, carried out in both Graz and Veszprém, indicated a quite different mechanism. Deviating from the case of the corresponding manganese(III) and cobalt(III) porphyrins, the triplet excited-state of the nickel(II) complex could not be quenched by the electron donor TEOA. Instead, it increased the lifetime of the excited state. However, the latter one could be quenched by the electron acceptor MV$^{2+}$, but only in the presence of TEOA. This observation indicated that Ni(II)TMPyP$^{4+}$ and TEOA formed an associate, the triplet excited state of which was oxidatively quenched by MV$^{2+}$, realizing a one-step electron transfer directly from the electron donor TEOA, without temporary reduction of the metalloporphyrin catalyst. Notably, the results of our steady-state absorption and emission experiments indicated an association of Ni(II)TMPyP$^{4+}$ and TEOA also in the ground state [20, 21, 34]. Scheme 2 summarizes the photocatalytic cycle functioning in this system.

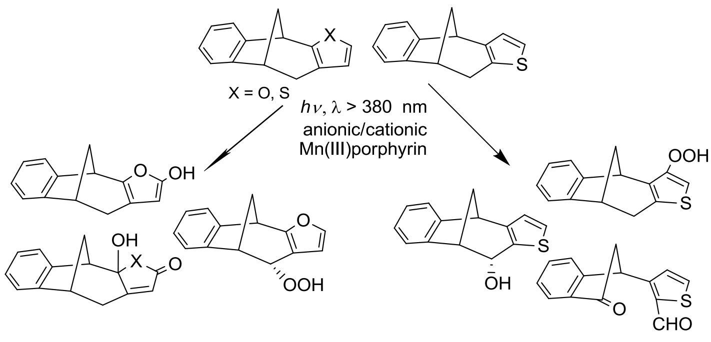


**Scheme 2.** Photocatalytic cycle based on Ni(II)TMPyP$^{4+}$ [34].

### *3.3. Photocatalytic oxygenation and oxidation with Mn(III) porphyrins*

#### *3.3.1. Photocatalytic oxygenation (preparative photocatalysis)*

Anionic and cationic manganese(III) porphyrins (Mn(III)TSPP$^{3-}$ and Mn(III)TMPyP$^{5+}$) have been applied as visible light-driven photocatalysts in preparative photochemistry. Photocatalytic oxygenations of furan and thiophene derivatives of benzobicyclo[3.2.1]-octadiene have been realized in this study carried out in a cooperation with Croatian organic chemists (Prof. I. Skorić and her colleagues). While the types of the end-products formed from the furan derivatives dramatically depended on the charge of the photocatalyst, the corresponding thiophene derivatives did not show such an effect (Scheme 3) [9].



**Scheme 3.** Oxygenation of bicyclic furan and tiophene derivatives by Mn(III) porphyrin based photocatalysis [9].

On the basis of our experiences with manganese(III) porphyrins mediated photocatalytic oxygenation of various bicyclic derivatives, in collaboration with our Croatian colleagues, we also studied such reactions with new bicyclic structures, which possess, for the first time in these processes, free double bond on the bicyclic ring (9-phenyl-, 9-(4-chlorophenyl)-, and 9-(4-methoxyphenyl)-tricyclo[6.3.1.0$^{2}$,$^{7}$]dodeca-2,4,6,10-tetraene, **1a**, **1b**, and **1c**, respectively). Visible-light driven photocatalysis of **1a** and **1b** led to the formation of the corresponding hydroperoxy derivatives **2** and **3**, respectively, in the presence of the anionic Mn(III) porphyrin, the cationic photocatalyst proved to be less efficient and less selective with **1a**. In the case of **1b**, also with the cationic porphyrin, the corresponding hydroperoxy derivative (**3**) was the main product at a shorter reaction time [41]. The formation of the hydroperoxy derivatives was attributed to the considerable π-stacking interaction between the phenyl ring and the porphyrin ligand in a very close proximity of the carbon atom to be functionalized in **1a** and **1b**. A dramatic change in the reactivity was observed for the methoxy derivative (**1c**). It gave only traces of identifiable products by using the anionic photocatalyst, while application of the cationic Mn(III) porphyrin resulted in a relatively efficient formation of an epoxy derivative due to the strong interaction between the electron-rich isolated double bond and the positively charged metalloporphyrin [41].

### *3.3.2. Photocatalytic oxidation (mineralization) of a pollutant*

Water-soluble manganese(III) porphyrins was also applied as photocatalysts for oxidative degradation of 4-*(*2-pyridylazo*)*-resorcinol (PAR) as a typical representative of the azo dyes, which cause considerable pollution of our waters. The intermediate and end-product analyses revealed that the photocatalytic oxidation mechanism in the presence of manganese(III) porphyrins strongly deviates from that observed with the corresponding free-bases, indicating the important role of the metal center in this process [10-12, 28].

## 4. Supplemental and summary

Comparing the content of the detailed final report to the original (planned ) program, it can be noticed that some experimental methods have not been applied, or have not provided the expected results. The previous cases occurred for technical reasons and shortage of time. Hence, although the suitable spectrograph has been purchased, the resonance Raman measurements could not be carried out due to the long-time failure of the laser system in Veszprém. This, however, could not hinder the development and study of photocatalytic systems. Fortunately, there have been appropriate lasers in the laboratory of our Austrian partner, thus, determinations of the triplet lifetimes and dynamic quenching experiments, originally planned in Veszprém, were realized in Graz. These measurements of substantial importance successfully compensated the (unexpected) inefficiency of the ESR experiments in Graz, which derived from the too wide and, thus, featureless signals. Hydrogen production experiments were also planned, at the end of the project, provided an optimum progress. These would have utilized our photocatalytic cycles generating methylviologen radicals, completed with an appropriate co-catalyst. Although these experiments could not be carried out due to the lack of time, the suitable reactor functioning with both LED and solar simulator (as light sources) has been developed and successfully tested with a heterogeneous photocatalytic system producing hydrogen. The equipment ensures the continuous monitoring of the amount of $H_2$ formed by a precise measurement of the mass of the liquid displaced by the gas evolved, using a PC for data storage. Right after the finalization of the detailed report, we noticed a very recent and hot publication (J. Catal., 2016, 344, 141), in which the $Ni(TEOA)_2^{2+}$ complex was utilized as an electron relay catalyst in a $H_2$ producing aqueous system applying fluorescein as sensitizer. This result indicates that our photocatalytic system based on a water-soluble Ni(II) porphyrin can be used for direct hydrogen generation if, instead of methylviologen, $Ni(TEOA)_2^{2+}$ is the electron relay. Such a system could be more homogeneous and stabile because both complexes (with TEOA and porphyrin ligands) have the same metal center (existing in excess in the solution).

Summarizing our achievements, on the basis of the results delivered by the photophysical and photochemical investigation of water-soluble metalloporphyrins, utilizing the kinetically inert complexes, visible-light-driven photocatalytic systems could be realized, which can be applied for hydrogen generation from water as well as functionalization (oxygenation) of special organic compounds. The latter type of reactions can also be used, under appropriate conditions (both in homogeneous systems and immobilized on solid supports), for oxidative degradation of organic pollutants. Our results have so far been published in 8 papers in internationally respected journals (this number exceeds the planned one) – their accepted manuscripts have been uploaded in the repository of the library of the Hungarian Academy of Sciences (the corresponding URLs are given at the references), however, the final articles are also accessible through the EISZ system, appearing in Elsevier journals. As the results summarized in this report suggest, at least 4 further publications are in preparation, regarding partly the photoinduced properties of the lanthanide(III) porphyrins, partly the photochemical behavior of the kinetically inert water-soluble metalloporphyrins. Besides, Muhammad Imran compiled a PhD dissertation from his results achieved in the frame of this project, moreover, he successfully defended his thesis well before the end of the project. The results of this project serve as bases for two additional PhD dissertation to be compiled by Melinda Anna Fodor and Melitta Patrícia Kiss, not to mention numerous diploma works, scientific compositions and conference presentations of our students. Thus, the realization of this project successfully contributed to the development of several young, talented researchers.

## References

| Sorszám | Közleményjegyzék | Dokumentum típusa | Impakt faktor | NKFI támogatás feltüntetve? | Támogató szervezetek |
|---|---|---|---|---|---|
| 1. | Valicsek Z; Horváth O: ***Formation of water-soluble cadmium porphyrin complexes: the effects of predistortion and the axial ligand***, Book of Abstracts, Debrecen Colloquium on Inorganic Reaction Mechanisms 2013, Debrecen, June 11-15, L24, 2013 | absztrakt | - | igen | TÁMOP (Hungarian Government, European Union, European Social Fund) |
| 2. | Valicsek Z; Kiss MP; Eller G; Szentgyörgyi C; Horváth O: ***Oligomerization of water-soluble lanthanide porphyrins***, Book of Abstracts,1st Symposium on Weak Molecular Interactions, Pécs, March 5-6, p. 70, 2013 | absztrakt | - | igen | TÁMOP (Hungarian Government, European Union, European Social Fund) |
| 3. | Valicsek Z; Patonay K; Horváth O: ***Formation of water-soluble bismuth(III) porphyrins: the role of the ligand's charge***, Book of Abstracts, Debrecen Colloquium on Inorganic Reaction Mechanisms 2013, Debrecen, June 11-15, P21, 2013 | absztrakt | - | igen | TÁMOP (Hungarian Government, European Union, European Social Fund) |
| 4. | Fodor MA; Horváth O; Fodor L; Grampp G; Wankmüller A: ***Photophysical and photocatalytic behavior of cobalt(III) 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin***, Inorganic Chemistry Communications 50, 110-112, 2014<br>URL: http://real.mtak.hu/id/eprint/41729 | folyóiratcikk | 1.777 | igen | TÁMOP, OMAA |
| 5. | Horváth, O; Imran M; Valicsek Z: ***Photophysical and photochemical investigation of water-soluble, anionic neodymium(III) porphyrins***, 20th International Conference on Photochemical Conversion of Solar Energy (IPS-20), Abstract Book, July 27 – August 1, Berlin, Germany, PoT 75, p. 157, 2014 | absztrakt | - | igen | TÁMOP, OMAA |
| 6. | Kiss MP; Imran M; Szentgyörgyi C; Valicsek Z*; Horváth O: ***Peculiarities of the reactions between early lanthanide(III) ions and an anionic porphyrin***, Inorganic Chemistry Communications 48, 22–25, 2014<br>URL: http://real.mtak.hu/id/eprint/41730 | folyóiratcikk | 1.777 | igen | TÁMOP, OMAA |
| 7. | Valicsek Z; Horváth O: ***Theoretical study on the geometrical and electronic structure of out-of-plane metalloporphyrins***, 8th International Conference on Porphyrins and Phthalocyanines, Abstract Book, Istanbul, Turkey, June 22-27, COPF-4-5, p. 395, 2014 | absztrakt | - | igen | TÁMOP |
| 8. | Valicsek Z; Horváth O: ***Distortion as the real origin of hyper-porphyrin spectra***, 8th International Conference on Porphyrins and Phthalocyanines, Abstract Book, Istanbul, Turkey, June 22-27, S46-015, p. 739, 2014 | absztrakt | - | igen | TÁMOP |
| 9. | Vuk D; Kikaš I; Molčanov K; Horváth O;* Škorić I*: ***Functionalization of the benzobicyclo[3.2.1]octadiene skeleton via photocatalytic oxygenation of thiophene and furan derivatives***, Journal of Molecular Structure 1063, 83-91, 2014<br>URL: http://real.mtak.hu/id/eprint/41734 | folyóiratcikk | 1.599 | igen | Croatian Ministry of Science, Education and Sports, TÁMOP (Hungarian Government, European Union) |

| | | | | | |
|---|---|---|---|---|---|
| 10. | Fodor MA; Horváth O; Fodor L; Horváth K; Szabó P: ***Vízoldható mangán(III)-porfirinek fotofizikai tulajdonságia és fotokatalitikus alkalmazása***, MKE 2. Nemzeti Konferencia, Program és előadás-összefoglalók, Hajdúszoboszló, augusztus 31.- szeptember 2. FK-P-3, 165. o., 2015 | absztrakt | - | igen | OMAA |
| 11. | Fodor MA; Horváth O; Szabó P; Horváth K: ***Photophysical and photocatalytic properties of water-soluble free-base and manganese(III) porphyrins***, The 21st International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Abstract Book, Kraków, July 5-9, PP028, p. 119, 2015 | absztrakt | - | igen | OMAA, OTKA |
| 12. | Fodor MA; Major MM; Horváth O; Grampp G; Wankmüller A: ***Water-soluble free-base and metalloporphyrins utilized in various photocatalytic systems***, 16th Blue Danube Symposium on Heterocyclic Chemistry, Abstract Book, Balatonalmádi, Hungary, June 14-17, P18, p. 74, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 13. | Imran M; Jurecska T; Kiss MP; Valicsek Zs; Horváth O: ***Formation, photophysics and photochemistry of water-soluble samarium(III) porphyrins***, 16th Blue Danube Symposium on Heterocyclic Chemistry, Abstract Book, Balatonalmádi, Hungary, June 14-17, P27, p. 83, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 14. | Imran M; Szentgyörgyi C; Eller G; Valicsek Z; Horváth O: ***Peculiar photoinduced properties of water-soluble, early lanthanide(III) porphyrins***, Inorganic Chemistry Communications 52, 60-63, 2015<br>URL: http://real.mtak.hu/id/eprint/41731 | folyóiratcikk | 1.762 | igen | TÁMOP, OMAA |
| 15. | Imran M; Valicsek Z; Horváth O: ***Photophysical and photochemical investigation of water-soluble porphyrin complexes of early lanthanide(III) ions***, 16th Blue Danube Symposium on Heterocyclic Chemistry, Abstract Book, Balatonalmádi, Hungary, June 14-17, P26, p. 82, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 16. | Imran M; Valicsek Z; Horváth O: ***Photophysical and photochemical investigation of water-soluble, anionic dysprosium(III) porphyrins***, 21st International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Abstarct Book, Krakow, Poland, July 5-9, PP41, p. 132, 2015 | absztrakt | - | igen | OMAA |
| 17. | Kiss MP; Imran M; Valicsek Z; Horváth O: ***Vízoldható neodímium(III)-porfirinek képződésének spektrofotometriai és reakciókinetikai vizsgálata***, MKE 2. Nemzeti Konferencia, Progrem és előadás-összefoglalók, Hajdúszoboszló, augusztus 31 – szeptember 2. A-O-16, 92. o., 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 18. | Kiss MP; Patonay K; Valicsek Z; Horváth O: ***Transformation reactions of p-type hyper-porphyrins in water***, 16th Blue Danube Symposium on Heterocyclic Chemistry, Abstract Book, Balatonalmádi, Hungary, June 14-17, P32, p. 88, 2015 | absztrakt | - | igen | TÁMOP, OMAA |

| | | | | | |
|---|---|---|---|---|---|
| 19. | Kiss MP; Valicsek Z; Horváth O: ***Kinetic investigation of the formation of samarium(III) and neodymium(III) porphyrins***, 16th Blue Danube Symposium on Heterocyclic Chemistry, Abstract Book, Balatonalmádi, Hungary, June 14-17, P31, p. 87, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 20. | Major MM: ***Fotokatalitikus nikkel-porfirin rendszer átfogó jellemzése***, TDK dolgozat, Pannon Egyetem, Veszprém, 2015 | szerkesztett mű | - | igen | TÁMOP |
| 21. | Major MM; Horváth O; Fodor MA; Valicsek Z; Fodor L: ***Kationos nikkel(II)-porfirin fotofizikai és fotokémiai tulajdonságainak vizsgálata***, MKE 2. Nemzeti Konferencia, Program és előadás-összefoglalók, Hajdúszoboszló, augusztus 31 – szeptember 2. FK-O-24, 46. o, 2015 | absztrakt | - | nem | |
| 22. | Valicsek Z; Horváth O: ***Study about the triplet-1 state of anionic metalloporphyrins***, 21st International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Abstract Book, Krakow, Poland, July 5-9, PP135, p. 226, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 23. | Valicsek Z; Horváth O: ***A fémion helyzetének hatása a porfirin-komplexek szingulett-1 fluoreszcenciájára***, MKE 2. Nemzeti Konferencia, Program és előadás-összefoglalók, Hajdúszoboszló, augusztus 31 – szeptember 2. A-P-7, 200. o., 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 24. | Valicsek Z; Imran M; Kiss MP; Szentgyörgyi C; Eller G; Jurecska T; Törőcsik R; Horváth O: ***Vízoldható, korai lantanoida(III)-porfirin komplexek fotoindukált tulajdonságainak vizsgálata***, MKE 2. Nemzeti Konferencia, Program és előadás-összefoglalók, Hajdúszoboszló, augusztus 31 – szeptember 2. FK-O-23, 45. o., 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 25. | Valicsek Z; Kiss MP; Imran M; Horváth O: ***Peculiarities of the reactions between early lanthanide(III) ions and an anionic porphyrin***, 9th International Conference on Chemical Kinetics, Abstract Book, Ghent, Belgium, June 28 – July 2, O79, p. 281, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 26. | Valicsek Z; Kiss MP; Imran M; Szentgyörgyi C; Eller G; Jurecska T; Törőcsik R; Horváth O: ***Vízoldható, lantanoida(III)-porfirin komplexek képződésének és fotoindukált tulajdonságainak érdekességei***, 49. Komplexkémiai Kollokvium, Előadás-összefoglalók, Siófok, május 26-28. E9, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 27. | Valicsek Z; Patonay K; Horváth O: ***The role of water and the ligand's charge in the formation kinetics of bismuth(III) porphyrins***, 9th International Conference on Chemical Kinetics, Abstract Book, Ghent, Belgium, June 28 – July 2, P50, p. 499, 2015 | absztrakt | - | igen | TÁMOP, OMAA |
| 28. | Fodor MA; Horváth O; Szabó P; Horváth K: ***Free-base and manganese(III) alkyl-pyridinium porphyrins in homogeneous and heterogeneous photooxidative systems***, Central European Conference on Photochemistry, Abstract Book, Bad Hofgastein, Austria, February 14-18, P21, p. 66, 2016 | absztrakt | - | igen | OTKA, OMAA |

| | | | | | |
|---|---|---|---|---|---|
| 29. | Fodor MA; Horváth O; Fodor L; Vazdar K; Grampp G; Wankmüller A: ***Photophysical and photochemical properties of manganese complexes with cationic porphyrin ligands: effects of alkyl substituents and micellar environment***, Journal of Photochemistry and Photobiology A: Chemistry, 328, 233-239, 2016<br>URL: http://real.mtak.hu/id/eprint/41733 | folyóiratcikk | 2.495 | igen | OTKA, OMAA |
| 30. | Horváth O; Valicsek Z; Fodor MA; Major MM; Imran M; Grampp G; Wankmüller A: ***Visible light-driven photophysics and photochemistry of water-soluble metalloporphyrins***, Coordination Chemistry Reviews, 325, 59-66, 2016<br>URL: http://real.mtak.hu/id/eprint/41722 | folyóiratcikk | 12.239 | igen | OTKA, OMAA |
| 31. | Imran M: ***Formation, photophysics and photochemistry of water-soluble lanthanide(III) porphyrins***, PhD Dissertation, University of Pannonia, 2016 | disszertáció | - | igen | OMAA |
| 32. | Kiss MP; Imran M; Valicsek Z; Horváth O: ***Spectrophotometric investigation of early lanthanide(III) porphyrins for potential biomedical applications***, XV. Italian-Hungarian Symposium on Spectrochemistry; Pharmacological research and analytical approaches, Abstract Book, Pisa, Italy, June 12-16, p. 160-161, 2016 | absztrakt | - | igen | OMAA |
| 33. | Kiss MP; Valicsek Z; Horváth O: ***Korai lantanoida-porfirin komplexek szerkezetének és képződésének érdekességei***, 50. Komplexkémiai Kollokvium, Kiadvány, Balatonvilágos, május 30 – június 1., E20, 2016 | absztrakt | - | igen | OTKA, TÁMOP, OMAA |
| 34. | Major MM; Horváth O; Fodor MA; Fodor L; Valicsek Z; Grampp G; Wankmüller A: ***Photophysical and photocatalytic behavior of nickel(II) 5,10,15,20-tetrakis(1-methylpyridinium-4- yl)porphyrin***, Inorganic Chemistry Communications, 73, 1-3, 2016<br>URL: http://real.mtak.hu/id/eprint/41732 | folyóiratcikk | 1.762 | igen | OMAA |
| 35. | Valicsek M; Imran M; Horváth O: ***Photoinduced properties of water-soluble porphyrin complexes of early lanthanide(III) ions***, Central European Conference on Photochemistry, Abstract Book, Bad Hofgastein, Austria, February 14-18, P16, p. 61, 2016 | absztrakt | - | igen | TÁMOP, OMAA |
| 36. | Valicsek Z; Kiss MP; Kovács M; Horváth O: ***Spectrophotometric study about the acetato- and fluoro-complexes of early lanthanide(III) ions***, Central European Conference on Photochemistry, Abstract Book, Bad Hofgastein, Austria, February 14-18, P20, p. 65, 2016 | absztrakt | - | igen | TÁMOP, OMAA |
| 37. | Valicsek Z; Harrach G; Sebestyén AK; Németh B; Horváth O: ***Formation and photoinduced properties of silver porphyrins as promising PDT reagents***, XV. Italian-Hungarian Symposium on Spectrochemistry; Pharmacological research and analytical approaches, Abstract Book, Pisa, Italy, June 12-16, p. 143-144, 2016 | absztrakt | - | igen | OMAA |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 38. | Valicsek Z; Horváth O: ***Possible application of out-of-plane metalloporphyrins in medical sciences***, XV. Italian-Hungarian Symposium on Spectrochemistry; Pharmacological research and analytical approaches, Abstract Book, Pisa, Italy, June 12-16, OS6/2, p. 103-1044, 2016 | absztrakt | - | igen | OMAA |
| 39. | Valicsek Z; Imran M; Horváth O: ***Photophysical and photochemical investigation of water-soluble, anionic erbium(III) porphyrins***, Central European Conference on Photochemistry, Abstract Book, Bad Hofgastein, Austria, February 14-18, P18, p. 63, 2016 | absztrakt | - | igen | TÁMOP, OMAA |
| 40. | Valicsek Z; Sebestyén AK; Németh B; Harrach G; Horváth O: ***Az ionerősség és az axiális ligandum hatása a vízoldható ezüst-porfirin komplexek képződésére és oligomerizációjára***, 50. Komplexkémiai Kollokvium, Kiadvány, Balatonvilágos, május 30 – június 1., E26, 2016 | absztrakt | - | igen | TÁMOP, OMAA |
| 41. | Vuk D; Horváth O; Marinić Ž; Škorić I: ***Functionalization of the benzobicyclo[3.2.1]octadiene skeleton possessing one isolated double bond via photocatalytic oxygenation***, Journal of Molecular Structure 1107, 70-76, 2016<br>URL: http://real.mtak.hu/id/eprint/41735 | folyóiratcikk | 1.602 | igen | University of Zagreb |