

PHOTOCATALYTIC ACTIVITY OF IMMOBILIZED METALLO-TETRAPYRROLE COMPLEXES IN HYDROGEN PEROXIDE MEDIA

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Abstract – Tetrapyrrolic macrocyclic compounds and their metal complexes are an important class of coordination compounds widely applied for development of materials with a broad range of functional properties, for example, highly sensitive redox systems for monitoring potentially toxic objects in solutions, or biocidal agents possessing an activity against pathogenic microorganisms, etc. The paper presents results of studying photocatalytic activity of silica immobilized metal-tetrapyrrole (i.e. tetraphenylporphyrin, phthalocyanine, and chlorophyll) complexes in hydrogen peroxide decomposition reaction. A linear correlation has been established between the photocatalytic activity of a number of *p*-, *d*⁰-, and *d*¹⁰-metal complexes of the studied macrocycles in the decomposition of hydrogen peroxide and their ability to generate a photopotential. These photophysical and photochemical characteristics are interrelated and can be used for evaluation and prediction of each other. In addition, the examined systems can be considered as a special treatment tool for destroying hazardous chemical compounds or harmful biological structures.

Keywords: photocatalytic activity, metal complexes, tetrapyrroles, hydrogen peroxide.

ФОТОКАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ ИММОБИЛИЗОВАННЫХ МЕТАЛЛОКОМПЛЕКСОВ ТЕТРАПИРРОЛОВ В СРЕДАХ, СОДЕРЖАЩИХ ПЕРОКСИД ВОДОРОДА

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Аннотация – Тетрапиррольные макроциклические соединения и их металлокомплексы являются важным классом координационных соединений, используемых для разработки материалов с широким спектром функциональных свойств, например, высокочувствительных сенсорных редокс-систем для мониторинга потенциально опасных объектов в растворах, или биоцидных материалов, активных в отношении патогенных микроорганизмов и др. В статье представлены результаты исследования фотокаталитической активности иммобилизованных на силикагелевой подложке металлокомплексов тетрафенилпорфирина, фталоцианина и хлорофилла в процессе разложения пероксида водорода. Установлена линейная корреляция между фотокаталитической активностью ряда *p*-, *d*⁰- и *d*¹⁰-металлокомплексов изученных макроциклов в разложении пероксида водорода и их способностью генерировать фотопотенциал. Эти свойства взаимосвязаны и могут быть использованы для оценки и предсказания друг друга. Кроме того, изученные системы могут рассматриваться как бинарные агенты для деструкции опасных химических веществ и биологических объектов.

Ключевые слова: фотокаталитическая активность, металлокомплексы, тетрапирролы, пероксид водорода.

INTRODUCTION

It is a common knowledge that a wide variety of vitally important biological and human medicine related processes proceed with the participation of tetrapyrrole molecules [1–4]. Photosensitive redox reactions involving metal-tetrapyrrole complexes and hydrogen peroxide are of special interest. Thus, photosynthesis photocatalyzed by chlorophyll, involves a step of donor electron interaction with carbon dioxide leading to the formation of energy-rich organic compounds along with oxygen generation [5]. Currently, it is anticipated that water molecules are oxidized to O₂, while hydrogen peroxide is an intermediate product of water oxidation reaction [6]. It is noteworthy that H₂O₂ oxidation reaction is less endothermic than oxidation of water molecule [7]. Photodynamic therapy of cancer and other pathologies applies processes where metal-tetrapyrrole complexes produce singlet oxygen [8] and reactive oxygen species, among them stable hydrogen peroxide molecule [9]. Consequently, *in vivo* pharmacologically active tetrapyrroles can be able to interact with H₂O₂ likewise. Decomposition of hydrogen peroxide in aqueous and salt solutions can yield reactive oxygen species [10]. Therefore, this process is attractive as a potential biocidal treatment tool against a number of harmful cells and bacteria.

Creating artificial photochemical active systems can also be useful for studying coordination and photochemical interaction of metal complexes of tetrapyrroles and reactive oxygen species. It is known that certain metal complexes with tetrapyrrolic macrocycles are effective catalysts of H₂O₂ decomposition in dark [11]. In this work, a photocatalytic activity of metal complexes of tetraphenylporphyrin (TPP) and phthalocyanine (Pc) in the process of H₂O₂ decomposition has been studied. Special attention is paid to examining dependence between photocatalytic activity of metal tetrapyrroles and their photovoltaic properties, which had been studied previously [12, 13].

EXPERIMENTAL

Metal complexes of Pc were synthesized and purified in Organic Intermediates and Dyes Institute (Moscow, Russia). Metal complexes of TPP were prepared and characterized in Ivanovo State University of Chemistry and Technology (Ivanovo, Russia). Chlorophyll *a* (MgChl) was purchased from Acros Organics (Belgium). Identification and concentration measurements of dyes were performed by UV-Vis spectroscopy in quartz cells (1 cm) on spectrophotometer DR/4000V (HACH-Lange, USA). Hydrogen peroxide and sodium bicarbonate (both laboratory reagent grade, Reakhim, Russia) were used without additional purification.

Immobilization of tetrapyrrole metal complexes on silica L 40/100 (Chemapol) was carried out by adding silica (1 g) to the solutions of MgChl in acetone, complexes of tetraphenylporphyrin in chloroform, and metal phthalocyanines in DMF. Then, the suspensions were kept in the darkness until solvent evaporation. Samples were repeatedly washed out with distilled water and dried to a constant weight in vacuum-exicator over CaCl₂.

Kinetic experiments were performed after introducing 10 ml of bicarbonate buffers (pH 8.5) containing 0.2 M H₂O₂ and 200 mg of silica together with one of the supported metal complexes in a photochemical reactor. The obtained suspensions

were irradiated by visible light using a halogen lamp (150 W) with condenser and a system of lenses, with constant stirring. All experiments were conducted at 20°C. Concentration of H₂O₂ was determined by titration in 0.2 M H₂SO₄ medium using 0.01 N KMnO₄ solution.

Quantum chemical calculations of H₂O₂ complexes were performed using 6-31G** procedure in the DFT-approximation with PBE1PBE exchange-correlation functional by Gaussian 03 program [14].

RESULTS AND DISCUSSION

Photocatalytic activity in the H₂O₂ decomposition reaction was revealed for both silica immobilized metal complexes of chlorophyll, and silica immobilized metal complexes of tetraphenylporphyrin and phthalocyanine. Kinetic parameters of photocatalytic activities are presented in the table.

Table. Kinetic parameters of photocatalytic activity of silica immobilized metal complexes of tetrapyrroles in H₂O₂ decomposition reaction (pH 8.5)^a

Metal complex	v_{im}^d , $\mu\text{mol}\cdot\text{g}^{-1}$	N/V , $\text{mol}\cdot\text{ml}^{-1}$	$k_{ob}\cdot 10^5$, s^{-1}	k_{ef} , $\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
MgChl	52	1.03	6.59	0.064
CrTPP	66	1.32	2.27	0.018
CuTPP	56	1.11	2.27	0.020
ZnTPP	55	1.10	4.35	0.040
CdTPP	52	1.03	0.60	0.006
SnTPP ^b	52	1.03	1.11	0.011
FeTPP ^b	21	0.41	18.0	0.439
MgTPP	49	0.98	5.0	0.051
YbTPP ^c	57	1.14	1.82	0.016
ZnPc	55	1.10	6.27	0.057
AlPc ^b	45	0.90	3.96	0.044
GaPc ^b	45	0.90	4.14	0.046
InPc ^b	45	0.90	5.49	0.061
MnPc	55	1.10	54.5	0.495
FePc	48	0.96	39.4	0.410
SiPc ^b	45	0.90	2.52	0.028
SnPc	45	0.90	2.88	0.032
VOpc	45	0.90	2.34	0.026

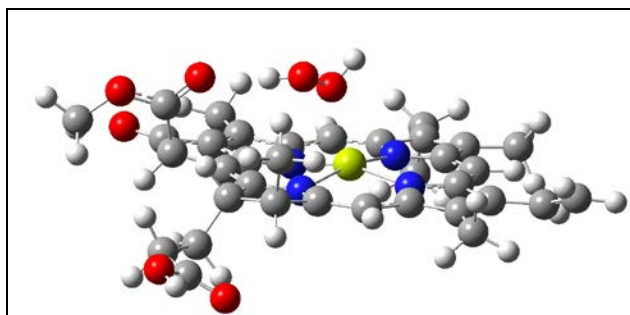
^a k_{ef} is the effective rate constant, N is the number of moles of (photo)catalyst, V is the volume of the reaction solution, k_{ob} is the observed rate constant which can be expressed as $k_{ef}(N/V)^n$ given that the rate of H₂O₂ decomposition $w = k_{ef}(N/V)^n [H_2O_2]^m$, where N/V , n and m are equal to 1 and do not change. The catalyst turnover number (TN) corresponds to the number of moles H₂O₂ per one mole of (photo)catalyst per hour. ^bThe coordination sphere of the metal (element) ion also includes one (for Fe^{III}, Al^{III}, Ga^{III}, In^{III}) or two (for Sn^{IV}, Si^{IV}) chloride anions. ^cYtterbium ion additionally comprises one molecule of acetylacetonate as extraligand on the third valence. ^dAmount of metal complex deposited per 1 g of silica.

Decomposition of H_2O_2 caused by visible light irradiation can be observed for all metal complexes studied. Tetrapyrrolic complexes with Fe^{III} , Mn^{II} , Cr^{II} , and Cu^{III} are active in H_2O_2 decomposition in the darkness. Catalytic activity of these tetrapyrrolic non-transition metal complexes does not change under the visible light irradiation. Complexes of TPP with magnesium, zinc, chlorophyll, as well as Pc complexes with zinc and non-transition metals of the IIIA group are found to be the most active in the process of H_2O_2 decomposition. It should be noted that the observed surface amount of metal complexes was much higher than a monolayer level quantity. Thus, the experimental kinetic data describe the cooperative activity of aggregates of metal-tetrapyrrole complexes immobilized on silica particles. It is important to note that aggregation of tetrapyrroles does not practically cause a decrease in coordination of hydrogen peroxide molecules and, consequently, does not affect the rate of H_2O_2 decomposition.

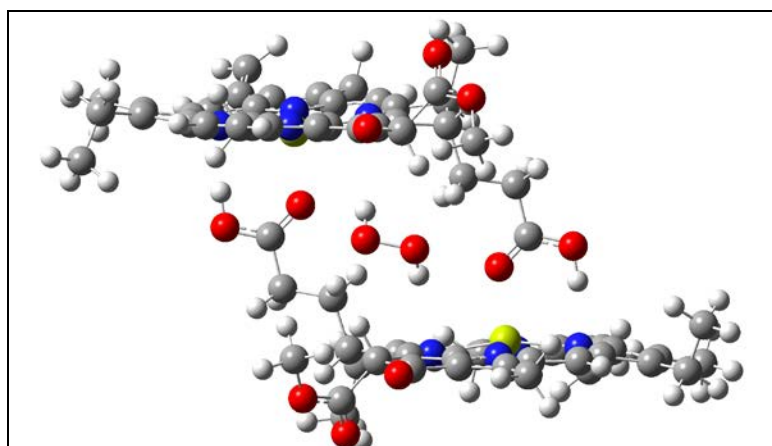
Indeed, quantum chemical calculations show that monomeric Chl, dimer, and trimer of Chl molecule model efficiently coordinate H_2O_2 molecule. Optimized structures of monomer ($\text{Chl}\dots\text{H}_2\text{O}_2$), dimer ($\text{Chl}\dots\text{H}_2\text{O}_2\dots\text{Chl}$), and trimer ($\text{Chl}\dots\text{H}_2\text{O}_2\dots\text{Chl}\dots\text{Chl}$) complexes of chlorophyll model with H_2O_2 are shown in Fig. 1. The calculated binding energy values for the complexes of chlorophyll monomer, dimer, and trimer with the hydrogen peroxide molecule are 72, 69, and 52 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. In addition, quantum chemical calculations demonstrate that although there can exist a plenty of local energy minima for binary systems of metal complexes and hydrogen peroxide, an arrangement of these small molecules in the vicinity of the metal ions of the complex is presumably the most energetically favourable position.

Earlier, a series of experiments studying the effect of Becquerel on photoelectrodes modified with various metal complexes of tetraphenylporphyrins and phthalocyanines was carried out to determine their activity in generating photopotential [12, 13]. A comparative analysis made in this work allowed to put forward a hypothesis of linear correlation between photoelectrochemical and photocatalytic properties of p -, d^0 -, and d^{10} -metal complexes of TPP and Pc, which was confirmed, as can be seen in Fig. 2.

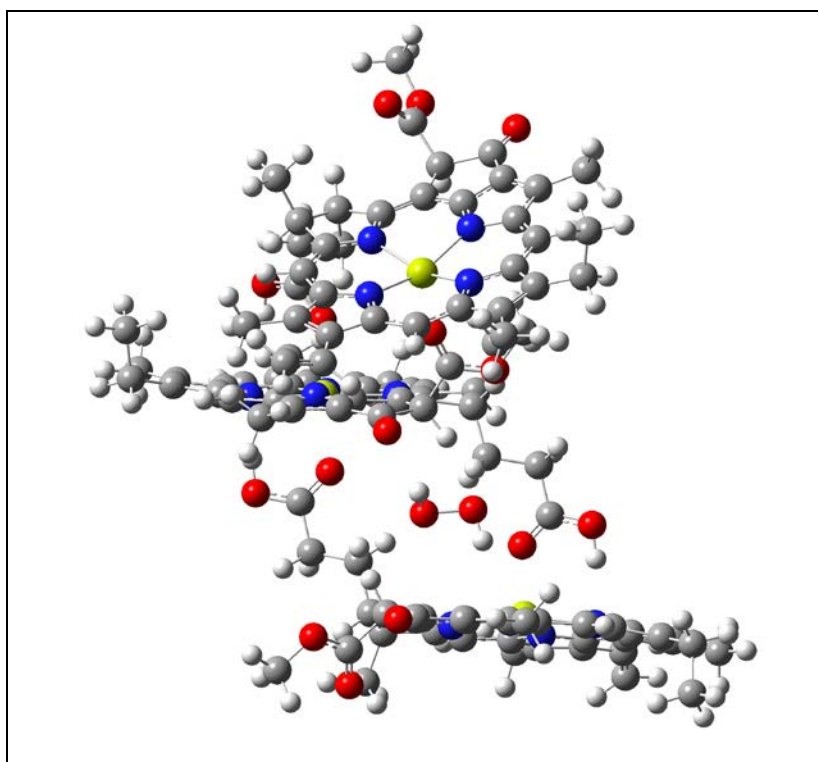
Meanwhile, no similar correlation was observed for the tetrapyrrolic complexes with other transition metals. Thus, the similarity between photovoltaic and photocatalytic properties of metal porphyrins exists only in the case of d^0 - and d^{10} -metal complexes of porphyrins and phthalocyanines which are capable to generate long-lived triplet excited states with high quantum yield [15]. Consequently, these characteristic properties are interrelated and can be used for evaluation and prediction of each other. For example, a difference between rates of dark and light-induced decomposition of H_2O_2 could be a key evaluation parameter in developing molecular devices converting solar energy to chemical generation of reactive oxygen species. Ultimately, the studied systems can be considered as binary agents applied for destroying hazardous chemical compounds or harmful biological structures.



a



b



c

Fig. 1. The most energetically favourable structures of three types of coordination complexes: Chl...H₂O₂ (*a*), Chl...H₂O₂...Chl (*b*), and Chl...H₂O₂...Chl...Chl (*c*) found according to quantum chemical calculations.

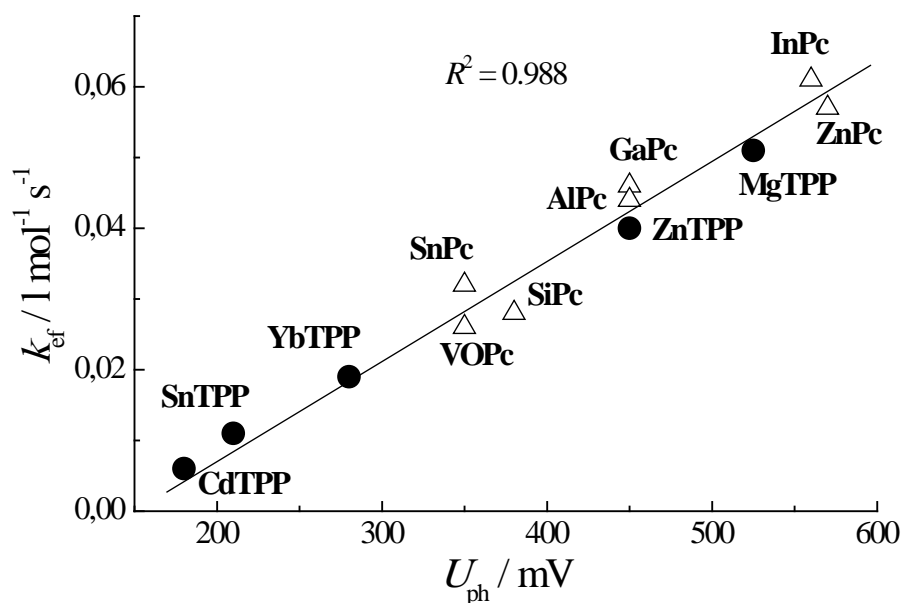


Fig. 2. Linear correlation between photocatalytic activity of metal complexes of tetraphenylporphyrin (circles) and phthalocyanines (triangles) and their photopotential generation ability.

CONCLUSION

In summary, a series of artificial chemically and photochemically active systems with hydrogen peroxide participation were prepared. The silica immobilized metal complexes of chlorophyll, porphyrins, and phthalocyanines were found to exhibit a photocatalytic activity in the reaction of H_2O_2 decomposition. In general, a linear correlation was revealed for the first time between the photovoltaic and photocatalytic properties of d^0 - and d^{10} -metal complexes of tetrapyrroles. Eventually, decomposition of hydrogen peroxide photocatalyzed by tetrapyrrolic metal complexes can be used for generating reactive oxygen species. On the one hand, the obtained data are important for the development of processes converting solar energy into the synthesis of reactive intermediates. On the other hand, the results are of interest for studying intracellular biochemical processes involving pharmacologically active metal complexes.

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