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CATALYSIS

Production of Hydrogen in a Ternary Photocatalytic System Based on Water-Soluble Palladium(II) Porphyrin

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Abstract—A new photocatalyst, water-soluble palladium(II) complex with *meso*-tetrakis(4-*N,N,N*-trimethylammoniophenyl)porphyrin, was suggested as a component of a photocatalytic system for water reduction to hydrogen. In the ternary system palladium(II) porphyrin–methyl viologen–triethanolamine, the metalloporphyrin phosphorescence is quenched only by methyl viologen by the mechanism of oxidative electron transfer. The reduced form of methyl viologen is accumulated in the solution, and hydrogen is evolved in the presence of colloidal platinum. The highest quantum yield of the formation of the reduced methyl viologen form and hydrogen in the system reaches 0.4. After 1-h irradiation of the system, 125 mol of hydrogen is evolved per mole of metalloporphyrin.

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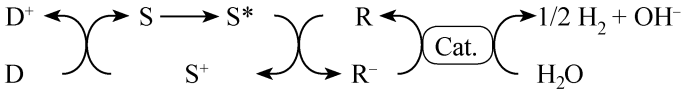
Reduction of fossil fuel resources requires search for alternative energy sources. It is particularly topical to use the solar radiation energy in photocatalytic processes for production of molecular hydrogen, a promising environmentally clean fuel. Resources of water, the main source of hydrogen, are practically inexhaustible on the Earth.

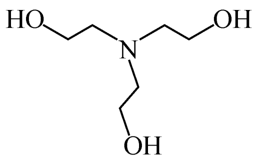
Various classes of photocatalysts that can be used in systems for hydrogen production from water have been studied by now. These include semiconductor materials [1] and molecular compounds such as organic dyes, metal polypyridine complxes, porphyrins, and metalloporphyrins [2–4].

Definite requirements are imposed upon a molecular photocatalyst: It should efficiently absorb light in the visible range, have a long-lived excited state in which it should be capable of reversible electron transfer, and be photochemically stable. Water-soluble metalloporphyrins meet all these requirements. Complexes of water-soluble porphyrins with zinc and some *p* metals are the most studied as photocatalysts [5–8]. However, of particular interest are metalloporphyrins with the long-lived triplet state whose lifetime is sufficient for the participation of these compounds in bimolecular photochemical redox processes. Such compounds include complexes of water-soluble porphyrins with platinum group metals. For these compounds, the probability of the population of the lowest triplet excited state is close to unity [9]. Bimolecular processes of energy transfer from the triplet excited state of such compounds to molecular oxygen, leading to the generation of singlet oxygen, were studied previously [10, 11].

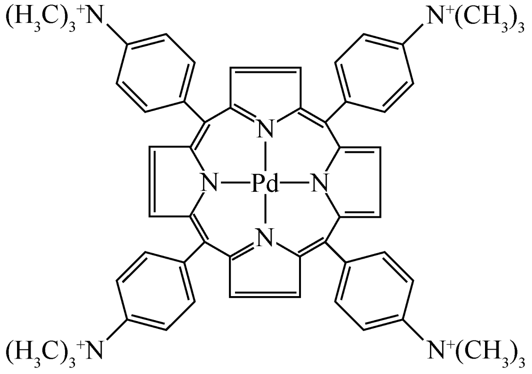
The aim of this study is to develop a model system for water reduction, acting in accordance with the scheme



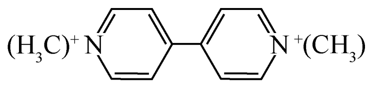
We used triethanolamine (TEOA) as irreversibly decomposing electron donor (D), methyl viologen (MV^{2+}) as an electron mediator (R), colloidal platinum as a heterogeneous catalyst of hydrogen evolution (Cat.), and, for the first time, the water-soluble complex of palladium(II) with *meso*-tetrakis(4-*N,N,N*-trimethylammoniophenyl)porphyrin, $[Pd(TTMAPP)](NO_3)_4$, as a photocatalyst (S):



D
TEOA



S
$[Pd(TTMAPP)]^{4+}$



R
MV^{2+}

We studied the quenching of the phosphorescence of the water-soluble palladium(II) porphyrin with methyl viologen and triethanolamine and the methyl viologen photoreduction and hydrogen evolution in the ternary system palladium(II) porphyrin–methyl viologen–triethanolamine.

EXPERIMENTAL

All the chemicals used in the study were purchased from Aldrich and Lenreaktiv and were used without additional purification. Solutions were made up in in ultrapure water prepared in a Simplicity® water treatment installation (Millipore S.A.S.).

Synthesis and purification of the water-soluble palladium(II) porphyrin were performed by the procedure described previously [12]. The purity of the metalloporphyrin was confirmed by thin-layer chromatography, elemental analysis, NMR spectra, and electronic absorption and phosphorescence spectra.

^1H NMR spectrum (DMSO-*D6*), δ, ppm: 8.77 s [8H (pyrrole)]; 8.42 d [8H (*o*-phenyl), $J_{o-m} = 9.16$ Hz]; 8.38 d [8H (*m*-phenyl), $J_{o-m} = 9.16$ Hz]; 3.87 s [36H (methyl)].

Absorption spectrum in H_2O, λ, nm ($\varepsilon \times 10^{-3}$, L mol^{-1} cm^{-1}): 410 (160), 521 (15.3), 552 (3.0). Phosphorescence spectrum and lifetime in H_2O, λ, nm ($\tau_0 \times 10^6$, s): 670 (290).

The NMR spectra were recorded with a Jeol ECX400A spectrometer, and the absorption spectra, with a T80+ spectrophotometer (PG Instruments). Luminescence studies were performed in an installation assembled on the basis of KSBU-1 spectroscopic and computational complex. An LGI-21 pulse nitrogen laser ($\lambda_{exc} = 337$ nm, $\tau_{pulse} = 10$ ns) was used as an excitation source.

Phosphorescence quenching experiments and photochemical studies were performed in a quartz cell ($l = 1$ cm) with a stopcock. The solutions were deaerated immediately before the experiment by passing high-purity argon for 15 min.

The oxidation and reduction potentials of the water-soluble palladium(II) porphyrin were determined by cyclic voltammetry with a P-8S potentiostat (Elins) in an aqueous solution (0.1 M Na_2SO_4) using a three-electrode electrochemical cell. Glassy carbon, platinum, and silver chloride electrodes (Cypress Systems) were used as working, auxiliary, and reference electrodes, respectively. All the potentials are given vs. standard hydrogen electrode.

A DRSh-250 mercury lamp with a set of glass color filters for cutting out the light with a wavelength of 546 nm and with an additional water filter for absorbing infrared radiation was used as an excitation source in photochemical studies. The luminous flux intensity determined with a ferrioxalate actinometer was 3.1 × 10^{-9} mol of quanta per second.

The constant values of the ionic strength and pH were maintained with phosphate buffer solution. The pH was monitored with an HI 2211 device (Hanna).

The heterogeneous colloidal platinum catalyst for hydrogen evolution was prepared by reduction of hydrogen hexachloroplatinate(IV) with sodium citrate, according to the procedure described in [13, 14].

Qualitative determination of hydrogen produced in the photocatalytic reaction was performed with a Kristall 2000M chromatograph (Khromatek). The volume of the evolved hydrogen was measured volumetrically with a microburet connected to the cell being irradiated.

All the studies were performed at room temperature, 22 ± 1°C. The Origin® 9.0 program was used for processing the experimental data.

RESULTS AND DISCUSSION

Redox properties of the complex $[Pd(TTMAPP)]^{4+}$ in the ground and triplet excited states. It is known that the highest occupied and lowest unoccupied molecular π orbitals in palladium(II) porphyrins ($Pd^{II}P$) are localized on the porphyrin macrocycle; therefore, oxidation of such porphyrins yields the radical cation ($Pd^{II}P^{\cdot+}$), and reduction, the radical anion ($Pd^{II}P^{\cdot-}$), with the oxidation state of the central ion remaining unchanged [9, 15]. The redox properties of the new photocatalyst, water-soluble palladium(II) porphyrin, were mainly studied by cyclic voltammetry. An anodic peak was observed on scanning the working electrode potential to the positive region from 0 to 0.9 V, and a cathodic peak was observed when scanning the potential in the reverse direction. The difference between the potentials of these peaks was 59 mV. The dependences of the peak current on the square root of the potential sweep rate are linear, suggesting the occurrence of the one-electron reversible oxidation of the metalloporphyrin, $[Pd(TTMAPP)]^{4+} - e \longleftrightarrow [Pd(TTMAPP)]^{5+}$, with the potential $E_{1/2}(PdP^{\cdot+}/PdP) = 0.72$ V. Scanning of the working electrode potential in the range from 0 to –1.0 V revealed no reduction peaks, i.e., the reduction potential is beyond the range of electrochemical stability of water as solvent. It is known [16] that the difference between the one-electron oxidation and reduction potentials for many porphyrins is approximately 2.2 V. Therefore, the potential of the palladium(II) porphyrin reduction, $[Pd(TTMAPP)]^{4+} + e \leftrightarrows [Pd(TTMAPP)]^{3+}$, can be estimated: $E_{1/2}(PdP/PdP^{\cdot-}) \approx -1.48$ V.

The redox potentials of palladium(II) porphyrin in the triplet excited state were calculated by the known relationships [3] using the ground-state potentials and the energy of the lowest triplet excited state, $E_T = 1.91$ eV, calculated from the phosphorescence spectrum:

$$E^\circ(PdP^{\cdot+}/{}^*PdP) = E_{1/2}(PdP^{\cdot+}/PdP) - E_T = -1.19\text{ V},$$
$$E^\circ({}^*PdP/PdP^{\cdot-}) = E_{1/2}(PdP/PdP^{\cdot-}) + E_T \approx 0.43\text{ V}.$$

All the redox potentials obtained are presented in the diagram below:

$$\begin{tikzcd}
 & {}^*[Pd(TTMAPP)]^{4+}\,(T) \arrow[dl, "0.43\text{ V}"'] \arrow[dr, "-1.19\text{ V}"] & \\
{[Pd(TTMAPP)]^{3+}} & {[Pd(TTMAPP)]^{4\cdot}} \arrow[l, "-1.48\text{ V}"'] \arrow[u, "h\nu", "1.91\text{ eV}"'] \arrow[r, "0.72\text{ V}"] & {[Pd(TTMAPP)]^{5+}}
\end{tikzcd}$$

Quenching of the $[Pd(TTMAPP)]^{4+}$ phosphorescence. The photocatalyst suggested in this study, water-soluble palladium(II) porphyrin, passes upon photoexcitation from the ground singlet state into the excited triplet state (T) of the lowest energy with the probability close to unity and exhibits phosphorescence in deaerated aqueous solution [12, 17] (Fig. 1a):

$$\begin{aligned} {}^*[Pd(TTMAPP)]^{4+}(T) \rightarrow {} & [Pd(TTMAPP)]^{4+} \\ & + h\nu\ (670\text{ nm}). \end{aligned} \qquad (1)$$

Addition of methyl viologen to the solution causes quenching of the palladium(II) porphyrin phosphorescence (Fig. 1). The Stern–Volmer plots of the decrease in the triplet state lifetime and in the phosphorescence intensity vs. concentration of methyl viologen as quencher coincide (Fig. 1b), suggesting dynamic character of quenching. From the dependences obtained, we determined the biomolecular rate constant of phosphorescence quenching, k_q:

$$\tau_0/\tau = I_0/I = 1 + k_q\tau_0[MV^{2+}], \qquad (2)$$

where τ_0 and I_0 are the lifetime and intensity of the phosphorescence without quencher, and τ and I are those at a quencher concentration $[MV^{2+}]$.

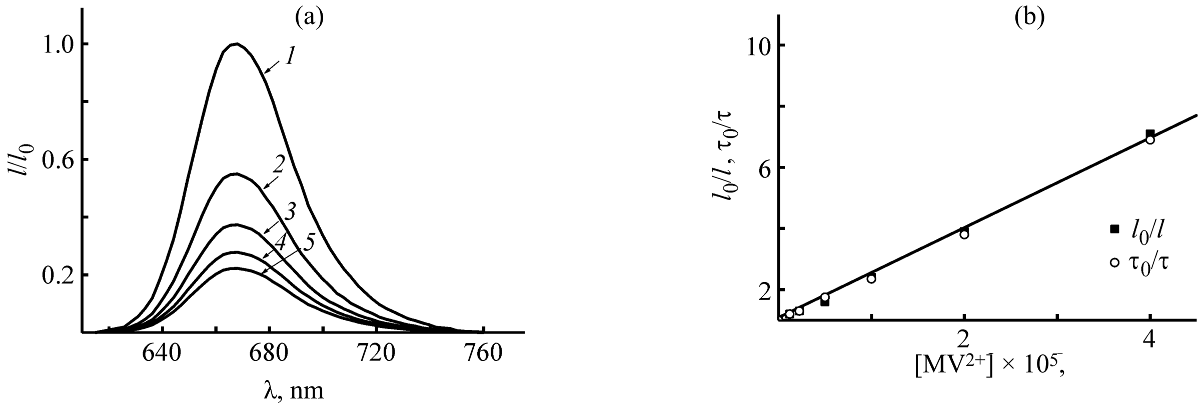


Fig. 1. (a) Variation of the phosphorescence spectrum of $[Pd(TTMAPP)](NO_3)_4$ with the MV^{2+} concentration and (b) Stern–Volmer plots for the decrease in the phosphorescence intensity and lifetime. (τ_0, I_0) Phosphorescence lifetime without quencher and (τ, I) those in the presence of the quencher, methyl viologen MV^{2+}, respectively (pH 7, μ = 0.1 M). (a) $[MV^{2+}]$, M: (*1*) 0, (*2*) 1×10^{-5}, (*3*) 2×10^{-5}, (*4*) 4×10^{-5}, and (*5*) 8×10^{-5}.

As the solution ionic strength μ was increased, the rate constant of the phosphorescence quenching increased, in accordance with the Debye–Hückel theory for reactions between like-charged ions [18]. At μ = 0.1 M, the quenching constant k_q was 7.9×10^8 L mol^{-1} s^{-1}.

Methyl viologen quenches the phosphorescence of the water-soluble palladium(II) porphyrin by the mechanism of oxidative electron transfer:

$$*[Pd(TTMAPP)]^{4+}\ (T) + MV^{2+} \rightarrow [Pd(TTMAPP)]^{5+} + MV^{\cdot+}. \quad (3)$$

The calculated negative value of the Gibbs free energy of the process indicates that it is thermodynamically possible: $\Delta G^\circ = -[E^\circ(MV^{2+}/MV^{\cdot+}) - E^\circ(PdP^{\cdot+}/{*PdP})] = -0.75$ eV. This value was obtained from the oxidation potential of palladium(II) porphyrin in the triplet excited state, $E^\circ(PdP^{\cdot+}/{*PdP}) = -1.19$ V, and the known reduction potential of methyl viologen, $E^\circ(MV^{2+}/MV^{\cdot+}) = -0.44$ V [19].

Triethanolamine does not noticeably quench the phosphorescence of the palladium(II) porphyrin (k_q = 1.1×10^5 L mol^{-1} s^{-1}). This is due to the fact that the reductive electron transfer

$$*[Pd(TTMAPP)]^{4+}(T) + TEOA \rightarrow [Pd(TTMAPP)]^{3+} + TEOA^{+} \quad (4)$$

is thermodynamically unfavorable, as indicated by the positive value of the Gibbs free energy of the process: $\Delta G^\circ = -[E^\circ({*PdP}/PdP^{\cdot-}) - E^\circ(TEOA^{+}/TEOA)]$ = 0.39 eV, determined from the reduction potential of the palladium(II) porphyrin in the triplet excited state, $E^\circ({*PdP}/PdP^{\cdot-}) = 0.43$ V, and the known oxidation potential of triethanolamine, $E^\circ(TEOA^{+}/TEOA) = 0.82$ V [19].

Thus, in the system containing the palladium(II) porphyrin, methyl viologen, and triethanolamine, only methyl viologen quenches the metalloporphyrin phosphorescence.

Photoreduction of methyl viologen and production of hydrogen. The absorption spectrum of the solution containing palladium(II) porphyrin and methyl viologen did not change upon irradiation, which is due to the occurrence of an efficient reaction between the products of reaction (3):

$$[Pd(TTMAPP)]^{5+} + MV^{\cdot+} \rightarrow [Pd(TTMAPP)]^{4+} + MV^{2+}. \quad (5)$$

However, if an irreversibly decomposing electron donor, triethanolamine, is added to the system, it reduces the oxidized form of the photocatalyst, palladium(II) porphyrin, to the initial state:

$$[Pd(TTMAPP)]^{5+} + TEOA \rightarrow [Pd(TTMAPP)]^{4+} + TEOA^{+}, \quad (6)$$

$$TEOA^{+} \rightarrow \text{oxidation products (very fast).} \quad (7)$$

When the deaerated solution containing the metalloporphyrin, methyl viologen, and triethanolamine was irradiated with a light with a wavelength of 546 nm, it acquired intense blue color characteristic of the reduced form of methyl viologen, $MV^{\cdot+}$. Figure 2 shows the changes observed in the absorption spectrum in the course of photolysis.

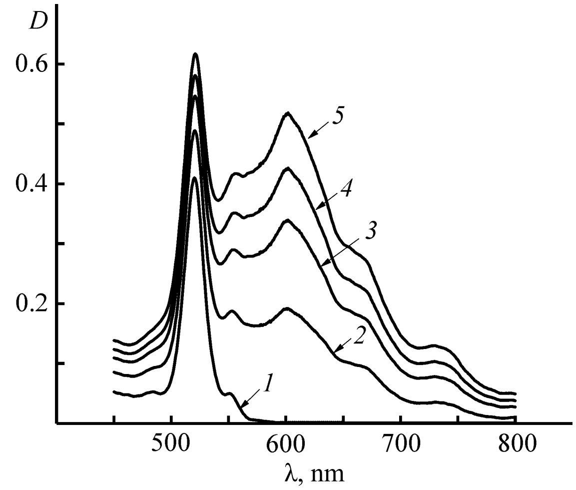


Fig. 2. Evolution of the absorption spectrum in the course of photolysis of the ternary system containing [Pd(TTMAPP)]$(NO_3)_4$ (2.5×10^{-5} M), methyl viologen (0.001 M), and triethanolamine (0.05 M). Time after the start of the experiment, min: (*1*) 0, (*2*) 15, (*3*) 30, (*4*) 45, and (*5*) 60 (λ_{exc} = 546 nm, pH 7, μ = 0.1 M). (*D*) Optical density and (λ) wavelength.

The arising broad absorption band with λ_{max} = 605 nm is assigned to $MV^{\cdot+}$ on the basis of published data [20, 21]. Upon aeration of the system, $MV^{\cdot+}$ is quantitatively oxidized with atmospheric oxygen to the initial MV^{2+}, with no loss of the photocatalyst, metalloporphyrin, and after the deaeration the process can be repeated many times.

The quantum yield of the $MV^{\cdot+}$ formation was determined from the dependence of optical density increase at 605 nm on the irradiation time, using the known molar extinction coefficient of $MV^{\cdot+}$, ε_{605} = 13700 L mol^{-1} cm^{-1} [20] and taking into account the fraction of the light at the excitation wavelength (546 nm), absorbed by the photocatalyst, palladium(II) porphyrin. As we found, the quantum yield of the $MV^{\cdot+}$ formation depends on the initial concentration of methyl viologen; the maximal quantum yield is 0.4.

It is known [22] that the reduced form of methyl viologen, $MV^{\cdot+}$, in the presence of a heterogeneous catalyst (e.g., colloidal platinum) at pH 5 can reduce water to molecular hydrogen:

$$MV^{\cdot+} + H_2O \xrightarrow{Pt} MV^{2+} + 1/2H_2 + OH^-. \quad (8)$$

Indeed, on adding colloidal platinum to the ternary system, the reduced form of methyl viologen did not accumulate, and the hydrogen evolution was confirmed chromatographically. The volume of the evolved hydrogen reached a maximum at after 160-min irradiation. The photocatalytic system showed high stability in the course of irradiation.

The quantum yield of hydrogen formation was determined from the initial part of the time dependence of the volume of the evolved hydrogen (Fig. 3). It appeared to be close to the quantum yield of the formation of the reduced methyl viologen form at the given concentration of methyl viologen ($\Phi_{1/2H_2} = \Phi_{MV^{\cdot+}}$).

We calculated the number of the photocatalyst turnovers, determined as the number of hydrogen moles evolved per mole of the metalloporphyrin [6]. As we found, 125 mol of hydrogen is formed per mole of the metalloporphyrin after 1-h irradiation. This value is not inferior to the values reached in the previously studied photocatalytic systems and in many cases exceeds them.

CONCLUSIONS

A new effective photocatalyst for the system of water reduction to molecular hydrogen was suggested. This system is extremely stable, with no decomposition of the photosensitizer.

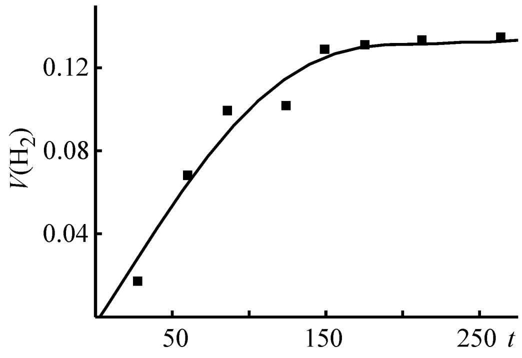


Fig. 3. Volume of the evolved hydrogen $V(H_2)$ as a function of the irradiation time *t* in the system containing [Pd(TTMAPP)]$(NO_3)_4$ (2.5×10^{-5} M), methyl viologen (0.002 M), triethanolamine (0.05 M), and colloidal platinum (4×10^{-5} M) (λ_{exc} = 546 nm, pH 7, μ = 0.1 M).

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