ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 6, pp. 1145–1152. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © E.A. Venediktov, E.Yu. Tulikova, V.E. Maizlish, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 6, pp. 1003–1010.

Photogeneration of Singlet Molecular Oxygen ($^1O_2$, $^1\Delta_g$) Using Monomeric and Aggregated Forms of Copper Tetra-4-(morpholine-4-yl)-tetra-5-(2-naphthoxy)phthalocyanine in Organic Solvents

E. A. Venediktov[a,b], E. Yu. Tulikova[a], and V. E. Maizlish[b]

[a] *Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
e-mail: eav@isc-ras.ru

[b] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*

Received April 21, 2011

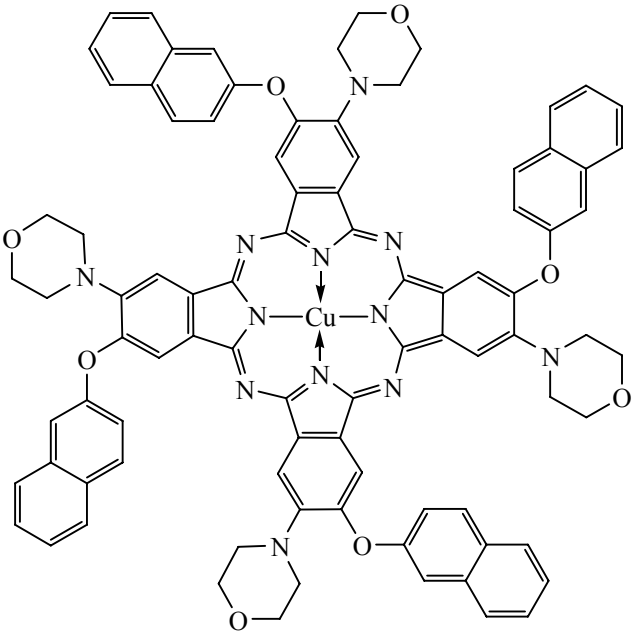
Abstract—Luminescence and chemical acceptors methods were used to study the photosensitized formation of singlet molecular oxygen ($^1O_2$, $^1\Delta_g$) by monomer and aggregated forms of copper tetra-4-(morpholine-4-yl)-tetra-5-(2-naphthoxy)phthalocyanine in benzene, benzene-d_6, acetone, DMF, and pyridine. The values of $^1O_2$ quantum yield were determined. The effectiveness of the $^1O_2$ photoproduction was shown to be reduced due mainly to the aggregation of the copper phthalocyanine molecules.

DOI: 10.1134/S1070363212060187

Copper phthalocyanines are important synthetic compounds with a wide range of applications in various fields of science and engineering, chemical engineering, and medicine: as pigments and dyes, materials for optics and electronics, catalysts, etc. [1]. The interest to the photocatalytic properties of copper phthalocyanine, in particular, to the ability of photochemical formation of singlet molecular oxygen ($^1O_2$, $^1\Delta_g$), is caused by the wide opportunities of its practical use in several areas of modern photomedicine [2, 3] and photochemical technology [4, 5].

Previously, the ability of copper phthalocyanines to generate $^1O_2$ in the light was noted in [5–9]. In some cases the published data are obviously contradictory [7, 10]. As the most common reason of this contradictt ion the aggregation of the molecules of copper phthalocyanine is suggested. However, by the example of copper tetra(5-*tert*-butylpyrazino)porphyrazine [(*t*-Bu)$_4$·PzcCu], a structural analog of copper phthalocyanine, it was proved that the quantum yield of $^1O_2$ (γ) fell sharply in coordinating solvents [11]. In solutions of copper tetra(4-*tert*-butyl)phthalocyanine [(*t*-Bu)$_4$PcCu] this dependence is manifested very weakly [9]. The question arises: Whether this behavior of copper phthalocyanine is of general character. In this connection, it was interesting to study further the photoproduction of $^1O_2$ in solutions of copper phthalocyanines extending their range.

In the present study, we investigated the photogeneration of $^1O_2$ with the use of copper tetra-4-(morpholine-4-yl)-tetra-5-(2-naphthoxy)phthalocyanine [(Mf)$_4$(Nf)$_4$PcCu] as a monomer or in aggregated state in organic solvents, including benzene, deuterobenzene (benzene-d_6), pyridine, DMF, and acetone.



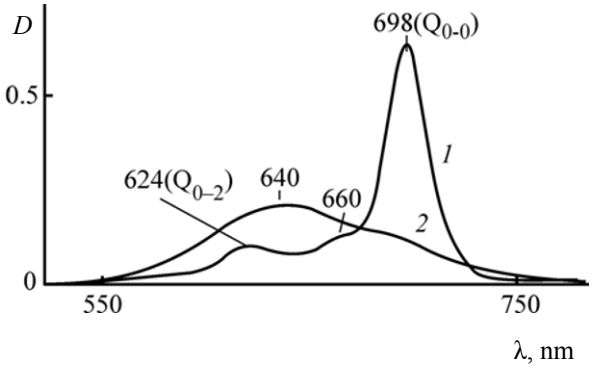


Fig. 1. Electron absorption spectra of $(Mf)_4(Nf)_4PcCu$ dissolved in (*1*) pyridine and (*2*) acetone.

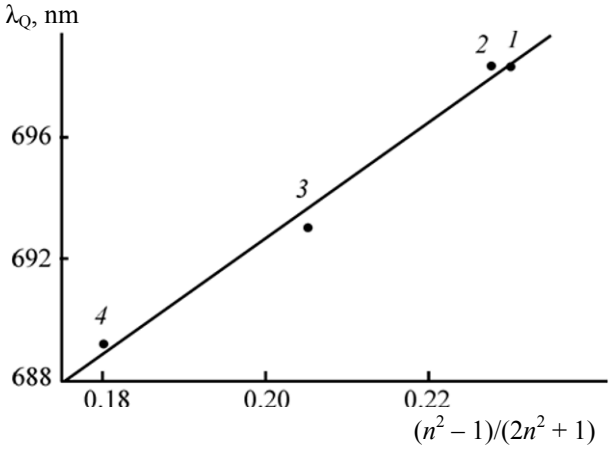


Fig. 2. The dependence on the refractive index n of the peak position of Q_{0-0} absorption band of the $(Mf)_4(Nf)_4PcCu$ monomer dissolved in (*1*) pyridine, (*2*) benzene, (*3*) DMF, and (*4*) acetone.

Electron absorption spectrum (EAS) of the $(Mf)_4(Nf)_4$·PcCu monomer in the visible region has a characteristic contour of the copper phthalocyanines with an intense Q_{0-0} band (Fig. 1, curve *1*) whose maximum (λ_Q) is located in the wavelength range from 685 to 700 nm depending on the solvent. In benzene, the Q_{0-0} band maximum is located at 698 nm (molar absorption coefficient $\varepsilon = 1.6\times10^5$ cm^{-1} mol^{-1} l). In acetone, the monomer Q_{0-0} band is very weak because of the high degree of aggregation of $(Mf)_4(Nf)_4PcCu$. Therefore, the assessment of its λ_Q was carried out using a dilute solution at the temperature of 333 K. As shown by measurements (Fig. 2), the value of λ_Q undergoes a blue shift in solvents with a lower refractive index (n) [12]. Similar behavior of Q_{0-0} band was observed in the solutions of the other copper phthalocyanines [9, 11, 13] as well as typically coordinately unsaturated metal phthalocyanines like zinc phthalocyanine [10]. This result indicates that the solvent effect on the Q_{0-0} band of $(Mf)_4(Nf)_4PcCu$ is determined primarily by universal interactions [14]. However, this fact, taking into account the assumption on the coordination unsaturated nature of copper phthalocyanine [15], which is confirmed by the results of [16], does not exclude specific solvation of $(Mf)_4(Nf)_4PcCu$ in coordinating solvents in the form of an additional (axial) coordination of molecules of the latter. However, the reason why such an interaction is not manifested in the EAS of metal phthalocyanines is far from clear. One of explanations is the assumption that in a high coordination environment the solvated metal phthalocyanines retain their original symmetry [17], for example, by joining two molecules of the solvent.

A characteristic feature of the UV absorption spectrum of $(Mf)_4(Nf)_4PcCu$ is the presence of an additional, not typical for PcCu and $(t\text{-Bu})_4PcCu$, absorption maximum at 314 nm adjacent to the short wavelength side of the Soret band (Fig. 3). Comparing the UV absorption spectra of $(Mf)_4(Nf)_4PcCu$, 4-(2-naphthoxy)-5-(morpholine-4-yl)phthalonitrile [(Mf)·(Nf)PN], and 4-*tert*-butyl-phthalonitrile (*t*-Bu-PN) (Fig. 3), we can conclude that this band is due to the electron transitions in the naphthoxyl fragments.

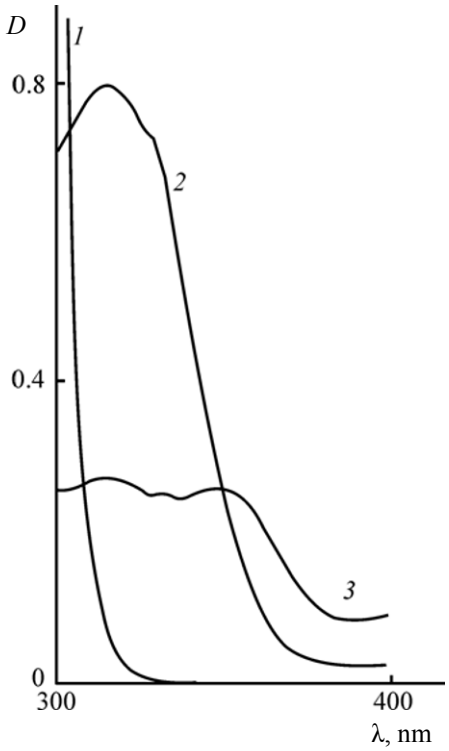
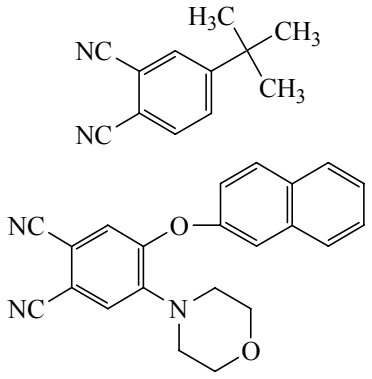


Fig. 3. UV absorption spectra of (*1*) (*t*-Bu)PN, (*2*) (Mf)(Nf)PN, and (*3*) $(Mf)_4(Nf)_4PcCu$ in benzene.



The compound $(Mf)_4(Nf)_4PcCu$ belongs to the group of the phthalocyanines soluble in organic solvents. However, its marked propensity to aggregation due to lyophobic interactions in solution (Fig. 1, curve *2*) is obvious. Although this property is typical of many copper phthalocyanines [18, 19], it is especially strong in the case of $(Mf)_4(Nf)_4PcCu$. In particular, in acetone the $(Mf)_4(Nf)_4PcCu$ is mainly in the form of an aggregate (Fig. 1, curve *2*). We used this advantage to estimate the γ value for an aggregated form of $(Mf)_4(Nf)_4PcCu$.

Comparing EAS of $(Mf)_4(Nf)_4PcCu$ in acetone and pyridine (Fig. 1), we can see that upon the $(Mf)_4(Nf)_4$·PcCu aggregation the Q_{0-0} absorption band disappears and a new broad absorption appears in the region of Q_{0-1} and Q_{0-2} transitions. In the spectrum of the acetone solution of $(Mf)_4(Nf)_4PcCu$ the maximum of this band is located at 640 nm (Fig. 1, curve *2*). In benzene, according to the measurement of differential EAS of solutions at different temperatures (295 and 333 K), it lies at 650 nm. As can be seen, the solvent affects the absorption band of the $(Mf)_4(Nf)_4PcCu$ aggregate like the *Q*-band of monomer.

The aggregation of $(Mf)_4(Nf)_4PcCu$ is reversible. A dilution and (or) an increase in the solution temperature lead to dissociation of the aggregates. However, the effect of acetone is very weak, indicating a high stability of such formations. The process of the formation and dissociation of $(Mf)_4(Nf)_4PcCu$ aggregates is accompanied by the changes in the intensity ratio of the absorption at the wavelengths of the maxima of Q_{0-0} and Q_{0-2} bands (D_{0-0}/D_{0-2}), which can be used to investigate the extent of the aggregation.

The $(Mf)_4(Nf)_4PcCu$ solution concentration used in the study of the luminescent and photochemical properties of the monomer were selected from the condition of achieving the upper limit of the ratio D_{0-0}/D_{0-2}. This condition is satisfied at the $(Mf)_4(Nf)_4PcCu$ concentration in benzene equal to and below 2.5×10^{-6} M ($D_{0-0}/D_{0-2} = 3.6$). The aggregation of $(Mf)_4(Nf)_4$·PcCu in pyridine is shown to occur to a much lesser extent than in benzene, due apparently to the axial coordination of pyridine molecules restricting the interlayer interaction of phthalocyanine molecules.

The photosensitized formation of $^1O_2$ in the solution of $(Mf)_4(Nf)_4PcCu$ was studied by the methods of luminescence and chemical acceptors. The $^1O_2$ luminescence was measured at 1270 nm with the excitation of the source solutions with the laser light at a wavelength of 337 nm. As the chemical acceptor of $^1O_2$ tetracene was used, and for the photoexcitation of solutions in this case the usual long-wavelength (red) light was used.

At the UV photoexcitation the absorption bands of the macroheterocyclic ligand and naphthoxyl substituents overlap (Fig. 3), therefore in order to determine the contribution of the latter in the photogeneration of $^1O_2$ we preliminary investigated the photochemical properties of benzene solutions of (Mf)(Nf)PN and (*t*-Bu)PN. The photoluminescence of $^1O_2$ was observed only in the (Mf)(Nf)PN solution. The measurement of γ for (Mf)(Nf)PN was performed by the relative method using palladium mesoporphyrin dimethyl ester (PdMP) as a reference photosensitizer of $^1O_2$. For PdMP, γ = 1.0 [20]. For (Mf)(Nf)PN γ value was found equal to 0.65.

In contrast to (Mf)(Nf)PN, the γ value at the UV irradiation of the solution of $(Mf)_4(Nf)_4PcCu$ is 0.30, and it should be regarded as a generalized value associated with the photochemical properties of both naphthoxyl substituents and macrocycle. Since the absorption spectra due to the transitions in these substructures overlap at the excitation wavelength, then the found difference in γ may indicate a lower ability of macrocycles $(Mf)_4(Nf)_4PcCu$ to photogeneration of $^1O_2$. The result obtained for $(t\text{-Bu})_4PcCu$ in [9] confirms indirectly this conclusion.

The potential ability of macrocycles $(Mf)_4(Nf)_4$·PcCu to the photogeneration of $^1O_2$ was investigated using the "energy criterion." For this purpose we studied $^1O_2$ quenching by the $(Mf)_4(Nf)_4PcCu$ molecules in benzene-d_6. In this solvent the lifetime of $^1O_2$ (τ_0) greatly increases [21, 22], and we could minimize the aggregation effect on the interaction of $^1O_2$ with $(Mf)_4(Nf)_4PcCu$ by reducing concentration of the latter. Figure 4 shows a dependence of the decay rate constant (*k*) of $^1O_2$ luminescence photosensitized with anthracene on the molar concentration of monomer

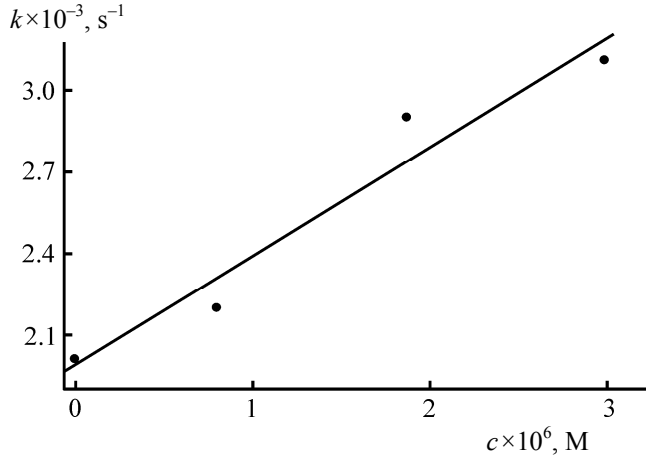


Fig. 4. Dependence of the rate constant of photosensitized $^1O_2$ luminescence decay on the concentration of $(Mf)_4(Nf)_4PcCu$ in benzene-d_6 (sensitizer anthracene, c = 5×10^{-5} M).

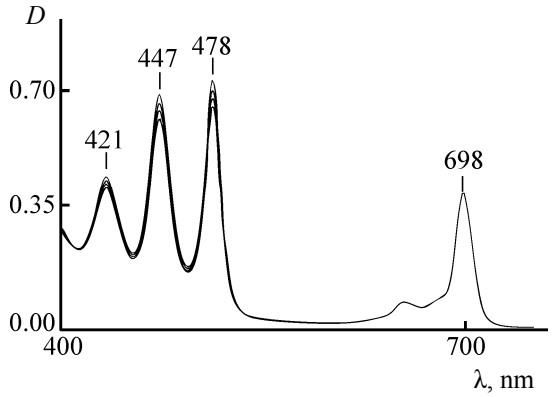


Fig. 5. Changes in the absorption spectrum of tetracene solution in pyridine at the photoexcitation by the light λ > 580 nm in the presence of $(Mf)_4(Nf)_4PcCu$, after 0, 10, 20, and 30 min of exposure.

$(Mf)_4(Nf)_4PcCu$ (c). As seen, this dependence is approximated by a straight line described by the equation

$$k = k_D + k_Q c. \quad (1)$$

Here, $k_D = 1/\tau_0$ is the $^1O_2$ luminescence decay rate constant in the absence of a quencher; k_Q is the bimolecular quenching rate constant. The experimental data using Eq. (1) give $k_Q = (4.0\pm0.7)\times10^8$ mol^{-1} l s^{-1}. This result shows that the value of k_Q is over tenfold less than the rate constant of a similar process where the basic mechanism of quenching is energy transfer from $^1O_2$ to the excited triplet levels of the phthalocyanine quenchers located below 94 kJ mol^{-1} [23]. In fact, the $^1O_2$ quenching in solution of $(Mf)_4(Nf)_4PcCu$ occurs likely along a mixed mechanism involving the exchange energy transfer and the formation of a charge transfer complex at the collision of the reactants. Nevertheless, from these data, we can conclude that the process of energy transfer is clearly endothermic in nature. This is possible when the energy of the triplet {trip-doublet (^2T) and (or) trip-quartet (^4T) [24, 25]} level of $(Mf)_4(Nf)_4PcCu$ lies higher than the $^1\Delta_g$ level of O_2. Since the $^1O_2$ photogeneration is a consequence of spin-allowed energy transfer from the excited triplet phthalocyanine molecules to $O_2(^3\Sigma_g^-)$ as a result of the exchange interaction [14, 26], we can conclude that from an energy viewpoint the photogeneration of $^1O_2$ by the $(Mf)_4(Nf)_4PcCu$ macrocycleis is an allowed process. This conclusion is confirmed by the method of photosensitized oxidation of tetracene at the photoexcitation of the reaction by the wavelength of the Q_{0-0} band of $(Mf)_4(Nf)_4PcCu$.

Figure 5 shows the EAS indicating the disappearance of the absorption bands of tetracene in the pyridine solution under the irradiation at λ > 580 nm in the presence of $(Mf)_4(Nf)_4PcCu$. A qualitatively similar effect was obtained with benzene and DMF. A special test showed that in the absence of $(Mf)_4(Nf)_4$·PcCu this reaction practically does not proceed. In acetone, where $(Mf)_4(Nf)_4PcCu$ is aggregated, the photosensitized oxidation of tetracene can also be observed. However, in this case the reaction is slow. According to [27], these results allow a conclusion that $(Mf)_4(Nf)_4PcCu$ is a photosensitizer of $^1O_2$ formation. Kinetic curves for this reaction allow the estimation of the γ value for $(Mf)_4(Nf)_4PcCu$.

Figure 6 shows the results of studying the kinetics of the tetracene photosensitized oxidation. As can be seen, the kinetic dependences in the coordinates $\ln(D_0/D_t)$-t are straight lines (D_0 and D_t are respectively initial and current optical densities at the long-wavelength absorption band of tetracene, t is the exposure duration). The data obtained show that the photosensitized oxidation of tetracene occurs in a pseudo-first order reaction [28]. Consequently, to determine the reaction rate the following equation can be applied:

$$-d[T]/dt = k_{eff}[T]. \quad (2)$$

Here [T] is tetracene concentration; $k_{eff} = k_r[^1O_2]$ is the effective rate constant; k_r is the rate constant of bimolecular reaction, $[^1O_2]$ is $^1O_2$ concentration. The k_{eff} values were obtained from the kinetic curves by the equation

$$k_{eff} = \ln (D_0/D_t)/t. \quad (3)$$

The k_{eff} values found show that the reaction rate is higher in the presence of $(Mf)_4(Nf)_4PcCu$ monomer rather than aggregate. However, it is obvious that the k_{eff} value for the monomer $(Mf)_4(Nf)_4PcCu$ in pyridine is 1.8 times higher than in benzene. If the result obtained with acetone can be qualitatively interpreted within the framework of reduction of photochemical activity of $(Mf)_4(Nf)_4PcCu$ due to its aggregation, then an adequate explanation of the difference of the kinetic data in pyridine and benzene from the standpoint of efficiency of the $^1O_2$ photogeneration can be given only considering the influence of the solvent on the $[O_2]$, [14, 29], k_r [30, 31] and τ_0 [21, 22, 30, 31]. Therefore, to investigate the causes of difference in the k_{eff} it is necessary to consider the mechanism of this reaction.

The photosensitized oxidation of tetracene can be represented as a set of elementary stages [7, 10, 14, 27]:

$$^1S_0 \xrightarrow{h\nu} {}^1S^* \rightarrow {}^3S^*,$$

$$^3S^* + O_2\,(^3\Sigma_g^-) \rightarrow {}^1S_0 + {}^1O_2\,(^1\Delta_g) \text{ or } O_2\,(^3\Sigma_g^-),\ k_T,$$

$$^1O_2 \xrightarrow{Solv} O_2 + h\nu\,(\sim 1270\text{ nm}),\ k_D,$$

$$^1O_2 + {}^1S_0 \rightarrow O_2 + {}^1S_0 \text{ and (or) the products of oxidation, } k_O,$$

$$^1O_2 + T \rightarrow \text{products of oxidation, } k_r.$$

Here $^1S_0$, $^1S^*$, and $^3S^*$ are the ground and excited singlet and triplet states of the sensitizer, respectively, *Solv* is solvent, k_T is the rate constant of the quenching of triplet molecules.

In the light of these elementary processes, the rate of decrease in the tetracene concentration in the quasistationary approximation can be written in the form of the Eq. (4):

$$-d[T]/dt = \frac{k_r\gamma[T]I}{k_D + k_Q[S] + k_r[T]}. \quad (4)$$

Here $[S]$ is the sensitizer concentration; $I = I_0\,(1-10^{-D})$ is the intensity of the absorbed light; I_0 is the intensity of the exciting light; D is the optical density of the solution at a wavelength of photoexcitation. If the reaction proceeds with insufficient $[O_2]$, then γ is given by Eq. (5) [7, 10, 32]:

$$\gamma = \frac{\gamma_T k_T[O_2]S_\Delta\tau_T}{1 + k_T[O_2]\tau_T}. \quad (5)$$

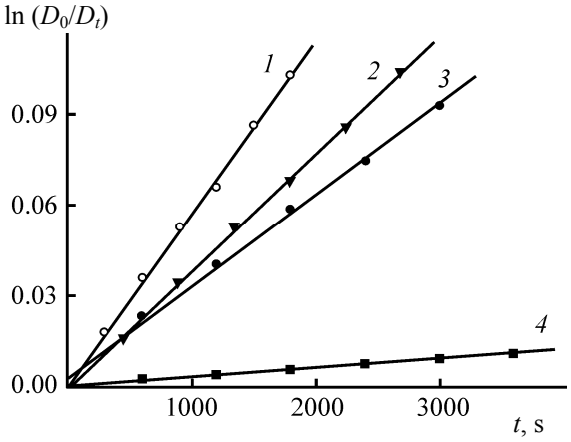


Fig. 6. Kinetic plots of the tetracene photosensitized oxidation reactions in the presence of $(Mf)_4(Nf)_4PcCu$ (*1*, *3,* and *4*) and (*t*-Bu) 4PzcCu (2) in pyridine (*1*), benzene (*2*, *3*) and acetone (*4*) obtained at the photoexcitation by light with $\lambda > 580$ nm.

Here, γ_T is the quantum yield of triplet molecules; τ_T is the lifetime of the triplet molecules; k_T is the bimolecular rate constant for the quenching of molecular oxygen triplet molecules; S_Δ is a probability of the $^1O_2$ formation at the quenching of the sensitizer triplet molecules by the molecular oxygen (for a weakly polar environment $S_\Delta \approx 1$ [32]).

With the known estimates of the k_D, k_Q, and k_r parameters, we can simplify equation (4). From the decay curves of the photosensitized luminescence of $^1O_2$ we obtain the limiting values of $k_D\times10^{-4}$: 3.3, 5.8, and 2.0 s^{-1} in benzene, pyridine and acetone, respectively. Hence, in the investigated solvents the values of τ_0 for $^1O_2$ are respectively 30, 17, and 50 μs. These values are well consistent with the data of [21, 22].

The parameter k_r for this reaction was studied in [30, 31, 33]. The interaction of $^1O_2$ with tetracene was shown to proceed by the chemical mechanism [33]. Therefore, the value of k_r is the same as the rate constant of the $^1O_2$ luminescence quenching by tetracene. In benzene-d_6 and acetone-d_6 the rate constants of $^1O_2$ luminescence quenching by tetracene are 1.4×10^7 and 2.3×10^7 $mol^{-1}\,l\,s^{-1}$, respectively [30]. Taking into account the weak effect of deuteration on the physicochemical properties of solvents [34], these values can be extended over the benzene and acetone solutions. For pyridine, the value of $k_r = 5.2\times10^7$ $mol^{-1}\,l\,s^{-1}$ was earlier obtained [31].

The value of k_Q for pyridine or acetone solutions is of the same order of magnitude. Consequently, the

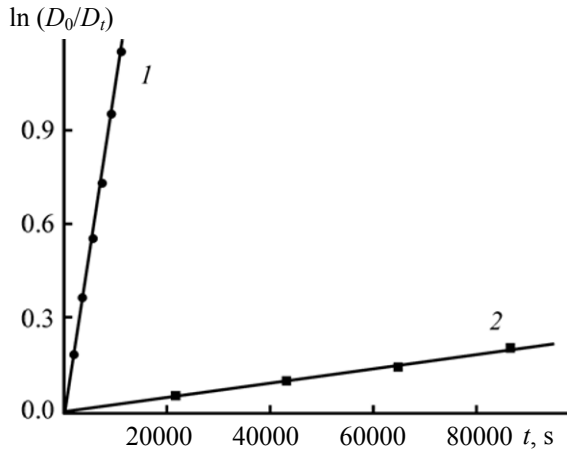


Fig. 7. Kinetic plots of the reaction of photosensitized oxidation of tetracene in the presence of protoporphyrin **IX** dimethyl ester (PP) (*1*) and $(Mf)_4(Nf)_4PcCu$ (*2*) in acetone, at the photoexcitation with a narrow band light with a peak at 631 nm.

kinetics of the oxidation of tetracene is determined by the inequality $k_D > k_Q[S] + k_r[T]$. Then, within this approximation, expression (4) can be rewritten in a simpler form (6):

$$-d[T]/dt = k_r\gamma\tau_0 I[T]. \quad (6)$$

From the joint consideration of Eq. (2) and Eq. (6) follows Eq. (7):

$$k_{eff} = k_r\gamma\tau_0 I. \quad (7).$$

Moreover, in the case of the $(Mf)_4(Nf)_4PcCu$ solutions in benzene and pyridine the difference in **I** can be ignored, taking into account the closeness of the EAS contours and *Q*-band positions for this compound. Then, the relationship between the relative values of γ and k_{eff} can be expressed as a ratio [Eq. (8)]:

$$\gamma/\gamma_b = \alpha/(\beta\delta). \quad (8)$$

Here α, β, and δ are the values of $k_{eff}/k_{eff,\,b}$, $k_r/k_{r,b}$, and $\tau_0/\tau_{0,b}$, respectively; index b corresponds to benzene. The ratio $\gamma/\gamma_b = 0.85$ found with this formula shows that the values of γ are close for the solutions in benzene and pyridine. This result indicates a weak dependence of γ for $(Mf)_4(Nf)_4PcCu$ on the solvent. Nevertheless, as in the case of $(t\text{-Bu})_4PcCu$ [9], the value of γ in pyridine is slightly less than in benzene. In accordance with Eq. (5), this fact may find its rational explanation in the reduced solubility of molecular oxygen in pyridine [29], considering also the short lifetime of $^2T/^4T$ states of the copper phthalocyanine molecule [24, 25].

To estimate γ we compared the kinetic data for the reaction in benzene in the presence of $(Mf)_4(Nf)_4PcCu$ and $(t\text{-Bu})_4PzcCu$ (γ = 0.16 [11]). Figure 6 shows the closeness of the values of $k_{eff,b}$ in the presence of $(Mf)_4(Nf)_4PcCu$ and $(t\text{-Bu})_4PzcCu$: Their ratio is about 1.3. It is important to note that despite the closeness of the contours of the EAS of sensitizers, they differ in the position of their Q_{0-0} bands. In the EAS of $(t\text{-Bu})_4PzcCu$ in benzene the Q_{0-0} band maximum lies at shorter wavelengths, at 634 nm [11]. Consequently, when for the photoexcitation an incandescent lamp is used, the reaction rate depends on the spectral emissivity of the source of light. According to [35], the spectral emissivity of such a lamp at the maximum of Q_{0-0} band of $(Mf)_4(Nf)_4PcCu$ is approximately 1.3 times higher than at the Q_{0-0} maximum of $(t\text{-Bu})_4PzcCu$ at the incandescent temperature about 3000 K. Consequently, in accordance with Eqs. (7) and (8), the value of γ for $(Mf)_4(Nf)_4PcCu$ should be approximately 1.7 times lower than that for $(t\text{-Bu})_4PzcCu$. Proceeding from this fact we can conclude that γ value for $(Mf)_4(Nf)_4PcCu$ is about 0.1. This value can be associated exclusively with the photochemical properties of the $(Mf)_4(Nf)_4PcCu$ macrocycle. From these data we can conclude that $(Mf)_4(Nf)_4PcCu$ is less effective in the reaction of photosensitized formation of $^1O_2$, but more active in quenching $^1O_2$, than, for example, the related compound $(t\text{-Bu})_4PcCu$ [9].

Finally, the γ value for the $(Mf)_4(Nf)_4PcCu$ aggregate was evaluated. We compared the kinetic data of the reactions of photosensitized oxidation of tetracene in acetone in the presence of either aggregated $(Mf)_4(Nf)_4PcCu$ or protoporphyrin **IX** dimethyl ester (PP), obtained by photoexcitation with the narrow band light with maximum intensity at 631 nm (half-width about 11 nm), which corresponds to the maximum of the first absorption band of PP [36]. As seen from Fig. 7, the rate of photosensitized oxidation of tetracene in a solution containing PP is much higher than in solution containing $(Mf)_4(Nf)_4PcCu$. The ratio of k_{eff} of these reactions is 46. If we consider that for PP γ = 0.77 [36], in accordance with Eq. (8) we obtain γ = 0.017 for the aggregated $(Mf)_4(Nf)_4PcCu$. Therefore, the photogeneration of $^1O_2$ with $(Mf)_4(Nf)_4$·PcCu aggregate is less effective than with the monomer.

Summarizing the main results, we can conclude that the aggregation is one of the most important factors in reducing the efficiency of photogeneration of $^1O_2$ by the $(Mf)_4(Nf)_4PcCu$ molecules.

EXPERIMENTAL

Compound $(Mf)_4(Nf)_4PcCu$ was synthesized and identified by the method [37] and subjected to further purification by column and thin layer chromatography on silica gel using as eluent first chloroform and then mixed solvent chloroform–methanol. Compounds $(t\text{-Bu})_4$PzcCu and PP were obtained and isolated according to the [38] and [39], respectively. The objects of study were the solutions of these compounds in benzene, benzene-d_6, pyridine, acetone, and DMF. Benzene of analytical grade, benzene-d_6 and acetone of high purity grade were used without further purification. Pyridine and DMF were purified according to procedures [12].

The time-resolved $^1O_2$ luminescence (1270 nm) was examined with a laser pulse fluorimeter LIF-200 equipped with a germanium photodetector PD-10 GA. The $^1O_2$ luminescence excitation was performed using the light from a nitrogen laser (wavelength 337 nm, pulse energy 20 uJ, pulse duration about 2 ns, pulse repetition frequency 30 Hz). In general, the resolution of the apparatus was no less than 2 μs. The $^1O_2$ luminescence separation was performed using an IKX-7 filter (thickness 5 mm) with the short-wavelength border of the transmission around 980 nm. The experimental setup is described in [40]. The $^1O_2$ lifetime ($\tau = 1/k$) was obtained from the luminescence decay curves in monoexponential approximation. The error in determining τ is about 5%.

Photochemical experiment was performed using highly stabilized light source of spectral complex KSVU-2 with the filament lamp OP-0.3-33. Photoexcitation of solutions was performed in the cell section of this complex through the condenser and filter KS-11 with short-wavelength transmission border 580 nm. These conditions allowed us to perform photoexcitation in the Q_{0-0} absorption bands of $(Mf)_4(Nf)_4PcCu$ and $(t\text{-Bu})_4$PzcCu with an optical density at the maxima $D \approx 0.4$. Tetracene oxidation with an initial concentration of about 7×10^{-5} M was monitored spectrophotometrically by the loss of absorption intensity at the peak of its first absorption band at 478, 475, and 472 nm in pyridine, benzene and acetone, respectively. Kinetic data were treated in the approximation of pseudo-first order reaction. The error in determining k_{eff} not exceeded 2%.

In experiments with aggregated $(Mf)_4(Nf)_4PcCu$ the irradiation was performed using a narrow-band light installation on Specol-10, containing a monochromator with a diffraction grating (651 lines per 1 mm) and a light source with a 30 W incandescent lamp.

Electron absorption spectra were recorded on a Specord-M40 spectrophotometer. Luminescence spectral measurements were performed using 1 cm quartz cells in the presence of air oxygen at about 295 K. In some cases the experiments were carried out at a specified temperature.

ACKNOWLEDGMENTS

The authors are grateful A.S. Semeikin, S.V. Efimova, and I.G. Abramov for presented compounds: PdMP, $(t\text{-Bu})_4$PzcCu, and (Mf)(Nf)PN.

REFERENCES

1. Mack, J. and Kobayashi, N., *Chem. Rev*., 2011, vol. 111, p. 281.
2. Pankratov, A.A., Yakubovskaya, R.I., Andreeva, T.N., Venediktova, Yu.B., Chissov, V.I., Butenin, A.V., Kogan, B.Ya., Vorozhtsov, G.N., Kaul', A.R., Rudoi, V.M., Dement'eva, O.V., Kartseva, M.E., and Fillipenko, M.A., *Ross. Bioterapevticheskii Zh*., 2009, vol. 8, p. 51.
3. RF Patent no. 2339414, 2008, *Byul. Izobret*., 2008, no. 33.
4. Iliev, V., Ilieva, A., and Bilyarska, L., *J. Mol. Catal., A: Chem*., 1997, vol. 126, p. 99.
5. Xiong, Z., Xu, Y., Zhu, L., and Zhao, J., *Environ. Sci. Technol*., 2005, vol. 39, p. 651.
6. Roeder, B., Naether, D., Lewald, T., Braune, M., Nowak, C., and Freyer, W., *Biophys. Chem*., 1990, vol. 35, p. 303.
7. Wilkinson, F., Helman, W.P., and Rose, A.B., *J. Phys. Chem. Ref. Data*, 1993, vol. 22, p. 113.
8. Bourdelande, J.I., Karzazi, M., Dicelio, L.E., Litter, M.I., Tura, G.M., Román, E.S., and Vinent, V., *J. Photochem. Photobiol*., 1997, vol. 108, p.273.
9. Venediktov, E.A. and Tulikova, E.Yu., *Zh. Obshch. Khim*., 2012, vol. 82, no. 2, p. 334.
10. DeRosa, M.S. and Crutchley, R.J., *Coordination Chem. Rev*., 2002, vols. 233–234, p. 351.
11. Venediktov, E.A., Tulikova, E.Yu., Efimova, S.V., and Koifman, O.I., *Dokl. Ross. Akad. Nauk*, 2010, vol. 435, p. 492.
12. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
13. Bayar, S., Dincer, H.A., and Gonca, E., *Dyes and Pigments*., 2009, vol. 80, p. 156.
14. Terenin, A.N., *Fotonika molekul krasitelei* (Photonics of Dye Molecules), Leningrad: Nauka, 1967.
15. Ghosh, A., Gossman, P.G., Aand lmlöf, J., *J. Am. Chem. Soc*., 1994, vol. 116, p., 1932.

16. Moons, H., Łapok Ł., Loas, A., Van Doorslaer, S., and Gorun, S.M., *Inorg. Chem*., 2010, vol. 49, p. 8779.
17. Day, P.N., Wang, Z., and Pachter, R., *J. Mol. Struct*., 1998, vol. 455, p. 33.
18. Monahan, A.R., Brado, J.A., and DeLuca, A.F., *J. Phys. Chem*., 1972, vol. 76, p., 1994.
19. Schutte, W.J., Sluyters-Rehbach, M., and Sluyters, J.H., *J. Phys. Chem*., 1993, vol. 97, p. 6069.
20. Dzhagarov, B.M., Gurinovich, G.P., Novichenkov, V.E., Salokhiddinov, K.I., Shul'ga, A.M., and Ganzha, V.A., *Khim. Fiz*., 1987, vol. 6, no. 8, p. 1069.
21. Ogilby, P.R. and Foote, C.S., *J. Am. Chem. Soc*., 1982, vol. 104, p. 2069.
22. Rodgers, M.A.J., *J. Am. Chem. Soc*., 1983, vol. 105, p. 6201.
23. Krasnovsky, A.A. Jr., Rodgers, M.A.J., Galpern, M.G., Rihter, B., Kenney, M.E., and Lukjanetz, E.A., *Photochem. Photobiol*., 1992, vol. 55, p. 691.
24. Nikolaitchik, A.V., Korth, O., and Rodgers, M.A.J., *J. Phys. Chem*., 1999, vol. 103, p. 7587.
25. Soldatova, A.V., Kim, J., Rosa, A., Ricciardi, G., Kenney, M.E., and Rodgers, M.A.J., *Inorg. Chem*., 2008, vol. 47, p. 4275.
26. Ermolaev, V.L., Bodunov, E.N., Sveshnikova, E.B., and Shakhverdov, T.A., *Bezyzluchatel'nyi perenos energii elektronnogo vozbuzhdeniya* (Radiationless Energy Transfer of Electron Excitation), Leningrad: Nauka, 1977.
27. Venediktov, E.A. and Krasnovskii, A.A., Jr., *Khimiya vysokikh energii* (Chemistry of High Enery), 1980, vol. 14.
28. Shmid, R. and Sapunov, V.N., *Neformal'naya kinetika* (Informal Kinetics), Moscow: Mir, 1985.
29. Bryk, D.B., Makitra , R.G., Pirig, Ya.N., and Stefanyg, Yu.V., *Zh. Prikl. Khim*., 1988, vol.61, p. 91.
30. Venedictov, E.A. and Tulikova, E.J., *Tetrahedron Lett*., 2003, vol. 44, p. 3215.
31. Venediktov, E.A. and Tulikova, E.Yu., *Zh. Fiz. Khim*., 2007, vol. 81, no. 8, p. 1375.
32. Firey, P.A. and Rodgers, M.A.J., *Photochem. Photobiol*., 1987, vol. 45, p. 535.
33. Krasnovskii, A.A. ml., Venediktov, E.A., and Chernenko, O.M., *Biofizika*, 1982, vol. 27, p. 966.
34. Rabinovich, I.B., *Vliyanie izotopii na fiziko-khimicheskie svoistva zhidkostei* (Effect of Isotopes on Physico-Chemical Properties of Liquids), Moscow: Nauka, 1968.
35. Zaidel', A.N. Ostrovskaya, G.V., and Ostrovskii, Yu.I., *Tekhnika i praktika spektroskopii* (Spectroscopy Technique and Practice), Moscow: Nauka, 1972.
36. Egorov, S.Yu., Krasnovskii, A.A. ml., Safronova, I.A., Bystrova, M.I., and Krasnovskii, A.A., *Dokl. Ross. Akad. Nauk*, 1988, vol. 299, p. 1266.
37. Fedotova, A.I., Maizlish, V.E., Shaposhnikov, G.P., Filimonov, S.N., and Abramov, I.G., *Zh. Obshch. Khim*., 2009, vol. 79, p. 846.
38. Gal'pern, M.G. and Luk'yanets, E.A., *Khim. Geterotsikl. Soed*., 1972, no. 6, p. 858.
39. Gurinovich, G.P., Sevchenko, A.N., and Solov'ev, K.N., *Spektroskopiya khlorofilla i rodstvennykh soedinenii* (Spectroscopy of Chlorophyll and Related Compounds), Minsk: Nauka i Tekhnika, 1968.
40. Venediktov, E.A. and Tokareva, O.G., *Kinetika i Kataliz*, 2000, vol. 41, p. 186.