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Solvent Effect on the Photogeneration of Singlet Molecular Oxygen by Copper Tetra(*tert*-butyl)phthalocyanine

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Abstract—The photogeneration of the singlet molecular oxygen ($^1O_2$) by copper tetra(4-*tert*-butyl) phthalocyanine in organic solvents of different nature was substantiated. The apparent quantum yields of $^1O_2$ in benzene and pyridine were determined. The data obtained indicate an influence of the coordinating properties of the solvent on the $^1O_2$ yield. However, this factor is not “critical” as in the case of photogeneration of $^1O_2$ by copper tetra(5-*tert*-butylpyrazino)porphyrazine.

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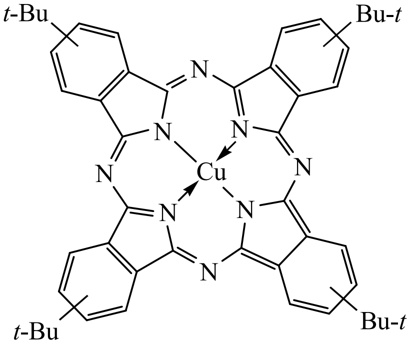
The interest in the photogeneration of singlet molecular oxygen ($^1O_2$, $^1\Delta_g$) by phthalocyanines is due to their application in a number of photochemical and photomedical technologies [1–4].

A photogeneration of $^1O_2$ by phthalocyanines proceeds as a quenching of their excited triplet states by O_2 ($^3\Sigma_g^-$) molecules through the mechanism of energy transfer [2, 5], and depends on both intramolecular (the macroheterocycle structure, the central atom nature) and external (solvation, aggregation) factors. As to copper phthalocyanine, the published data on the effectiveness of this process are contradictory. Usually this situation is attributed to a tendency of copper phthalocyanine to aggregation (see, for example, [2]). However, in [6] by an example of the $^1O_2$ photogeneration by copper tetra(5-*tert*-butylpyrazino)porphyrazine it has been shown that the important external factors affecting the yield of $^1O_2$ may include the coordinating ability of the solvent. This effect is apparently due to the competitive quenching of excited triplet molecules of the sensitizer by the solvent due to its axial coordination [7–10].

The purpose of this study is to investigate the influence of the coordinating ability of solvent on the photogeneration of $^1O_2$ by copper phthalocyanine by an example of behavior in the process of copper tetra-(4-*tert*-butyl)phthalocyanine [(*t*-Bu)$_4$PcCu], the most convenient object for this purpose owing to its good solubility in many organic media.



The electron absorption spectrum of the (*t*-Bu)$_4$PcCu solutions is typical of most metallphthalocyanines, with an intense *Q*-band at 670–680 nm [11, 12]. The band position depends on the solvent. In benzene, the band maximum (λ_Q) occurs at 677.5 (±0.5) nm, and its decimal molar absorption coefficient is equal to 1.7×10^5 ($\pm0.2\times10^5$) cm^{-1} mol^{-1} l. With the increase in the solvent refractive index, the λ_Q value undergoes a red shift (Fig. 1). These data can be interpreted within the framework of universal solvation of (*t*-Bu)$_4$PcCu [13].

A good qualitative example of photochemical activity of (*t*-Bu)$_4$PcCu is its ability to sensitize the photooxidation of the $^1O_2$ acceptors. The results of one such experiment on the sensitized photobleaching of tetracene solution in pyridine are shown in Fig. 2. Similar results were obtained with the other, less basic, solvents. Accounting for the oxidative nature of this process, whose mechanism has been substantiated in detail in [14–16], these data allow a preliminary

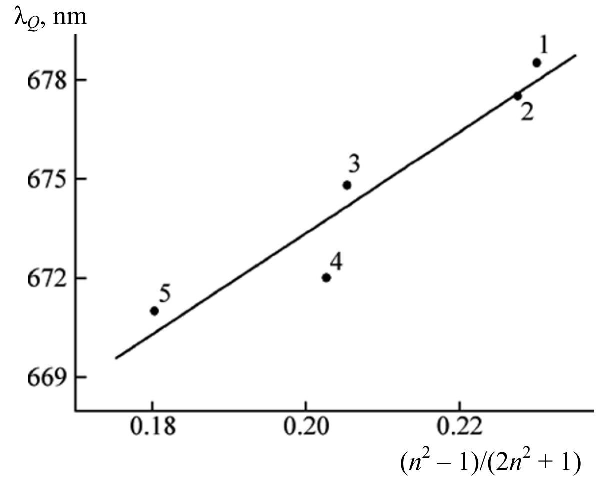


Fig. 1. The dependence of the Q-band peak position in the electron absorption spectrum of copper tetra(4-*tert*-butyl)-phthalocyanine in a solution vs. the refractive index of the solvent: (1) pyridine, (2) benzene, (3) DMF, (4) 1,4-dioxane, and (5) acetone.

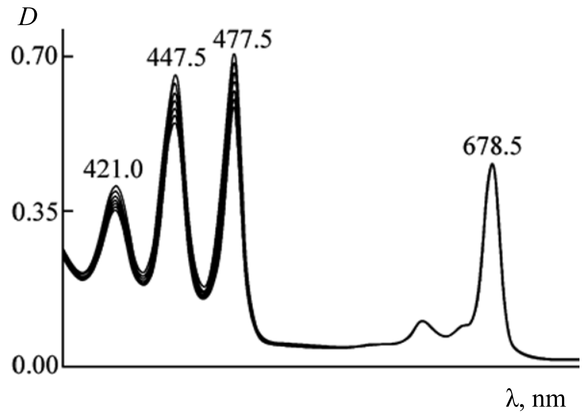


Fig. 2. Changes in the electron absorption spectrum of tetracene solution in pyridine at the photooxidation sensitized with copper tetra(4-*tert*-butyl)phthalocyanine.

conclusion on the ability of $(t\text{-Bu})_4$PcCu to the photogeneration of $^1O_2$ in the solution regardless of the solvent nature. In addition, we obtained a direct evidence of the photogeneration of $^1O_2$ in solution of $(t\text{-Bu})_4$PcCu. We found that the $(t\text{-Bu})_4$PcCu excitation in solution results in a two-component afterglow in the region of the $^1O_2$ radiation (1270 nm). The intense luminescence component is characterized by a lifetime of less than 10 μs, that is a typical lifetime of excited triplet $(t\text{-Bu})_4$PcCu [2] molecules rather than $^1O_2$ in the investigated media [17–22]. Since the $(t\text{-Bu})_4$PcCu fluorescence is not specific [2, 11], the observed short-living luminescence retaining its high level also in the absence of oxygen can be attributed to the $(t\text{-Bu})_4$PcCu phosphorescence, whose peak lies in the region of 1065–1100 nm [2, 11]. The level of long-living components of the glow is associated with solvent and with the content in solution of atmospheric oxygen. In nitrogen atmosphere, this emission is absent. An estimate shows that in benzene in the presence of air its lifetime is about 30 μs being of the same order as that of the $^1O_2$ luminescence [17–22]. In addition, in deuterobenzene it increases (Fig. 3) reaching typical for the $^1O_2$ luminescence value 5×10^{-4} s. A similar value was obtained for a solution of the palladium mesoporphyrin-IX dimethyl ether complex (PdMP-IX), a typical $^1O_2$ photosensitizer (Fig. 3) [23]. In specially arranged experiments we found also that such luminescence in the $(t\text{-Bu})_4$PcCu and PdMP-IX solutions is not observed in nitrogen atmosphere, and it appears only after saturation of the solution with the atmospheric oxygen. Hence, it is clear that long-living component of the observed luminescence is connected with the emission by $^1O_2$. However, measuring the latter in nondeuterated environments, especially in pyridine, was complicated due to the strong overlapping with the $(t\text{-Bu})_4$PcCu phosphorescence. In this regard, direct measurement of the quantum yield of $^1O_2$ (γ_Δ) were performed only in deuterobenzene where the $^1O_2$ luminescence recording is the most reliable.

Before determination of γ_Δ we studied quenching of $^1O_2$ by $(t\text{-Bu})_4$PcCu molecules. The latter is extremely important to optimize conditions for measuring γ_Δ, particularly in deuterated media. For this purpose we studied the kinetics of the $^1O_2$ luminescence decay in deuterobenzene in the presence of $(t\text{-Bu})_4$PcCu at various concentrations. Since the luminescence intensity of $^1O_2$ in $(t\text{-Bu})_4$PcCu solution was relatively low, to increase the resolution of the method we carried out the experiments in the presence of anthracene as an auxiliary $^1O_2$ photosensitizer (γ_Δ is about 0.83 in air-saturated solution [21]). As seen from Fig. 4, the rate constant for the $^1O_2$ luminescence decay ($k = 1/\tau$) increases linearly with increasing $(t\text{-Bu})_4$PcCu concentration. These findings suggest enhancement of nonradiation deactivation of $^1O_2$ in solution. This dependence is described by the Stern–Volmer equation (1):

$$1/\tau = 1/\tau_0 + k_Q[Q], \qquad (1)$$

where τ_0 and τ are the $^1O_2$ luminescence lifetimes in pure solvent and in the presence of a quencher, k_Q is the bimolecular quenching rate constant. Processing

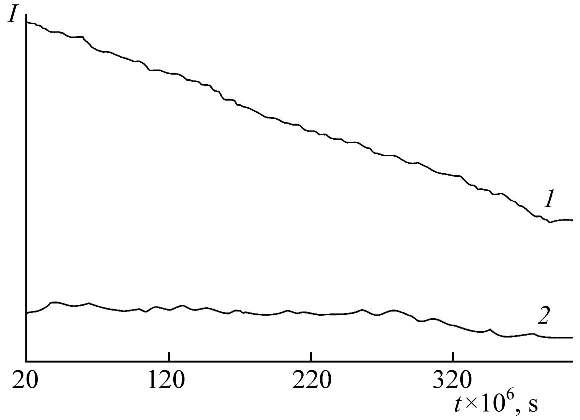


Fig. 3. The curves of decay of the sensitized $^1O_2$ photoluminescence in solutions of (*1*) palladium mezoporphyrin-IX dimethyl ether and (*2*) copper tetra(4-*tert*-butyl)-phthalocyanine.

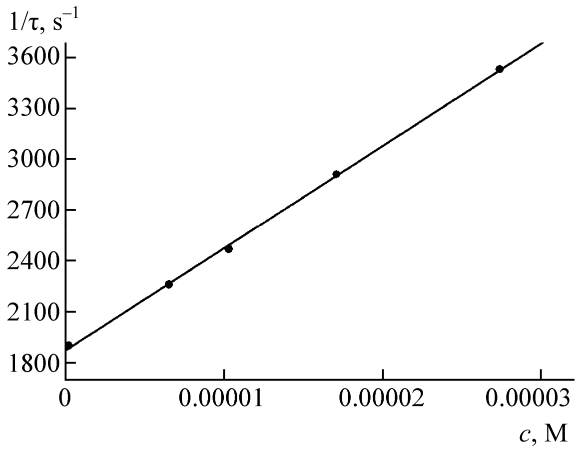


Fig. 4. The dependence of the reciprocal value of lifetime of the sensitized $^1O_2$ photoluminescence in benzene-d_6 on the concentration of copper tetra(4-*tert*-butyl)phthalocyanine (sensitizer anthracene).

data with Eq. (1) gives for (t-Bu)$_4$PcCu $k_Q = (6.2\pm0.2)\times 10^7$ mol^{-1} l s^{-1}. The obtained value is quite high in the series of related compounds [24, 25] . Under these conditions (t-Bu)$_4$PcCu showed a high photochemical stability. Consequently, we can conclude on the predominantly physical nature of the $^1O_2$ quenching. In view of these results, for measureming γ_Δ was chosen a working concentration of (t-Bu)$_4$PcCu to which corresponded optical density of the solution at the photoexcitation wavelength (337 nm) equal to 0.45.

Measurement of luminescence γ_Δ was carried by a relative method using PdMP-IX as a reference (γ_Δ = 1.0 [23]). Figure 3 shows the $^1O_2$ luminescence decay curves in the solutions of (t-Bu)$_4$PcCu and PdMP-IX in deuterobenzene recorded under equal other conditions. In both cases, the luminescence decay is exponential, and its intensity is significantly higher in the solution of PdMP-IX than of (t-Bu)$_4$PcCu. The ratio of the initial $^1O_2$ luminescence intensity deter-mined from the curves of luminescence decay in the monoexponential approximation, is 4.8. According to [21], this value should be proportional to the ratio of initial $^1O_2$ concentrations and, consequently, to the ratio of γ_Δ in these solutions. In view of the above data, from the found ratio follows that the experimental γ_Δ value for (t-Bu)$_4$PcCu is equal to 0.21± 0.03.

To assess the effect of solvent on γ_Δ, we considered a photogeneration of $^1O_2$ by the (t-Bu)$_4$PcCu molecules in a limited number of solvents: in benzene and most strongly coordinating pyridine [26]. For the reasons stated above, to solve this problem we used chemical data based on the analysis of the kinetics of the tetracene photooxidation sensitized by the (t-Bu)$_4$PcCu molecules.

Figure 5 shows the change in the tetracene optical density at a wavelength of 477 nm for the photooxidation sensitized by (t-Bu)$_4$PcCu in benzene and pyridine. From the results obtained it is evident that the reaction rate of tetracene photooxidation in pyridine is higher than in benzene. The data obtained can be approximated by straight lines also in the coordinates ln (D_0/D_t)–t (where D_0 and D_t are the initial and current densities, respectively, of the tetracene optical absorption band). The slope the lines gives the values of effective reaction rate constant (k_{ef}) in pyridine and benzene, as well as their ratio, which is equal to 1.4. To use this ratio to calculate γ_Δ the differences in τ_0 [17–22] and in the rate constant of tetracene photooxidation (k_r) [27] connected with the solvent properties should be taken into account. For this purpose we consider the tetracene photooxidation reaction kinetics in more detail.

The sensitized photooxidation of tetracene can be described taking into account the photophysical properties of $^1O_2$ and (t-Bu)$_4$PcCu as in the following scheme:

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

$${}^3S + O_2\,({}^3\Sigma_g^-) \rightarrow S + {}^1O_2\,({}^1\Delta_g),\ k_{et},$$

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

$${}^1O_2 + S \rightarrow O_2 + S \text{ and its oxidation product, } k_Q,$$

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

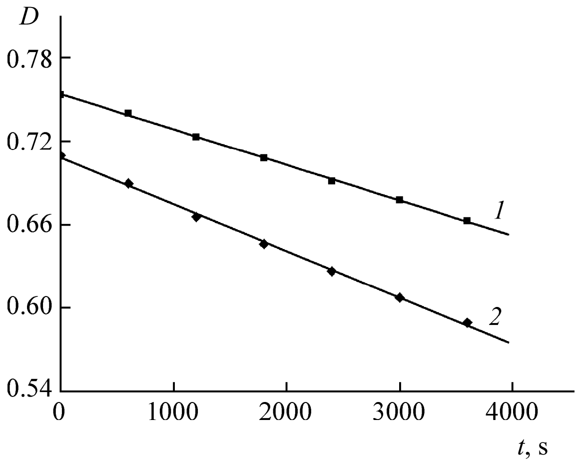


Fig. 5. Change in optical density of tetracene at λ ~477 nm at its photooxidation in (*1*) benzene and (*2*) pyridine sensitized with copper tetra(4-*tert*-butyl)phthalocyanine.

Here, S, ^{1}S, and ^{3}S are ground state and excited singlet and triplet states of (t-Bu)$_4$PcCu, *Solv* means solvent, T is tetracene; k_{et} is the rate constant of energy transfer from ^{3}S to O$_2$ ($^3\Sigma_g^-$); $k_d = 1/\tau_0$ is the rate constant of the ^{1}O$_2$ deactivation in the solvent.

Applying the principle of quasi-stationary approximation, we can write the equation for the overall reaction rate:

$$-d[T]/dt = \frac{k_r \gamma_\Delta [T] I}{k_d + k_Q[S] + k_r[T]}, \qquad (2)$$

where [S] and [T] are concentrations of (t-Bu)$_4$PcCu and tetracene, respectively; $I = I_0(1-10^{-D})$ is the intensity of the absorbed light; I_0 is the intensity of exciting light; D is the optical density of the solution at the excitation wavelength; t is the irradiation duration.

Provided $k_d > (k_Q \cdot [S] + k_r \cdot [T])$, expression (2) takes the following form:

$$-d[T]/dt = k_r \gamma_\Delta \tau_0 I [T]. \qquad (3)$$

Since the dependences in the coordinates ln (D_0/D_t)–t are linear, the rate of reaction can be written in the form of Eq. (4) [28]:

$$-d[T]/dt = k_{ef}[T]. \qquad (4)$$

From Eqs. (3) and (4) follows that

$$k_{ef} = k_r \gamma_\Delta \tau_0 I. \qquad (5)$$

Since the electron absorption spectra of (t-Bu)$_4$PcCu in benzene and pyridine are virtually identical (Fig. 1), the ratio of γ_Δ for these solvents can be found from Eq. (6):

$$\gamma_{\Delta,\,py}/\gamma_\Delta = \frac{\alpha}{\beta\delta}, \qquad (6)$$

where α, β, and δ are the ratios of $k_{ef,py}/k_{ef}$, $k_{r,py}/k_r$, and $\tau_{0,py}/\tau_0$, respectively, and the subscript (py) denotes the parameters in pyridine. The value of τ_0 necessary for the calculation of $\gamma_{\Delta,py}/\gamma_\Delta$ we measured by the method of time-resolved ^{1}O$_2$ luminescence with anthracene as a sensitizer. The values of τ_0 found in this way were 30.3 and 17.2 μs in benzene and pyridine, respectively. According to [27], the value of k_r in pyridine is 3.7 times higher than in benzene. Based on the results of [14, 16], we got for k_r in benzene the rate constant of ^{1}O$_2$ luminescence quenching by tetracene equal to 1.4×10^7 mol^{-1} l s^{-1} [28], and for pyridine we obtain: $k_r = 5.2\times10^7$ mol^{-1} l s^{-1}. Finally, we have $\gamma_{\Delta,py}/\gamma_\Delta$ = 0.67. Hence, using for (t-Bu)$_4$PcCu the γ_Δ value in deuterobenzene, we obtain $\gamma_{\Delta,py} \approx 0.14$. As seen from these data, in a strongly coordinating solvent, pyridine, the efficiency of the photogeneration of ^{1}O$_2$ molecules by (t-Bu)$_4$PcCu is reduced, like in the case of copper tetra(5-*tert*-butylpyrazino)porphyrazine [6], but not significantly.

Thus, these results confirm the ability of (t-Bu)$_4$PcCu to sensitize ^{1}O$_2$ photogeneration. In a strongly coordinating solvent the yield of ^{1}O$_2$ decreases. However, this effect is negligible. Thus the photo-chemical behavior of (t-Bu)$_4$PcCu is more favorable as compared with that of copper tetra(5-*tert*-butylpyrazino)porphyrazine in a similar process [6], which can be attributed to the weak influence of the donor solvent on the lifetime of the (t-Bu)$_4$PcCu "triplet" state.

EXPERIMENTAL

The compounds (t-Bu)$_4$PcCu and PdMP-IX were prepared in the Ivanovo State University of Chemistry and Technology. (t-Bu)$_4$PcCu was additionally purified by column and then thin layer chromatography on silica gel using as eluent chloroform and methanol. PdMP-IX was purified by column chromatography on alumina (Grade II activity), using as eluent benzene. The objects of study were solutions of these compounds in benzene, deuterobenzene, 1,4-dioxane, DMF, acetone, and pyridine, which were prepared in accordance with common procedures [29].

To measure the ^{1}O$_2$ luminescence, we used a laser pulse fluorimeter LIF-200 equipped additionally with a germanium photodetector PD-10 HA and operational amplifier, as described in [30]. The luminescence was measured using a glass filter IKS-7 (short-wave boundary transmission at 980 nm) using a nitrogen laser as a source of photoexcitation (wavelength 337 nm, pulse energy 20 μJ, pulse duration 2 ns, repetition rate 30 Hz). In the installation thus designed the time resolution is defined by the operational amplifier; it was 2 μs or better. The measurement of luminescence started at 20 μs after photoexcitation. We used the standard method of processing the luminescence decay curves based on the exponential dependence, which allowed us to obtain the initial luminescence intensity at $t = 0$ and the lifetime of $^1O_2$ τ_Δ with an error of only 5%. The $^1O_2$ quantum yield γ_Δ in benzene-d_6 was determined by a relative method by comparing the initial intensity of luminescence in solutions $(t\text{-Bu})_4$PcCu ($c = 1\times10^{-5}$ M) and PdMP-IX ($c = 3.3\times10^{-5}$ M) at the optical density values at the excitation wavelength $D_{337} = 0.45$. In the experiments on the quenching of $^1O_2$ luminescence, to increase the resolution of the installation we used the combined photosensitizer $(t\text{-Bu})_4$PcCu + anthracene (5×10^{-5} M).

In photochemical experiments we used a highly stable light source of spectral complex KSVU-2 with OP-0.3-33 incandescent lamp. The excitation light passed through the condenser and the boundary glass filter KS-11 with short-wavelength transmission border 580 nm. These conditions allowed us to carry out the excitation of the solution in the region of $(t\text{-Bu})_4$PcCu Q-band ($D = 0.4$). The irradiation was performed using a glass cell 1 cm thick. The tetracene oxidation at the initial concentration in solution of about 7×10^{-5} M was monitored spectrophotometrically by the decrease of absorption at the peak of the its first absorption band at 471–478 nm, depending on the nature of the solvent. We used the standard treatment of kinetic data in the approximation of the reaction pseudo-first order. The error in determining k_{ef} was less than 5%.

Electron absorption spectra were recorded on a Specord-M40 double-beam spectrophotometer.

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