

Kinetic Measurements of Singlet Oxygen Phosphorescence in Hydrogen-Free Solvents by Time-Resolved Photon Counting

A. A. Krasnovsky^{1,2,a*}, A. S. Benditkis¹, and A. S. Kozlov¹

¹Federal Research Center of Biotechnology, A. N. Bach Institute of Biochemistry,
Russian Academy of Sciences, 119071 Moscow, Russia

²M. V. Lomonosov Moscow State University, Faculty of Biology, 119234 Moscow, Russia

^ae-mail: phoal@mail.ru

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Abstract—Solvents lacking hydrogen atoms are very convenient models for elucidating the properties of singlet oxygen, since the lifetime of singlet oxygen in these solvents reaches tens milliseconds. Measuring intrinsic infrared (IR) phosphorescence of singlet oxygen at 1270 nm is the most reliable method of singlet oxygen detection. However, efficient application of the phosphorescence method to these models requires an equipment allowing reliable measurement of the phosphorescence kinetic parameters in the millisecond time range at low rates of singlet oxygen generation, which is a technically difficult problem. Here, we describe a highly sensitive LED (laser) spectrometer recently constructed in our laboratory for the steady-state and time-resolved measurements of the millisecond phosphorescence of singlet oxygen. In the steady-state mode, this spectrometer allows detection of singlet oxygen phosphorescence upon direct excitation of oxygen molecules in the region of dark-red absorption bands at 690 and 765 nm. For kinetic measurements, we used phenalenone as a photosensitizer, microsecond pulses of violet (405 nm) LED for excitation (irradiance intensity, <50 μW/cm²), a photomultiplier and a computer multichannel scaler for time-resolved photon counting. The decays of singlet oxygen in air-saturated CCl₄, C₆F₆, and Freon 113 and quenching of singlet oxygen by phenalenone and dissolved molecules of triplet oxygen were measured. The relative values of the radiative rate constants of singlet oxygen in these media were determined. The results were compared with the absorption coefficients of oxygen measured by our group using the methods of laser photochemistry. Critical discussion of the obtained results and the data of other researchers is presented.

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Photosensitized IR phosphorescence of singlet (${}^1\Delta_g$) oxygen (1O_2) (Fig. 1) is widely used for investigating the properties of singlet oxygen and photodynamic photosensitizers in connection with numerous theoretical and applied problems of photophysics, photochemistry, and photomedicine [1, 2].

The first measurements of singlet oxygen phosphorescence in hydrogen-free solvents (CCl₄, Freon 113, and CS₂) were performed by one of the authors of this paper in 1976–1977 ([3] and references therein). Initially, the phos-

phorescence had been detected using spectrometers with mechanical phosphoroscopes and photodetector systems based on cooled photomultiplier tubes with the spectral response S-1 (FEU-83). The construction and the principles of operation of these spectrometers have been described in detail in [3, 4] and in following publications ([1] and references therein). These devices allowed measurements of excitation spectra, emission spectra, and lifetimes of phosphorescence of ≥ 0.7 ms. It was found that the lifetime of singlet oxygen (τ_Δ) in these solvents is > 20 ms [3], which is much greater than the value of ~ 1 ms previously obtained using singlet oxygen traps [5]. Detailed studies of phosphorescence in CCl₄ led to the conclusion that τ_Δ decreases with the increase in the concentration of photosensitizer pigments due to the quenching of 1O_2 by non-excited pigment molecules. The maximal $\tau_\Delta \sim 30$ ms

Abbreviations: cw, continuous wave (waveform); DPBF, 1,3-diphenylisobenzofuran; Freon 113, 1,1,2-trifluoro-1,2,2-trichloroethane; IR, infrared; LED, light-emitting diode; TPP, tetraphenylporphyrin.

* To whom correspondence should be addressed.

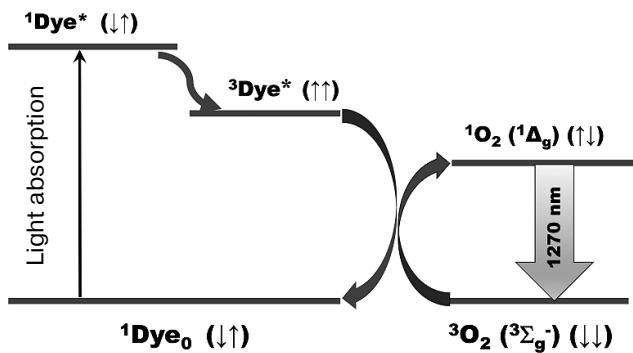


Fig. 1. Mechanism of photosensitized IR phosphorescence of singlet oxygen. $^1\text{Dye}_0$, $^1\text{Dye}^*$ and $^3\text{Dye}^*$ are molecules of photosensitizer pigments in the ground and excited singlet and triplet states; $^3\text{O}_2$ and $^1\text{O}_2$ are oxygen molecules in the ground and singlet states.

was obtained in pheophytin *a* solution (1 μM) in CCl_4 additionally purified by double distillation at the excitation light power density of 300–700 $\mu\text{W}/\text{cm}^2$. Similar lifetime was observed in the commercial samples of high-purity ($\geq 99.5\%$) CCl_4 without additional distillation [3]. Under these conditions, no destruction of the photosensitizers was observed within the period of irradiation. Quenching of $^1\text{O}_2$ by air oxygen was not studied in these experiments.

Therefore, it was found that the solvents, molecules of which do not have hydrogen atoms, are exceptionally convenient models for elucidating the properties and reactivity of singlet oxygen by the phosphorescence method. Using CCl_4 and $\tau_\Delta \sim 30$ ms, the rate constants of $^1\text{O}_2$ quenching have been measured for many biologically important compounds including porphyrins, chlorophylls, carotenoids, water, 1,4-diazobicyclo[2.2.2]octane, α -tocopherol, etc. The obtained rate constants coincided with those measured by other methods, which confirms that the above τ_Δ value obtained by the phosphorescence method was correct ([1, 3] and references therein).

In 1979, a group from the Institute of Physics, Minsk, constructed a spectrometer for the time-resolved phosphorescence measurements after irradiation with short pulses of lasers or flash lamps using a photomultiplier FEU-83 as a photodetector and a storage oscilloscope [6–8]. In particular, they observed biphasic nonexponential decay of oxygen phosphorescence in CCl_4 upon excitation with high-power laser pulses. The authors proposed that this effect was due to the recombination of $^1\text{O}_2$ molecules occurring at high $^1\text{O}_2$ concentrations. The decay became exponential with the lifetime of 30 ms [6] with the decrease in the pulse power to the minimal value (7 mJ). Therefore, the authors arrived to the τ_Δ value similar to that obtained in our experiments. In solvents containing hydrogen atoms, the phosphorescence lifetime decreased to 10–100 μs [6–8].

In 1987, Schmidt and Brauer constructed a setup with a mercury lamp for phosphorescence excitation and

a germanium photodiode for phosphorescence detection. The exciting light was passed through a mechanical chopper to obtain light pulses with 10 ms duration and 2.5 Hz repetition rate. The time constant of the photodiode and its amplifying system was 5.1 ms. To eliminate distortion of the kinetic curves by the instrument hardware function, the signal was processed with a computer program to account for a slow response of the photodetector system. Hence, the resulting curves depended on the efficiency of the applied software. Using this setup, the following values of τ_Δ were obtained: 87 ms in CCl_4 , 99 ms in Freon 113, and 24 ms in hexafluorobenzene [9, 10].

In parallel, Losev et al. reported the results of time-resolved and steady-state measurements of τ_Δ in CCl_4 and CS_2 using photodiodes as photodetectors [11, 12]. The authors found that at the minimal power of excitation light and the minimal photosensitizer (Pd-mesoporphyrin) concentration, τ_Δ was ~ 30 ms at room temperature in both solvents. At lower temperature (193 K), a 30% increase in the lifetime was observed. The discrepancy with the data of the Schmidt's group was explained by a higher degree of solvent purification in Schmidt's experiments. It is of interest that some authors [6, 9–12] raised the question of the involvement of air oxygen in the quenching of singlet oxygen phosphorescence. However, they all came to the conclusion that this process is not efficient.

In 1991, Schmidt's group improved the procedure of data processing and established that after removal of air, the phosphorescence lifetime increased by 1.5–2 times. Increasing the concentration of oxygen to a partial pressure of 1 bar decreased τ_Δ to 10–20 ms [13]. It was concluded that air oxygen reduces the lifetime of singlet oxygen in aerated solutions. In aerated CCl_4 , the lifetime of singlet oxygen was 59 ± 5 ms, which is 1.5 times less than the value reported by this group earlier (87 ms) [9, 10]. Smaller τ_Δ values were also obtained in Freon 113 (72 ms) and hexafluorobenzene (21 ms) [13]. The same values were reported in the review paper of Schweitzer and Schmidt [14] with no clear explanation of the reasons for the discrepancy with the earlier data [9, 10]. Until now, these experiments have not been repeated by anyone, although it is obvious that their verification is of fundamental importance.

More recently, kinetic parameters of singlet oxygen phosphorescence in CCl_4 were investigated by several groups. Bagrov et al. used a flash lamp, a germanium photodetector, and fullerenes C_{70} and C_{60} as photosensitizers. At room temperature and excitation power density of 10 mJ/cm^2 , τ_Δ varied between 22 and 55 ms [15, 16]. In agreement with Salokhiddinov et al. [6] and Losev et al. [11, 12], the authors observed that the phosphorescence lifetime in CCl_4 decreased with the increase in the excitation power and solution temperature.

Wang et al. reproduced these experiments using a Hamamatsu IR photomultiplier. At the lowest power of laser pulses (10 mJ), the lifetime in C_{60} (200 μM) solution

in CCl_4 was 16–17 ms [17]. Simultaneously, they observed oxygenation of C_{60} and quenching of $^1\text{O}_2$ by the oxygenation products. Hasebe et al. [18] used Pt(II)-meso-tetra(pentafluorophenyl)porphin (7.4 μM) as a sensitizer and pulses of Nd:YAG laser (8 ns, 10 Hz) for excitation. The obtained τ_Δ value in CCl_4 was 5.04 ms. Extrapolation of the data to the photosensitizer zero concentration leads to $\tau_\Delta \sim 14$ ms (no information about the pulse energy was provided).

The discrepancies in the determined values of the singlet oxygen lifetime in hydrogen-free solvents have caused doubts in the reliability of the used model systems. As a result, some researchers question or even refuse to use them. To obtain reliable information, one needs instrumentation that could measure the stationary intensity and temporal parameters of phosphorescence under a very low excitation power, at which the nonlinear and destructive effects described above are excluded. The first spectrometers developed in our laboratory [3] have solved this problem in general. Although they provided the measurements of the spectral parameters and average lifetime of phosphorescence, these devices did not allow recording the phosphorescence decay traces.

By the present time, the technique for detection of singlet oxygen phosphorescence has been significantly improved. The instruments with time-resolved photon counting are the most effective for kinetic measurements. The first setup of this type designed for measurement of singlet oxygen phosphorescence with microsecond resolution was constructed in our laboratory [19, 20]. Later, its nanosecond modification operating in the regime of time-correlated single photon counting was constructed [21]. At present, such devices are widely used by many researchers ([1, 2] and references therein). However, as mentioned above, all of them have been designed for studying rapidly decaying delayed light emissions.

A new setup recently constructed by our group and briefly described in our preliminary publications [22, 23] has been specially designed for investigation of slowly decaying delayed light emissions using the time-resolved photon counting technique. Here, we used this setup for kinetic measurements of photosensitized phosphorescence of singlet oxygen in solvents weakly deactivating $^1\text{O}_2$ upon excitation by LED pulses, whose energy is 3–4 orders lower than in all the above-mentioned papers employing the pulsed technique. We also demonstrated that this device can be used to record phosphorescence of singlet oxygen in pigment-free solvents occurring upon direct excitation of oxygen by dark-red light that corresponds to the oxygen absorption bands at 690 and 765 nm.

MATERIALS AND METHODS

The functional layout of the new spectrometer is shown in Fig. 2. For the steady-state luminescence

measurements, a light-emitting diode (LED) was used with the emission maximum at 399 nm and a half-width of 14 nm (Polironik, Russia). The photodiode radiation was focused into a 5-mm spot on the surface of a quartz cell containing the analyzed solution. The intensity of the exciting light was monitored by a ThorLabs PM-100D power meter with a S120VC sensor head (Thorlabs, USA). In separate experiments, diode lasers with the emission maxima of 765 nm (half-width, 2 nm; power, up to 1 W) (LAMI Helios, Russia) and 690 nm (half-width, 3 nm; power, up to 5 W) (Milon-Lakhta, Russia) were used. The laser radiation power was measured using an Ophir ORION-TH instrument with a 20C-SH sensor head (Ophir, Israel). The phosphorescence of singlet oxygen was measured at a 90° angle with a cooled photomultiplier FEU-112 (S1 spectral response) (Ekran, Russia) through IR filters transmitting IR light at $\lambda \geq 950$ nm and one of three interchangeable interference light filters with the transmission peaks at 1230, 1270, and 1310 nm and a half-width of 10 nm. The steady-state phosphorescence intensity was measured with a digital high-resistance millivoltmeter (Econix-Expert, Russia); the obtained data were processed with a computer.

For kinetic measurements, a pulse LED (Polironik) with an operating unit (Alcom Medica, Russia) was used for sample irradiation with 405-nm monochromatic light (band half-width, 14 nm) with a pulse duration of 10 μs and pulse repetition rate of 5 or 10 Hz. The average power of the exciting light was 15–30 μW ; the energy of one pulse was 3 μJ . The photomultiplier signal was sent through a preamplifier to a computer board that worked in two modes – time-resolved multichannel photon counting or time-resolved single photon counting (Parsek, Russia). The time constant of the recording system was ~ 10 ns. The counting board was started by an additional pulse of the operating unit synchronized with the LED pulse. The counting board divided the time interval between the pulses into 1024 channels; the kinetic curves were obtained by accumulating the photopulses in each channel. In this work, we did not use the method of time-correlated single photon counting.

The analyzed solution (1.5 ml) was placed in a 1-cm quartz cell. Phenalenone (perinaphthenone, 1H-phenalen-1-one) or tetraphenylporphyrin (Aldrich, EU) were used as photosensitizers. The concentration of phenalenone was calculated using the molar absorption coefficient at the absorbance maximum ($9700 \text{ M}^{-1}\cdot\text{cm}^{-1}$) [24]. In some experiments, the singlet oxygen trap 1,3-diphenylisobenzofuran (DPBF) was used (Acros Organics, Belgium). CCl_4 (Labtech, Russia), hexafluorobenzene (Piminvest, Russia), and Freon 113 (1,1,2-trifluoro-1,2,2-trichloroethane) (Ruskhimprom, Russia) with $\geq 99.5\text{--}99.8\%$ purity were used as solvents. The absorption spectra were recorded with an SF-56 spectrophotometer (LOMO Spektr, Russia).

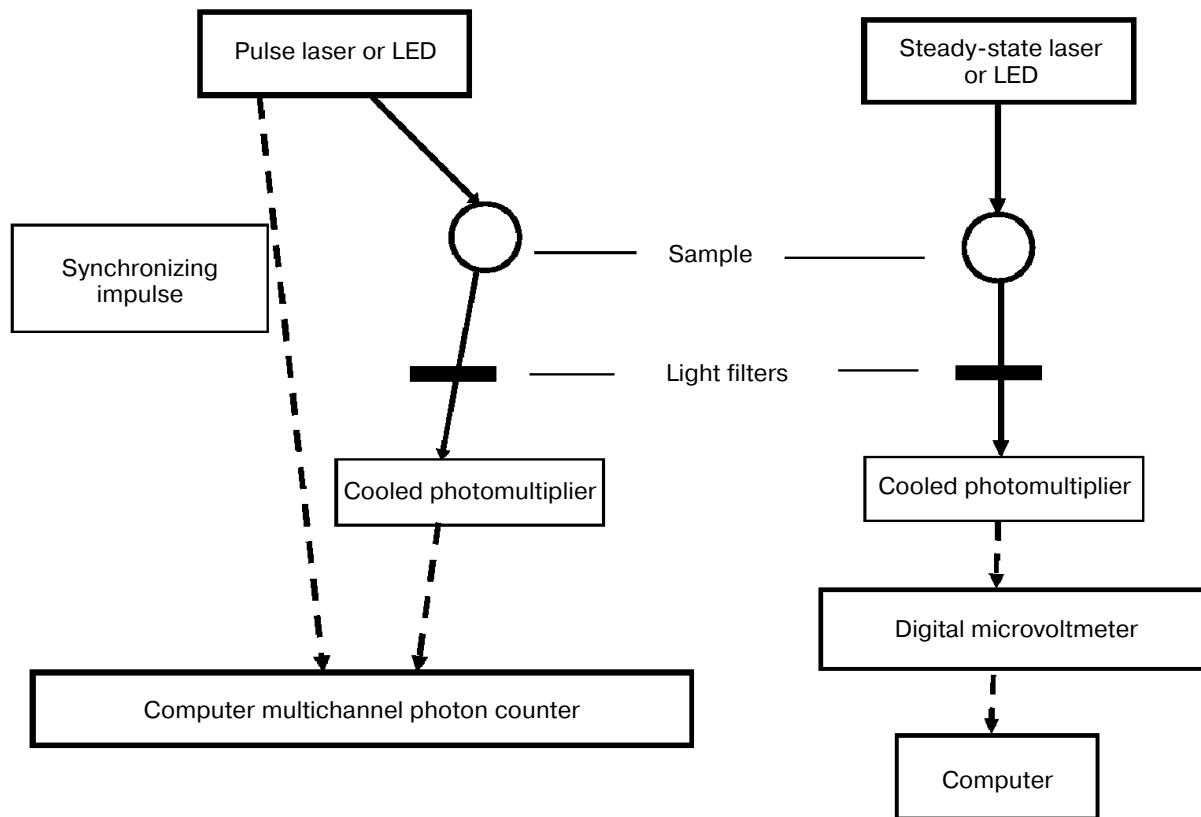


Fig. 2. Block diagram of laser (LED) spectrometers for stationary and time-resolved measurements of singlet oxygen IR phosphorescence (1270 nm) in the solvents that weakly deactivate singlet oxygen.

RESULTS AND DISCUSSION

Steady-state measurements. Measurements of the steady-state photomultiplier signal in the direct photocurrent registration mode showed that illumination of air-saturated solutions of phenalenone or tetraphenylporphyrin in CCl_4 , hexafluorobenzene, or Freon 113 with continuous or pulsed LED radiation at ~ 400 nm resulted in ${}^1\text{O}_2$ phosphorescence with the spectral maximum at 1270 nm (Fig. 3). Addition of 50% acetone led to a sharp decrease in the ${}^1\text{O}_2$ lifetime and weakened the photosensitized phosphorescence ~ 500 times (Fig. 3). The IR phosphorescence in the air-saturated solvents was also observed in the absence of photosensitizers upon irradiation with LEDs at 400 nm [16, 25, 26]. However, the quantum efficiency of this phosphorescence was several orders of magnitude lower than in the photosensitizer-containing solutions. Therefore, it did not affect the overall intensity of photosensitized phosphorescence.

In the stationary mode, the spectrometer allows the recording of the oxygen phosphorescence upon irradiation of pigment-free solutions with 765- and 690-nm laser diodes (1-3 W), i.e., at the wavelengths corresponding to the oxygen absorption bands. The ability of a

765-nm laser to excite oxygen phosphorescence has already been described by Ogilby's group [27] and in our previous publications [22, 23]. In this work, we report also the excitation of oxygen by irradiation at 690 nm (1-3 W) (Fig. 3) (see [23] for preliminary data).

Acetone quenched the phosphorescence (Fig. 3): the phosphorescence intensity in the presence of 50% acetone corresponded to the level of the intrinsic luminescence of the quartz cell. It should be noted that Fig. 3 shows the phosphorescence intensity curves normalized to 1. In reality, the quantum efficiency of photosensitized phosphorescence is about five orders of magnitude higher than the quantum efficiency of phosphorescence caused by the dark-red light in the absence of the photosensitizer. Detailed analysis of the emission caused by dark-red lasers is beyond the scope of this work and will be presented in a separate publication.

In all solvents under cw excitation at 399 nm, the intensity of phosphorescence photosensitized by phenalenone linearly depended on the intensity of the exciting light (I_{ex}) in the range of 0.05-4 mW (data not shown). At higher intensities, some deviation from linearity was observed, which was relatively weak in hexafluorobenzene but distinctly noticeable in CCl_4 and Freon

113. For example, at the maximum photodiode power (200 mW), the phosphorescence intensity in CCl_4 was twice as low as it would be expected at the linear dependence on the exciting light intensity observed at $I_{\text{ex}} \leq 4 \text{ mW}$.

Kinetic measurements. The phosphorescence kinetic curves recorded at 1270 nm using the time-resolved photon counting setup after irradiation of phenalenone solutions with 10- μs LED pulses (405 nm) are shown in Figs. 4-6. The decay times were determined from the slopes of the kinetic curves on a semi-logarithmic scale. To obtain

this parameter, the averaged luminescence traces from a quartz cell with a pure solvent were subtracted from the phosphorescence kinetic curves of phenalenone solutions obtained under the same irradiation conditions. The first 10 μs of the resulting kinetic curve were omitted due to possible contribution of ${}^1\text{O}_2$ accumulation by the triplet molecules of the photosensitizer. The final part of the curves was discarded because of significant distortions due to the signal noise. Figure 4 demonstrates that the phosphorescence decays are exponential. In air-saturated

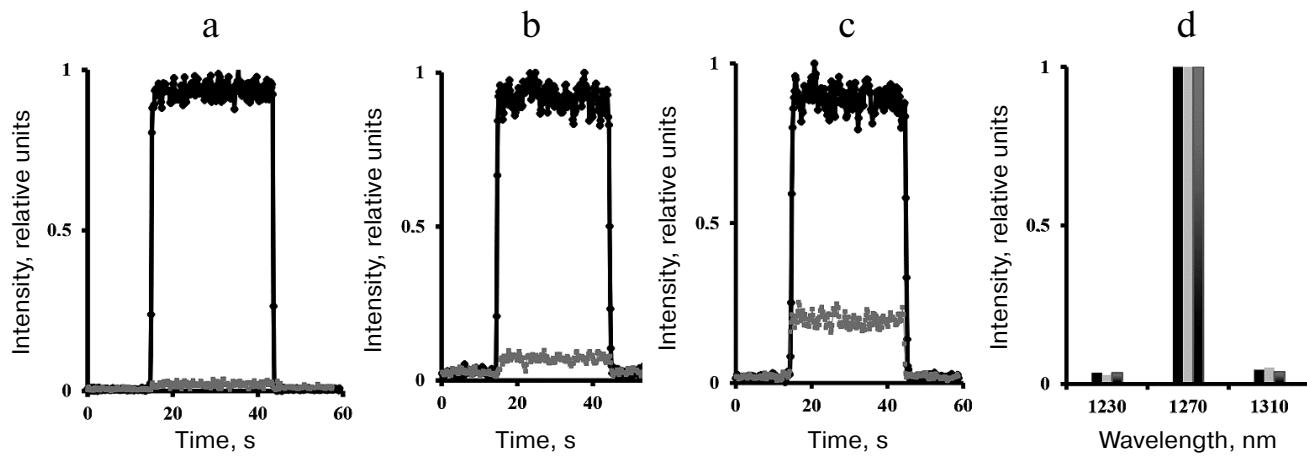


Fig. 3. Intensity and spectrum of ${}^1\text{O}_2$ phosphorescence upon photosensitized (a, d) and direct (b-d) excitation of oxygen in air-saturated CCl_4 . a) Solution of phenalenone excited with cw LED 399 nm (4 mW) in the absence of acetone (upper curve) and after addition of 50% acetone (lower curve); b) in the absence of phenalenone upon oxygen excitation with a 765-nm diode laser (900 mW); c) in the absence of phenalenone upon oxygen excitation with a 690-nm diode laser (1-3 W); d) phosphorescence spectra corresponding to the curves (a)-(c) after subtraction of luminescence observed in the presence of acetone (from left to right).

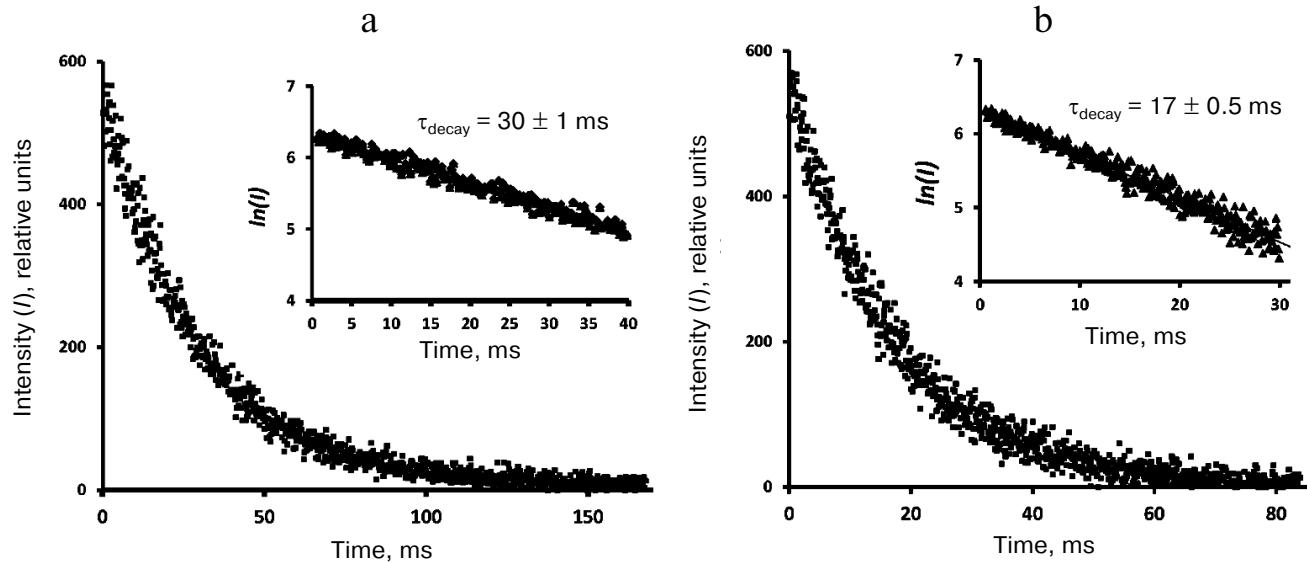


Fig. 4. Decays of ${}^1\text{O}_2$ phosphorescence in phenalenone (35 μM) solutions in CCl_4 after irradiation by 10 μs pulses of LED (405 nm) in the presence of air (a) and after saturation with oxygen (b). The curves were obtained at a pulse repetition rate of 5 Hz as a result of 30-min signal accumulation; duration of one channel, 164 μs ; average excitation power, 15 μW . Insets, decay curves in the semi-log scale.

CCl_4 containing $\sim 30 \mu\text{M}$ phenalenone, the phosphorescence decay time was $30 \pm 1 \text{ ms}$ (Fig. 4). Therefore, it coincides with the value reported in our earlier papers [3] and publications of the Minsk group [6–8, 11, 12], being half as much as reported by the Schmidt's group (59 ms) [13, 14].

In the air-saturated hexafluorobenzene (Fig. 5), the lifetime was 16 ms. This value coincides with the result of our previous measurements performed with a setup with a phosphoroscope [3, 28] and is close enough to the latest data from the Schmidt's group (21 ms) [13, 14]. In aerat-

ed Freon 113, the lifetime was $\sim 37 \text{ ms}$ (Fig. 6), which is 2 times smaller than in Schmidt's work ($72 \pm 5 \text{ ms}$) [13, 14].

We also studied the influence of the concentrations of the photosensitizer and oxygen on the phosphorescence decay times. Figures 4–6 show that saturation of the solutions with pure oxygen (bubbling oxygen for 20 min increases its concentration in the solution by 4.8 times) caused the 1.5–1.7-fold increase in the phosphorescence decay rates. Also, the decay rates increased with the phenalenone concentration increase. These facts indicate that $^1\text{O}_2$ is physically quenched by phenalenone (Ph) and

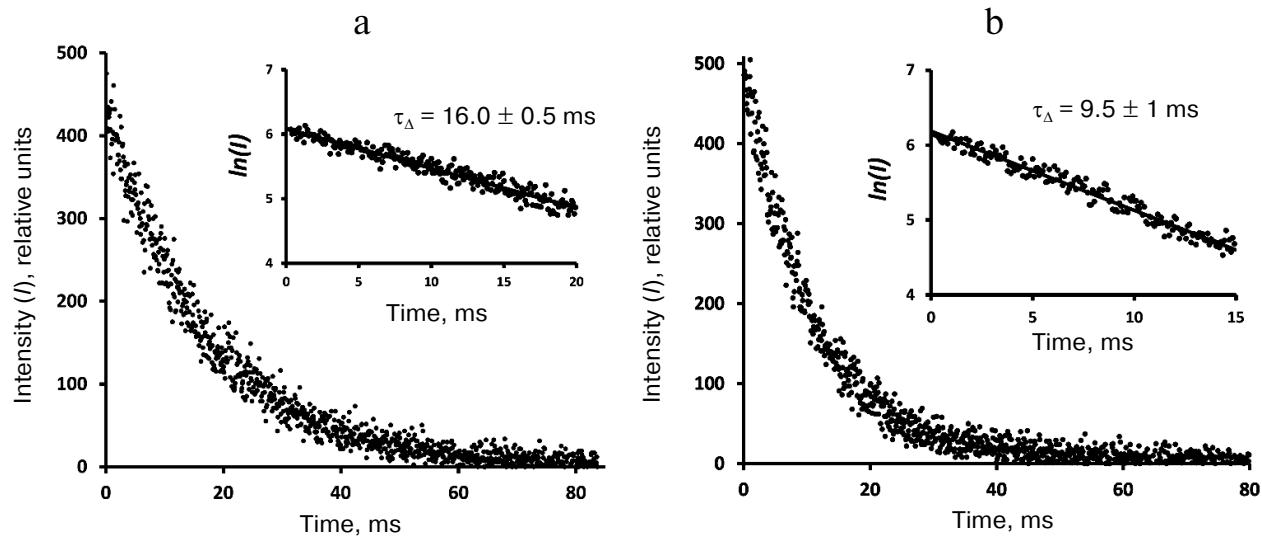


Fig. 5. Decays of $^1\text{O}_2$ phosphorescence in phenalenone ($35 \mu\text{M}$) solutions in hexafluorobenzene after irradiation with 10- μs LED pulses (405 nm) in the presence of air (a) and after saturation with oxygen (b). The curves were recorded at a pulse repetition rate of 10 Hz as a result of 20-min signal accumulation; duration of one channel, 82 μs ; average excitation power, 30 μW . Insets, decay curve in the semi-log scale.

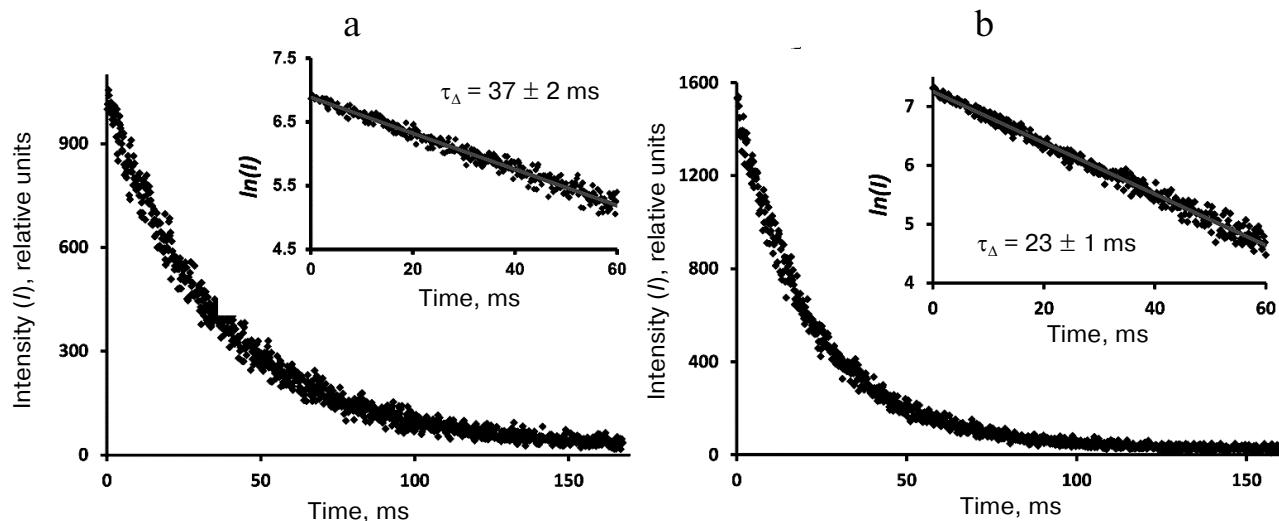


Fig. 6. Decays of $^1\text{O}_2$ phosphorescence in phenalenone ($35 \mu\text{M}$) solutions in Freon 113 after irradiation by 10- μs LED pulses (405 nm) in the presence of air (a) and after saturation with oxygen (b). The curves were recorded at the pulse repetition rates of 5 Hz as a result of 30-min signal accumulation; duration of one channel, 164 μs ; average excitation power, 15 μW . Insets, decay curves in the semi-log scale.

Table 1. Rates constants for $^1\text{O}_2$ quenching by triplet oxygen (k_{ox}) and phenalenone (k_{ph}) and the decay rate constants (k_{obs}) and lifetimes (τ_{Δ}) of singlet oxygen phosphorescence in solutions saturated with air and oxygen

Solvents	[O ₂], M [29, 30]	k_{obs} , s ^{-1*} ($\tau_{\Delta} = 1/k_{\text{obs}}$, ms)	k_{ox} , M ⁻¹ .s ⁻¹	$k_0 + k_{\text{ph}}[\text{Ph}]$, s ^{-1**} ($\tau = 1/k_0 + k_{\text{ph}}[\text{Ph}]$, ms)	$k_{\text{ph}} \times 10^{-5}$, M ⁻¹ .s ⁻¹	k_0 , s ^{-1***} ($\tau_0 = 1/k_0$, ms)
CCl ₄	2.6; air 12.4; oxygen	33 (30 ms) 59 (17 ms)	2600	27 (38 ms)	1.7 ± 0.3	~20 (50 ms)
Hexafluorobenzene	4.4; air 21; oxygen	62.5 (16 ms) 105 (9.5 ms)	2600	51 (20 ms)	1.0 ± 0.1	~48 (21 ms)
Freon 113	3.2****; air 15.4; oxygen	27 (37 ms) 44 (23 ms)	1400	22 (45 ms)	1.0 ± 0.1	~19 (53 ms)

* Measurements in the presence of air and 35 μM phenalenone.

** Calculated decay rate constants and lifetimes of $^1\text{O}_2$ in solvents in the absence of oxygen.

*** Calculated decay rate constants and the lifetimes of $^1\text{O}_2$ in solvents in the absence of oxygen and phenalenone.

**** Oxygen concentration was taken from the data of Table 2 (see below).

Table 2. Relative values of k_r for IR $^1\text{O}_2$ emission band and relative values of molar absorption coefficients in the oxygen absorption maximum at about 1270 nm (ε_{1270}) calculated using relative k_r values. Comparison with the absolute values of A_{1270} and ε_{1270} obtained by the method of laser photochemistry [22, 34, 35]

Solvents	n^2	I_{Δ}/I_{399} , rel. units (± 10%)	τ_{Δ} , ms (± 2%)	k_r , rel. units (± 15%)	ε_{1270} , rel. units (± 15%)	$A_{1270} \times 10^5$, (1 cm)	$\varepsilon_{1270} \times 10^3$, M ⁻¹ .cm ⁻¹
CCl ₄	2.13	1	30	1.0	1.0	1.33	5.1
Hexafluorobenzene	1.9	0.57	16	0.94	1.05	2.2	5.0
Freon 113	1.85	0.92	37	0.68	0.78	1.3	4.0*

* This value was obtained by multiplying the relative value of ε_{1270} in Freon 113 (0.78) by the absolute value of ε_{1270} in M⁻¹.cm⁻¹ in CCl₄ (5.1).

triplet oxygen. The quenching efficiency can be described by the following version of the Stern–Volmer equation:

$$k_{\text{obs}} = k_0 + k_{\text{ox}}[\text{O}_2] + k_{\text{ph}}[\text{Ph}], \quad (1)$$

where k_{obs} is the observed phosphorescence decay rate ($k_{\text{obs}} = 1/\tau_{\text{decay}}$) in solutions containing phenalenone and oxygen; k_0 is the decay rate in pure solvent; k_{ox} and k_{ph} are the rate constants for $^1\text{O}_2$ quenching by triplet oxygen and phenalenone, respectively. It follows from the Eq. (1) that:

$$(k_{\text{obs}})_{\text{oxygen}} - (k_{\text{obs}})_{\text{air}} = k_{\text{ox}}([\text{O}_2]_{\text{oxygen}} - [\text{O}_2]_{\text{air}}). \quad (2)$$

Table 1 shows the k_{ox} values calculated using Eq. (2), the decay times indicated in Figs. 4–6, and the literature data on the oxygen concentration in air-saturated solutions [29, 30]. The k_{ox} values obtained in CCl₄ and hexafluorobenzene reasonably correlate with the data of Schmidt's and other research groups [13, 14, 31]. A somewhat smaller constant was obtained in Freon 113.

However, it should be noted that to our knowledge, there is no reliable information on the solubility of oxygen in this solvent. Therefore, to estimate k_{ox} , we calculated [O₂]_{air} using the data of the present work on the phosphorescence quantum efficiency and oxygen absorption coefficients. The results of these calculation are presented in Table 2. The obtained k_{ox} values appear to be reasonable. It should be noted that the boiling point of Freon 113 is 47°C; therefore, at room temperature, the volatility of this solvent is higher compared to other solvents. Hence, Freon 113 saturation by oxygen after oxygen purging might be less complete.

The dependences of the decay rates of $^1\text{O}_2$ phosphorescence on phenalenone concentration in hexafluorobenzene and Freon 113 are linear in the Stern–Volmer coordinates (Fig. 7). Similar linear dependence was found in CCl₄, although in this solvent, the data were more scattered (not shown). The k_{ph} values obtained in our experiments are shown in Table 1. These values are somewhat lower than the values measured in our laboratory earlier (3·10⁵ M⁻¹.s⁻¹ in CCl₄) [28], and slightly

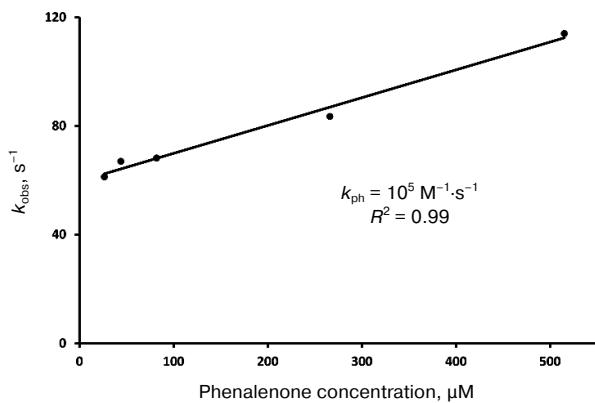


Fig. 7. Quenching of singlet oxygen phosphorescence by phenalenone in air-saturated hexafluorobenzene; k_{obs} is the rate constant of deactivation of singlet oxygen phosphorescence; R^2 is the coefficient of determination.

greater than the values reported by the Schmidt's group ($3.5 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$) [13, 14].

Radiative constants and absorption coefficients. It is known that the lifetime of singlet oxygen (τ_{Δ}) is mainly characterized by nonradiative deactivation of ${}^1\text{O}_2$, whereas the intensity of ${}^1\text{O}_2$ phosphorescence is determined by the radiative rate constant (k_r); its phosphorescence quantum yield (Φ_r) can be calculated as:

$$\Phi_r = k_r \cdot \tau_{\Delta}. \quad (3)$$

The radiative rate constant characterizes the electronic structure and the state of oxygen molecule and, according to the generally known Einstein relation, is directly proportional to the molar absorption coefficient:

$$\varepsilon_{1270} \sim k_r / n^2. \quad (4)$$

Our spectrometer allowed us to compare the radiative rate constants of ${}^1\text{O}_2$ deactivation in the studied solvents. Phenalenone solutions with the same optical density of 0.12 ± 0.005 at 399 nm were used for the measurements. The k_r constants were calculated using the following equation for the steady-state intensity (I_{Δ}) of photosensitized phosphorescence:

$$I_{\Delta} = (K/n^2)\Phi_{\Delta} I_{399} \alpha (1 - 10^{-A_{\text{ph}}})k_r \cdot \tau_{\Delta}, \quad (5)$$

where K is a proportionality coefficient accounting for the device design; I_{Δ} and I_{399} are the intensities (in photons per second) of photosensitized phosphorescence and the exciting light, respectively; n is the solvent refractive index; Φ_{Δ} is the quantum yield of singlet oxygen generation by phenalenone (equal to ~1) [24, 32]; A_{ph} is the phenalenone absorbance in the excitation region

(399 nm); α is a coefficient showing the extent of overlapping of the LED emission band with the absorption band of phenalenone. Therefore,

$$k_r = (n^2 I_{\Delta}/I_{399})/\tau_{\Delta} K\Phi_{\Delta} \alpha(1 - 10^{-A_{\text{ph}}}), \quad (6)$$

where $K\Phi_{\Delta} \alpha(1 - 10^{-A_{\text{ph}}})$ is the same for all solutions, therefore it was not taken into account in calculating the relative values of k_r . The relative values of the molar absorption coefficient for the same band were calculated from the relative values of k_r using the Einstein equation (4). The obtained values are summarized in Table 2. The I_{Δ}/I_{399} ratio and the values of k_0 and ε_{1270} in CCl_4 were set to be 1. It follows from Table 2 that in all solvents studied in this work, the constants k_r and ε_{1270} are rather similar within the indicated confidence interval. There is a tendency for some decrease in k_r and ε_{1270} in Freon 113, which has been mentioned earlier [33].

Over the past 15 years our laboratory has developed a photochemical method for measuring absorbance (A_{1270} and A_{765}) and molar absorption coefficients (ε_{1270} and ε_{765}) for the absorption maxima of oxygen dissolved in many organic solvents and water. This method is based on the kinetic analyses of the rates of chemical trapping of singlet oxygen upon direct laser excitation of oxygen molecules (Fig. 8) [22, 33–35]. The most accurate results were obtained from comparative analysis of the chemical trapping rates upon direct (V_{dir} , M/s) and photosensitized (V_{psr} , M/s) oxygen excitation [22, 33–35]. In this work, the absorbance of oxygen A_{1270} (A_{765} was not considered in the present paper) was calculated using the following equation:

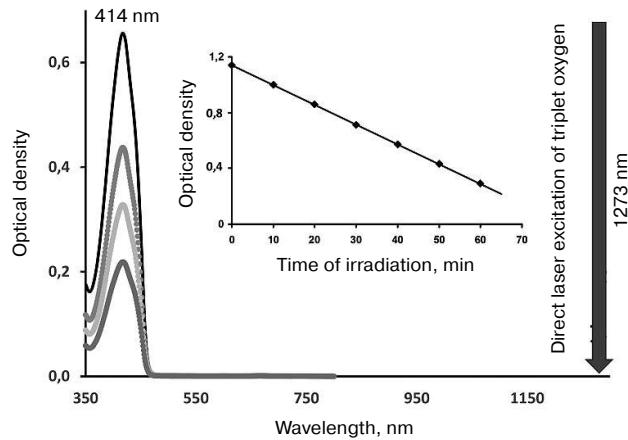


Fig. 8. Principles of singlet oxygen detection using the laser photochemistry method. The absorption spectrum of the singlet oxygen trap 1,3-diphenylisobenzofuran (maximum, 414 nm). The trap is bleached by the laser radiation at 1273 nm corresponding to the absorption maximum of dissolved oxygen. The absorbance of oxygen at 1270 nm is $\sim 10^{-5}$ [22, 33–35], therefore, on the scale of this figure, this maximum is not seen.

$$A_{1270} = (V_{\text{dir}}/I_{1270})/(V_{\text{psr}}/I_{511}) \Phi_{\Delta}(1 - 10^{-4}\rho_{\text{ps}})/(\alpha_{\text{las}} 2.3), \quad (7)$$

where I_{1270} and I_{511} are the fluence rates (in photons/second) for direct and photosensitized [tetraphenylporphine (TPP) was used as a photosensitizer in most cases mainly] excitation of oxygen, respectively; Φ_{Δ} is the quantum yield of singlet oxygen generation by porphyrin ($\Phi_{\Delta} = 0.73$); ρ_{ps} is the optical density of TPP at the excitation wavelength (511 nm); α_{las} is the extent of overlapping of the diode laser emission band and the oxygen absorption spectrum [22, 34, 35]. The obtained values of A_{1270} are shown in Table 2. Given that

$$A_{1270} = \varepsilon_{1270} [\text{O}_2] l, \quad (8)$$

where $l = 1$ cm, one can easily obtain the values of ε_{1270} using known oxygen concentrations (see Table 2).

To our knowledge, the exact value of oxygen solubility in Freon 113 has not been described yet, and only the estimates are available [13, 31]. This value can be determined using our data from Table 2. For this purpose, we used the ε_{1270} value in CCl_4 obtained by the laser photochemistry methods [22, 34, 35]. The ε_{1270} value in Freon 113 was calculated by multiplying ε_{1270} in CCl_4 by the relative value of ε_{1270} , which has been obtained from the photosensitized phosphorescence of oxygen. Using A_{1270} in Freon 113 measured by the method of laser photochemistry and Eq. (8), we arrived to $[\text{O}_2] = 3.2$ mM. In Table 2, this value was used to calculate the rate constant for $^1\text{O}_2$ quenching by triplet oxygen. Interestingly, a similar procedure, after some improvement, can be applied to estimating the oxygen solubility in any medium that allows spectral measurements.

Thus, the spectrometers developed in our lab provide reliable measurements of the kinetic parameters of singlet oxygen phosphorescence in solvents, in which the lifetime of $^1\text{O}_2$ reaches tens of milliseconds. From the technical point of view, the designed spectrometers are more advanced and informative than all the instruments used previously to study the kinetic parameters of oxygen phosphorescence in such solvents. As indicated, the kinetic curves were measured upon the irradiation with a very low-intensity exciting light (15–30 μW), which is orders of magnitude lower than used previously. This excludes the contribution of nonlinear effects observed earlier [6]. The temporal resolution of the photodetector system (nanoseconds) could not introduce distortions in the decay kinetics. The kinetic measurements performed with these instruments led to the value of the singlet oxygen lifetime in CCl_4 (30 ms) similar to those obtained in our first papers [3] and subsequent works of the Minsk researchers [6–8, 11, 12]. However, this value is twice as little as the value obtained by the Schmidt's group [13, 14]. In Freon 113, the measured lifetime was 37 ms, which is also a half of the value obtained by the Schmidt's group [13, 14]. In hexafluorobenzene, our data and the

data of the Schmidt's group [13, 14] were rather similar (Table 1 and Figs. 5 and 6).

More recently, other groups have reported the values of τ_{Δ} in CCl_4 , which were within 14–55 ms [15–18]. Unfortunately, the information on the conditions for their measurements is insufficient for detailed analysis of the results. The authors mostly assumed that the higher τ_{Δ} values obtained by the Schmidt's group were due to a higher purity of the solvents used in the experiments. Indeed, Schmidt and colleagues indicated that “all solvents were purified by repeated chromatography on columns with Al_2O_3 ”. In our experiments and in the experiments of other groups, highly purified commercial solvents were used without further purification or after additional distillation. On the other hand, it is obvious that the phosphorescence setup developed by the Schmidt's group is not perfect (see the introductory section). So, it cannot be ruled out that the delay of the most slowly decaying curves was due to technical problems. Nevertheless, our measurements confirm the observation of the Schmidt's group that $^1\text{O}_2$ is quenched by triplet air oxygen and phenalenone. The quenching rate constants obtained in our experiments are in a reasonable agreement with the Schmidt's data.

By comparing the phosphorescence quantum yields in phenalenone solutions, the relative rates of $^1\text{O}_2$ radiative deactivation were determined. It was established that the relative values of radiative constants and relative absorption coefficients obtained using the laser photochemistry methods are virtually similar. The rationale for this idea in regard to a wider range of solvents has been given in our previous publications [1, 22, 33–35]. In addition, as mentioned above, the designed devices open up new possibilities for studying $^1\text{O}_2$ generation and quenching. Also, as Fig. 3 indicates, they open new prospects in studying the generation of singlet oxygen by dark-red light in pigment-free aerated systems.

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Conflict of Interest

The authors declare no conflict of interest.

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