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## PHOTONICS

# Determination of the Quantum Yield of Singlet Oxygen Sensitized by Halogenated Boron Difluoride Dipyrromethenes

**R. T. Kuznetsova[a], *, Iu. V. Aksenova[a], D. E. Bashkirtsev[a], A. S. Shulev[a], E. V. Antina[b], M. B. Berezin[b], and N. A. Bumagina[b]**
[a] *Tomsk State University, Tomsk, 634050 Russia*
[b] *Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia*
**e-mail: kuznetrt@phys.tsu.ru*

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**Abstract**—The spectral–luminescent, photophysical, and photochemical properties of dichloro-, dibromo-, and diiodo-derivatives of boron dipyrromethenate (BODIPY) have been studied, as well as the feasibility of generating singlet oxygen ($^1O_2$) via its photosensitization by the dihalogenated derivatives of $BF_2$ dipyrromethene in solutions. Quantum yields of singlet oxygen have been determined using 1,3-diphenylisobenzofuran as the $^1O_2$ trap. The lowest fluorescence quantum yields have been shown to correspond to the maximum yields of singlet oxygen. It has been found that the best $^1O_2$ photosensitizer among the three test dihalotetraphenylaza-BODIPY is dibromotetraphenylaza-BODIPY, which in addition possesses the highest photostability. Diiodotetramethyl-BODIPY results in the singlet oxygen yield close to unity, but it has significantly lower photostability. The yield of singlet oxygen is affected by the solvent. Dibromtetraphenylaza-BODIPY and diiodotetramethyl-BODIPY may find use as a medium in photodynamic therapy and photocatalysis of oxidation reactions.

*Keywords*: dipyrromethenes, BODIPY, photosensitivity, singlet oxygen, chemical traps

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The last decade has seen intense development of a new class of synthetic chemical compounds, the complexes of p- and d-block elements with dipyrromethenes [1, 2], which can significantly alter both chromophore properties (absorption and emission regions and their intensity) and emission efficiency with fluorescence quantum yields of 1 to <0.01, depending on the central atom and the ligand structure [3]. Therefore, this class of compounds is the most promising for studying the relation of the spectral-and-luminescent properties and photonics of the compounds to their structure with the aim of the subsequent selection and synthesis of a particular structure to solve a certain practical problem of creation of a high-tech optical device. Thus, alkyl, phenyl, and benzyl derivatives of boron dipyrromethenate (BODIPY), which have a fluorescence yield close to unity, can be used as a laser active medium for both liquid and solid-state tunable lasers operating in the range of 500–615 nm [3–6]. Introduction of the propargylamino group into the *meso*-position of the molecule shifts the spectral characteristics to shorter wavelengths (effective generation of stimulated emission at 470 nm has been achieved [5]). Halogen substitution substantially reduces the efficiency of fluorescence and causes the emergence of long-lived phosphorescence in both frozen solutions and solid matrices at room temperature, which is quenched by ambient oxygen, a property that is used to create oxygen sensor media [7, 8]. The replacement of carbon in the *meso*-position of the $BF_2$ dipyrromethene molecule by nitrogen (aza-BODIPY) leads to a long-wavelength shift of band maxima in the spectra and a decrease in the fluorescence efficiency [3] due to the appearance of closely arranged energy states of different orbital natures and multiplicities, which increases the probability of intersystem crossing. The subsequent halogenation of the dipyrromethene core of aza-BODIPY would further increase the intersystem crossing probability, i.e., the triplet and phosphorescence yields, which might enhance the response of sensor media. However, the study of the luminescence characteristics of tetraphenylaza-BODIPY has shown that neither tetraphenylaza-BODIPY nor any of its halogenated derivative exhibits phosphorescence, a fact that can be explained by a decrease in the lifetime of the $T_1$ state as a result of not only nonradiative processes of intersystem crossing from the $T_1$ state, but also the effective quenching of this state by molecular oxygen to give its singlet form ($^1O_2$) [9, 10].

The formation of singlet oxygen via its photosensitization by organic compounds that have a high triplet yield involves energy transfer from the BODIPY triplet

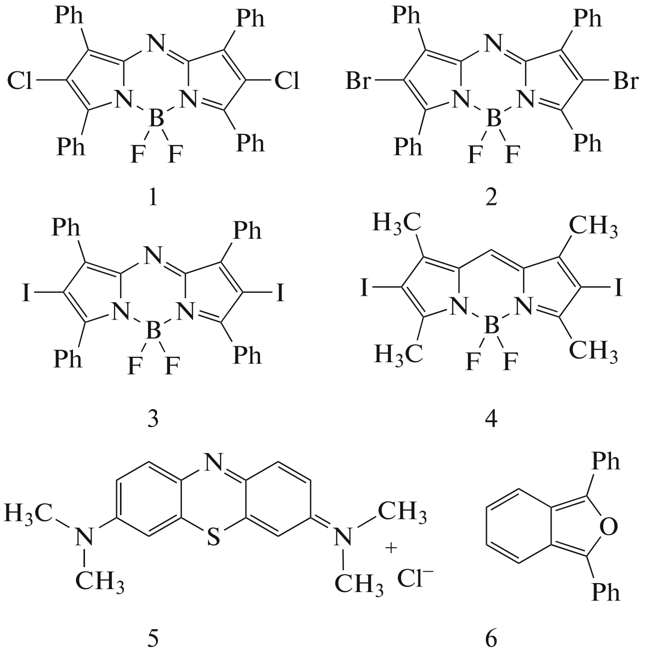

**Fig. 1.** Structural formulas of (**1**) dichlorotetraphenylaza-BODIPY ($Cl_2Ph_4$-aza-BODIPY), (**2**) dibromotetraphenylaza-BODIPY ($Br_2Ph_4$-aza-BODIPY), (**3**) diiodotetraphenylaza-BODIPY ($I_2Ph_4$-aza-BODIPY), (**4**) diiodotetramethyl-BODIPY ($I_2(CH_3)_4$BODIPY), (**5**) methylene blue (MB), and (**6**) 1,3-diphenylisobenzofuran (DPBF).

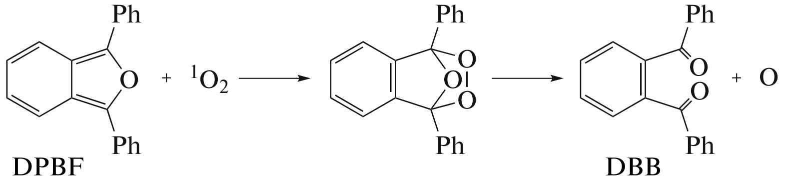

**Fig. 2.** Scheme of the reaction of diphenylisobenzofuran (DPBF) with $^1O_2$ to form the UV photoproduct DBB [11].

to $^3O_2$ in the triplet collision complex (reaction (1)) [11, 12]:

$$[^3T(BODIPY) + {}^3O_2] \rightarrow S_0(BODIPY) + {}^1O_2. \quad (1)$$

Media that generate $^1O_2$ with a high yield hold promise for use in photodynamic therapy (PDT) [11–13] and as photocatalysts for processes based on the participation of $^1O_2$ in photooxidation reactions [14].

In this regard, the aim of the present spectroscopic study was to explore the possibility of generating $^1O_2$ and determining its quantum yield via photosensitization by dichloro, dibromo, and diiodo derivatives of tetraphenyl aza-BODIPY, which do not exhibit phosphorescence, and their well-phosphorescing analogue diiodotetramethyl-BODIPY, using the technique of chemical degradation of $^1O_2$ traps during their interaction with singlet oxygen.

## OBJECTS AND METHODS OF STUDY

Figure 1 shows the structural formulas of the test photosensitizers, which are $BF_2$ complexes of halogenated dipyrromethenes (**1–4**); the singlet oxygen trap diphenylisobenzofuran (DPBF) (**6**); and the methylene blue (MB) dye (**5**), which is the currently known singlet-oxygen photosensitizer [11, 12, 14] used in this study as the standard with a quantum yield of $\varphi^{MB}(^1O_2) = 0.52$ [15]. The method for determining the quantum yield of halo-BODIPY-photosensitized singlet oxygen with the use of $^1O_2$ traps is based on the chemical interaction of DPBF in the ground electronic state (Fig. 2) with excited singlet oxygen $^1O_2$ generated via reaction (1).

Quantum yields $\Phi^X(^1O_2)$ were determined according to Eq. (2) [11, 13]:

$$\Phi^X(^1O_2) = \Phi^{MB}(^1O_2)(k^X/k^{MB}) \times \left[\left(1 - T^{MB}_{\lambda\,\mathrm{exc}}\right)\Big/\left(1 - T^{X}_{\lambda\,\mathrm{exc}}\right)\right], \quad (2)$$

where $\Phi^{MB}$ is the known yield of $^1O_2$ sensitized by the standard MB, $k^X$ is the decay rate of DPBF in a mixture with test dipyrromethenate X, and $k^{MB}$ is the DPBF decay rate in a mixture with the standard MB. The rate was determined from the slope (Fig. 3) of the plot of absorbance $A$ at maximum of the DPBF absorption band (410 nm) versus the time of irradiation at the sensitizer absorption band (640 or 535 nm), at which DPBF does not absorb light (i.e., singlet oxygen can be generated via reaction (1) alone). $T^{MB}$ and $T^X$ refer to the transmittance of the solutions with methylene blue (standard) and the test photosensitizer (X), respectively, at the excitation wavelength (here, the factor $(1 - T_{\lambda exc})$ takes into account the light absorbed by the photosensitizer to cause the formation of excited triplet complexes). In the case of compound **4**, the excitation was carried out to its long-wavelength absorption at $\lambda = 535$ nm, at which DPBF likewise does not absorb light. The standard (MB) was also excited at this wavelength, and its yield at a wavelength excitation of 535 nm was evaluated with respect to that in the case of excitation in the long-wavelength band (640 nm), since the intensity of the excitation source at these wavelengths was the same for an SM 2203 spectrometer.

The experiment was conducted in the sample compartment of the modified SM 2203 spectrometer by placing in the compartment a cell with the solution of the photosensitizer–DPBF mixture prepared in the dark (spectral slit width was 10 nm during irradiation or 5 nm for recording absorption spectra). To retain the excitation geometry in different experiments, close values of transmittance of the mixtures at the excitation wavelength ($T = 0.15$–$0.2$, $c_{BODIPY} = 1$–$2 \times 10^{-5}$ mol/L) and close "trap" concentrations ($c_{DPBF} \cong 2 \times 10^{-5}$ mol/L) were chosen. To exclude appreciable consumption of dissolved molecular oxygen during the generation of $^1O_2$, the working mixtures were sparged with pure oxygen at a constant flow rate (20 $cm^3$/min).

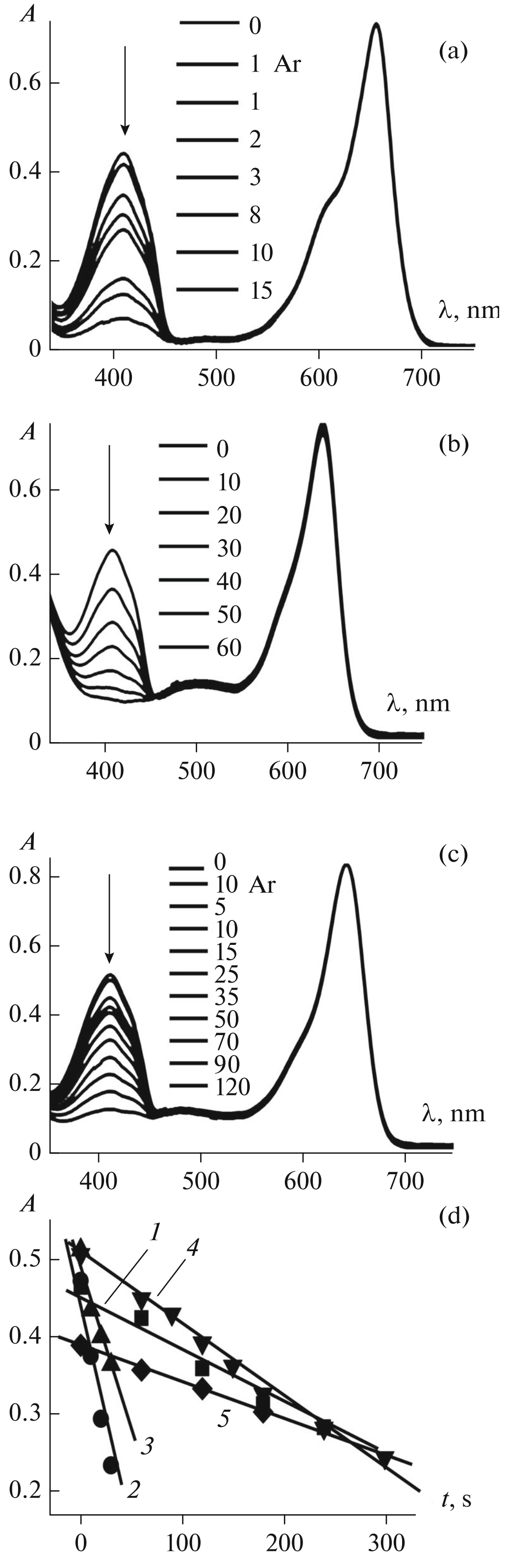

**Fig. 3.** Change in the absorption spectra of a DPBF mixture with the dyes: (a) methylene blue in ethanol, (b) $Br_2Ph_4$-aza-BODIPY in acetonitrile, and (c) $I_2Ph_4$-aza-BODIPY in ethanol, depending on the time of irradiation at $\lambda = 640$ nm. The irradiation time is given in (a, c), minutes and (b) seconds. (d) Dependence of absorbance at the DPBF absorption band maximum (410 nm) upon the time of irradiation of mixtures with the dyes (*1*) methylene blue in ethanol, (*2*) $Br_2Ph_4$-aza-BODIPY in acetonitrile, (*3*) $I_2(CH_3)_4$BODIPY in ethanol, (*4*) $I_2Ph_4$-aza-BODIPY in acetonitrile, and (*5*) $Cl_2Ph_4$-aza-BODIPY in acetonitrile. Irradiation wavelength: (*1*, *2*, *4*, *5*) 640 or (*3*) 535 nm.

The error of the $^1O_2$ yield was calculated on the basis of three independent measurements of the DPBF decay rate in freshly prepared MB–DPBF mixtures. The measurement error of the DPBF decay rate was 5%, and its error in the subsequent calculation of $\Phi(^1O_2)$ by Eq. (2) was 12%.

Halogenated boron(III) dipyrromethenates were synthesized at the Institute of Solution Chemistry (Ivanovo) [16]. As has been noted in [16], $Br_2Ph_4$-aza-BODIPY is unstable in proton-donor alcohols and electron-donor DMF. The concentration of a $Br_2Ph_4$-aza-BODIPY (compound **2**) solution at room temperature is reduced two- to threefold 3 h after its preparation. It can be assumed that the dye degradation under these conditions involves the nucleophilic displacement of the bromine atoms and the subsequent reduction of the imine bond of the *meso*-aza bridge by the bromide anions and oxidative degradation of the azadipyrrol core. In inert nonpolar solvents, compound **2** is stable. No effects of this kind have been detected for compounds **1** and **3**: their solutions in ethanol are stored for a long time without significant change; i.e., this property is associated with the dibromo substitution in tetraphenylaza-BODIPY. In connection with this, compounds **1**, **3**, and **4** were studied in ethanol and acetonitrile, and compound **2** was examined in acetonitrile, acetone, cyclohexane, and toluene (all of the reagent grade) using only freshly prepared solutions. Methylene blue and DPBF available from Aldrich were used without further purification.

The spectral-and-luminescent characteristics of the mixtures were recorded on a SOLAR SM 2203 spectrofluorimeter (Belarus). Photochemical and lasing properties were studied using excitation by the second harmonic of an Nd : YAG laser (532 nm, 20 MW/cm$^2$), the lasing and pumping energies were measured with an OPHIR NOVA II power meter (Israel) and a Gentec ED100A DUO energy detector (Canada) with an error 3%, and lasing spectra were recorded with an AVANTES spectrometer (the Netherlands) accurate to 0.5 nm. Photostability parameters (absolute quantum yield of phototransformations) were determined by measuring the change in absorbance upon the Nd : YAG second harmonic excitation (532 nm, 20 MW/cm$^2$) of the compounds, with the error being 7%. The setup used and the measurement procedures are detailed in [3, 6, 9].

## RESULTS AND DISCUSSION

Figure 3 shows changes caused by 640 nm irradiation in the absorption spectra of solutions of the photosensitizers mixed with DPBF (Figs. 3a–3c) and linear plots of absorbance at the maximum of the DPBF absorption band versus the irradiation time (Fig. 3d), as constructed on the basis of these changes. From the presented data it follows that the irradiation of the mixtures at wavelengths at which the trap DPBF does not absorb causes its degradation, whereas the concentration of the irradiated photosensitizer itself remains almost unchanged providing that the irradiated volume of the solution is maintained constant during the measurement. Based on the processing of these and other relevant relationships for the four $Hal_2$-BODIPY species in different solvents, we calculated by Eq. (2) values for the quantum yield of singlet oxygen. The calculation results together with the spectral–luminescent, photophysical, and photochemical properties are given in Tables 1 and 2.

Analysis of the data presented in Table 1 shows that substitution of the halogen atoms for the alkyl and benzyl groups in the 4,4’-position (β-substitution) of the dipyrromethene core leads to a long-wavelength shift (10–12 nm) in the spectra and an enhancement of intersystem crossing as a result of the heavy atom effect; i.e., a decrease in the fluorescence yield and appearance of phosphorescence in some cases [1, 5, 7, 8]. In the case of *meso*-aza substitution, even in the absence of halogen atoms in the 4,4’-positions, there is a significant red shift (75 nm) and a decrease in the fluorescence yield to 0.2 due to the appearance of energy states differing in type ($\pi\sigma^*$, $n\pi^*$, $\pi\pi^*$) and multiplicity; as a result, intersystem crossing is also enhanced [3, 5]. The introduction of different halogens in the 4,4'-position of aza-BODIPY hardly alters the position of the absorption and fluorescence bands (Table 1 and [3]), and the fluorescence quantum yields depend on the halogen type, making 0.2–0.3 for $Cl_2$- and $I_2$-$Ph_4$-aza-BODIPY, remaining almost unchanged as compared with nonhalogenated $Ph_4$-aza-BODIPY (see [3]). The fluorescence lifetimes measured are consistent with the data on quantum yields: the lower the fluorescence yield (i.e., the greater the contribution of nonradiative processes), the shorter the fluorescence lifetime (Table 1). Note that even lasing was obtained in the case of $Cl_2Ph_4$-aza-BODIPY [9, 10]. For $Br_2Ph_4$-aza-BODIPY, the quantum yield and the fluorescence lifetime are an order of magnitude lower ($\gamma_{fl}$ is as low as 0.02–0.04 and $\tau_{fl}$ = 0.08 ns). The fluorescence of $I_2(CH_3)_4$BODIPY is also low ($\gamma_{fl} = 0.04$, Table 1), but this compound exhibits phosphorescence is solid media and is used as an oxygen sensor medium [5, 7, 8]. On the other hand, $Ph_4$-aza-BODIPY and its halogenated derivatives are not phosphorescent, and the yield of the T state estimated experimentally and by quantum-chemical calculation is an order of magnitude higher for $Br_2Ph_4$-aza-BODIPY than for $Cl_2$- and $I_2Ph_4$-aza-BODIPY [10], a finding that is consistent with the experimental data on photonics (Tables 1, 2).

The results given in Table 2 show that all of the test $Hal_2$-BODIPY species generate singlet oxygen $^1O_2$ with varying efficiency depending on the structure of

**Table 1.** Spectral–luminescent and photochemical properties of dihalo-BODIPY

| Compound, solvent | $\lambda_{abs}$, nm ($\varepsilon$, L mol$^{-1}$cm$^{-1}$) | $\lambda_{fl}$, nm ($\lambda_{exc}$, nm | $\tau_{fl}$, ns | $\gamma_{fl}^{exp}$ [$\gamma_{fl}^{exp}$] ($\lambda_{exc}$, nm) | $\varphi_{phot}$ × $10^5$ |
|---|---|---|---|---|---|
| $Cl_2Ph_4$-aza-BODIPY, ethanol | 645 (50000) | 679 (570) | 0.9 | 0.28 (570)<br>0.06 (290) | |
| $Cl_2Ph_4$-aza-BODIPY*, ethyl acetate | 645 (60500) | 677 (590) | | 0.25 (590)<br>0.05 (315) | 1.3 |
| $Br_2Ph_4$-aza-BODIPY, ethyl acetate | 643 (68500) | 673 (550) | 0.08 | 0.025 (590) | 0.13 |
| $Br_2Ph_4$-aza-BODIPY, toluene | 651 (65000) | 685 (570) | | 0.03 (570) | |
| $Br_2Ph_4$-aza-BODIPY, acetonitrile | 639 (38000) | 672 (570) | 0.08 | 0.02 (570)<br>0.003 (310) | |
| $Br_2Ph_4$-aza-BODIPY, acetone | 641 (39500) | 672 (570) | | 0.02 (570) | |
| $Br_2Ph_4$-aza-BODIPY, cyclohexane | 647 (30500) | 677 (570) | | 0.04 (570)<br>0.008 (310) | |
| $I_2Ph_4$-aza-BODIPY, ethyl acetate | 646 (77350) | 672 (600) | | 0.26 (600)<br>0.05 (320) | |
| $I_2Ph_4$-aza-BODIPY, ethanol | 647 (64000) | 674 (600) | 0.8 | 0.32 (600)<br>0.06 (320) | 0.18 |
| $I_2Ph_4$-aza-BODIPY, cyclohexane | 646 (60500) | 674 (600) | | 0.24 (600)<br>0.07 (320) | |
| $I_2(CH_3)_4$BODIPY**, ethanol | 535 (51600) | 550 (500) | 0.27 | 0.04 (500) | 35 |

* $Cl_2Ph_4$-aza-BODIPY in ethyl acetate generates laser radiation: $\lambda_{exc}$ = 532 nm, $\lambda_{las}$ = 685 nm, efficiency = 1.3%.
** $I_2(CH_3)_4$BODIPY in ethanol phosphoresces at 77 K: $\lambda_{phosph}$ = 792 nm, $\gamma_{phosph}$ = 0.6 ($\lambda_{exc}$ = 520 nm).

the ligand core, the halogen introduced, and the solvent. The maximum value of the yield was obtained for $Br_2Ph_4$-aza-BODIPY compared with the $Cl_2$- and $I_2$-aza-substituted counterparts in the case of irradiating the mixture at 640 nm ($\Phi(^1O_2)$ = 1.73, which was greater than that for the MB standard). A value close to unity (within the margin of error) was obtained for $I_2(CH_3)_4$BODIPY in ethanol by exciting at 535 nm. The quantum yields of singlet oxygen for all $Hal_2Ph_4$-aza-BODIPY and MB in polar acetonitrile are greater than in the nonpolar solvents, a difference that may be due to different lifetimes of $^1O_2$ in these media: 60–75 μs in acetonitrile and 12, 17, and 29 μs in absolute ethanol, cyclohexane, and toluene, respectively [12, 13]. It should be noted that the $^1O_2$ yield for $Br_2Ph_4$-aza-BODIPY in acetonitrile was found to be greater than unity, a fact that may be associated with an increase in the rate of the DPBF reaction with $^1O_2$ in a specifically solvating solvent, suggesting its passing to a chain reaction as discussed in [11]. In addition, the $Br_2Ph_4$-aza-BODIPY fluorescence in acetonitrile is less effective compared with cyclohexane (Table 1), indicating a greater yield of triplets for this compound in acetonitrile and also facilitating the transformation of the mechanism of the reaction shown in Fig. 2 into the chain mechanism [11]. Of the two most effective $^1O_2$ photosensitizers $I_2(CH_3)_4$BODIPY and $Br_2Ph_4$-aza-BODIPY, the one that is less subject to phototransformation is better to use for practical application; i.e., it is $Br_2Ph_4$-aza-BODIPY, whose phototransformation yield is two orders of magnitude lower (Table 1).

The less efficient generation of $^1O_2$ by $Cl_2Ph_4$-aza-BODIPY compared with $Br_2Ph_4$-aza-BODIPY and $I_2Ph_4$-aza-BODIPY is easy to understand: the yield of triplets in $Cl_2Ph_4$-aza-BODIPY solutions is the smallest because of a lower value of the spin–orbit coupling operator; hence, as shown in [10], the intersystem crossing rate constant is 4.5 × $10^9$ s$^{-1}$ for Br2Ph4-aza-BODIPY versus 5.7 × $10^8$ s$^{-1}$ for $Cl_2Ph_4$-aza-BODIPY. The compound $I_2Ph_4$-aza-BODIPY "drops out" of this series, although it must have a higher triplet yield according to the above reasoning. As follows from the data in Table 2, the $^1O_2$ yield in ethanol and acetonitrile with this photosensitizer is indeed higher than that with $Cl_2Ph_4$-aza-BODIPY, but it significantly lower than the yield with Br2Ph4-aza-BODIPY in the same solvents. Bearing in mind that the yield of $^1O_2$ in the presence of $I_2(CH_3)_4$BODIPY as a photosensitizer is higher than that with $I_2Ph_4$-aza-BODIPY, we can assume that the reason behind this distinction is associated with the nature of substitution with the $Br_2$ ions, causing the existence of nπ*-type energy states, which have a substantial effect on the time characteristics of the triplets. As shown above, the sta-

**Table 2.** Values for the DPBF degradation rate ($k$), the factor correcting light absorption at an irradiation wavelength ($1 - T_{\lambda\ \mathrm{exc}}$), and the quantum yield of singlet oxygen generated by photosensitization with halogenated boron dipyrromethenates ($\Phi(^1O_2)$)

| Photosensitizer, solvent, $\lambda_{\mathrm{exc}}$, nm | $k = \Delta(A_0 - A_t)_{410}/\Delta t$: DPBF decay rate × $10^3$ (±5%), $\mathrm{s}^{-1}$ | $(1 - 10^{-\log 1/T}) = (1 - T_{\lambda\mathrm{exc}})$ (±1%) | $\Phi(^1O_2)$ (±12%) |
|---|---|---|---|
| MB, ethanol, 640 | 0.85 | 0.75 | 0.52 [13] |
| MB, acetone, 640 | 1.33 | 0.74 | 0.84 |
| MB, acetonitrile, 640 | 1.8 | 0.74 | 1.1 |
| MB, ethanol, 535 | 0.5 | 0.29 | 0.82 |
| $Cl_2Ph_4$-aza-BODIPY, ethanol, 640 | 0.032 | 0.81 | 0.02 |
| $Cl_2Ph_4$-aza-BODIPY, acetonitrile, 640 | 0.5 | 0.83 | 0.28 |
| $Br_2Ph_4$-aza-BODIPY, acetone, 640 | 1.4 | 0.74 | 0.89 |
| $Br_2Ph_4$-aza-BODIPY, toluene, 640 | 1.33 | 0.77 | 0.83 |
| $Br_2Ph_4$-aza-BODIPY, cyclohexane, 640 | 0.83 | 0.82 | 0.47 |
| $I_2Ph_4$-aza-BODIPY, ethanol, 640 | 0.053 | 0.82 | 0.03 |
| $I_2Ph_4$-aza-BODIPY, cyclohexane, 640 | 0.35 | 0.84 | 0.19 |
| $I_2Ph_4$-aza-BODIPY, acetonitrile, 640 | 0.83 | 0.84 | 0.46 |
| $I_2(CH_3)_4$BODIPY, ethanol, 535 | 2 | 0.85 | 1.09 |

bility of this derivative is lower in proton-donating solvents. An understanding of this phenomenon invites further investigation.

## CONCLUSIONS

The efficiency of generation of singlet oxygen via its photosensitization by halogenated derivatives of BODIPY has been determined, as well as their spectral–luminescent, lasing, and photochemical properties, thereby allowing some features of the relationships revealed to be explained.

The most effective singlet-oxygen photosensitizers suitable for practical application are $Br_2Ph_4$-aza-BODIPY and $I_2(CH_3)_4$BODIPY used at excitation wavelengths of 640 and 535 nm, respectively: both are superior in singlet-oxygen generation efficiency to methylene blue, a well-known photosensitizer for this spectral region; however, $Br_2Ph_4$-aza-BODIPY is 270 times more photostable than $I_2(CH_3)_4$BODIPY and, therefore, is preferable for practical use. On the basis of these photosensitizers, media for photodynamic therapy and photocatalysis of chemical oxidation reactions can be created.

The violation of the trend of change in the quantum yield of singlet oxygen generated by the photosensitizers in the order: $Cl_2Ph_4$-aza-BODIPY < $Br_2Ph_4$-aza-BODIPY < $I_2Ph_4$-aza-BODIPY calls for further investigation to reveal the causes of the selective ability of the dibromo derivatives as compared to the dichloro- and diiodo-substituted counterparts regarding the yield of triplets and generation of singlet oxygen.

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