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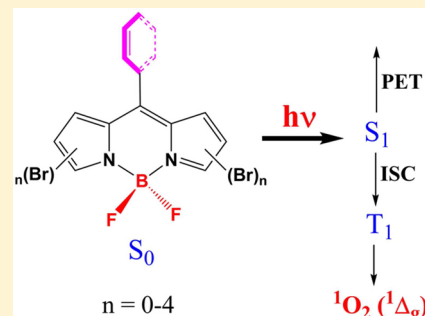
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Singlet Oxygen Generation and Triplet Excited-State Spectra of Brominated BODIPY

Xian-Fu Zhang^{*,†,‡} and Xudong Yang[†][†]Chemistry Department & Center of Instrumental Analysis, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei Province, 066004 China[‡]MPC Technologies, Hamilton, Ontario, Canada L8S 3H4

ABSTRACT: The excited triplet-, singlet-, and ground-state properties as well as singlet oxygen generation capability of four brominated BODIPY dyes were measured in toluene with laser flash photolysis, fluorescence spectroscopy, time-correlated single-photon counting, and absorption spectroscopy. The triplet–triplet (T_1 – T_n) absorption spectra were identified for four dyes **1B**, **2B**, **4B**, and **6B** substituted with one, two, four, and six Br atoms, respectively. The triplet quantum yield (Φ_T) of a usual BODIPY dye is negligible and has rarely been studied. So is the case for the parent compound **0B** (8-phenyl boron-dipyrromethene), in which no Br atom is present. The substitution of the first Br atom into the π ring of BODIPY allowed a dramatic increase of Φ_T from 0.0 of **0B** to 0.39 for **1B**. The further addition of Br number increased Φ_T to 0.46, 0.50, and 0.66 for **2B**, **4B**, and **6B**, respectively. The triplet lifetimes τ_T are also fairly long, which is 43, 39, 36, and 26 μ s, for **1B**, **2B**, **4B**, and **6B**, respectively. The brominated BODIPY dyes are therefore efficient singlet oxygen photosensitizers with the formation quantum yield of 0.39, 0.45, 0.49, and 0.64 for **1B**, **2B**, **4B**, and **6B**, respectively. The result indicates their potential application in photodynamic therapy of cancer. The fluorescence properties of the dyes were also measured.



■ INTRODUCTION

Boron-dipyrromethene complexes (BODIPY) are well-known fluorophores,^{1,2} which are used as laser dyes,^{3–5} labeling reagents,⁶ fluorescent switches,⁷ chemosensors,⁸ and OLEDs.⁹ These applications are based on their photophysics of the lowest-lying excited singlet state (S_1), mainly involving $S_1 \leftrightarrow S_0$ electronic transitions. (S_0 is the ground state.)

New applications based on their T_1 (the lowest-lying excited triplet state) photophysics have also appeared recently, including singlet oxygen photosensitizers for PDT^{10–12} (photodynamic therapy of cancer) and NIR photon upconversion.^{13–15} These dyes generally show intense and narrow absorption and fluorescence bands in the visible region, high fluorescence quantum yields, as well as good thermal and photochemical stability.^{1,2} BODIPY dyes usually exhibit negligible efficiency of T_1 formation due to the high fluorescence quantum yields.

T_1 is the key intermediate that leads to the formation of singlet oxygen ($^1\Delta_g$) by energy-transfer process: $T_1 + O_2 \rightarrow S_0 + O_2 (^1\Delta_g)$, where $O_2 (^1\Delta_g)$ is the reactive oxygen species that plays the main role to damage tumor tissues in PDT.¹⁰ Because of the very low efficiency of T_1 formation, heavy atoms (such as Br, I) are often incorporated into the BODIPY structure to enhance the spin–orbit coupling.^{10,12} The in vitro or in vivo tests showed that the halogenated BODIPYs could effectively kill tumor cells.^{11,16} However, there has been no associated study focusing on the triplet T_1 properties for these BODIPY dyes, such as the effect of the type, position, and number of halogen atoms. Also, the triplet properties for usual BODIPY dyes are rarely studied due to the negligible T_1 formation efficiency, although the synthesis and fluorescence properties

of BODIPY have been extensively carried out by many researchers.^{1,2,16–18} In this study, we report the effect of bromine substitution on the triplet state and singlet oxygen generation of BODIPY dyes (Figure 1).

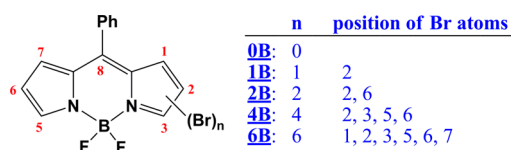


Figure 1. Chemical structure of brominated BODIPYs.

■ EXPERIMENTAL SECTION

Chemicals. The synthesis and characterization for these compounds have been described before.¹⁶ Toluene is of analytical grade and used after redistillation.

Solution Preparation. A dye was first dissolved in toluene to make a stock concentrated solution ca. 1 mM. Then, the dye was diluted in another vial to accommodate the absorbance at the instruments requirements.

Absorption Measurements. Ground-state UV–vis absorption spectra were recorded on a StellarNet BLACK Comet C-SR diode array miniature spectrophotometer connected to deuterium and halogen lamp by Optical fiber using 1 cm matched quartz cuvettes at room temperature.

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Table 1. Absorption, Triplet State, and Fluorescence Properties of Brominated BODIPYS in Toluene^a

	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{max}}^{\text{T-T}}$ (nm)	τ_{T} (μs)	Φ_{T}	Φ_{Δ}	$\lambda_{\text{max}}^{\text{em}}$ (nm)	Φ_{f}	τ_{f} (ns)	χ^2
0B	501			0	0	522	0.044	0.44(99%), 5.13	1.00
1B	521	420	43	0.39	0.39	543	0.071	0.73(98.5%), 1.75	0.99
2B	540	420, 435	39	0.46	0.45	565	0.053	0.76(95%), 2.11	1.02
4B	559	435, 450	36	0.50	0.49	576	0.065	0.25(2%), 3.47	1.00
6B	556	460	26	0.66	0.64	569	0.014	0.82(83%), 2.54	1.05

^aExperimental error for Φ_{f} , Φ_{T} , and Φ_{Δ} is $\sim 10\%$. $\lambda_{\text{abs}}^{\text{max}}$: absorption maximum. $\lambda_{\text{max}}^{\text{T-T}}$: T_1-T_n absorption maximum. τ_{T} : triplet lifetime. Φ_{T} : quantum yield for triplet formation. Φ_{Δ} : quantum yield for singlet oxygen formation. $\lambda_{\text{max}}^{\text{em}}$: emission maximum. Φ_{f} : fluorescence quantum yield. τ_{f} : fluorescence lifetime. χ^2 : chi-square values for τ_{f} fitting.

Fluorescence Measurements. Fluorescence spectra were recorded using an Edinburgh Instruments FLS920 fluorospectrometer, with 2 nm slits for excitation at 480 nm and emission from 490 to 750 nm. All spectra were corrected for the sensitivity of the photomultiplier tube. The fluorescence quantum yield (Φ_{f}) was computed by using

$$\Phi_{\text{f}} = \Phi_{\text{f}}^0 \cdot \frac{F_{\text{s}}}{F_0} \cdot \frac{A_0}{A_{\text{s}}} \cdot \frac{n_{\text{s}}^2}{n_0^2} \quad (1)$$

in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound, and s represents samples. Rhodamine 6G in ethanol was used as the reference ($\Phi_{\text{f}} = 0.95$).¹⁹ The sample and reference solutions were prepared with the same absorbance (A_{i}) at the excitation wavelength (near 0.090 in a 1 cm quartz cell). All solutions were air-saturated.

Fluorescence lifetime of the S_1 state was measured by time-correlated single photon counting method (Edinburgh FLS920 spectrophotometer) with excitation at 379 nm by a portable diode laser (69 ps fwhm), and emission was monitored at the peak maximum. The lifetime values were computed by the F900 software that came with the instrument.

Laser Flash Photolysis. Nanosecond transient absorption measurements were obtained using LP920 (Edinburgh Instruments). The excitation source was a Q-switched Nd/YAG laser (BRIO) of 4 ns full width at half-maximum with third harmonic (355 nm) generation. The 355 nm beam was directed onto one side of a 1 cm square silica cell containing the sample (absorbance around 0.2) after bubbling Ar gas during 20 min. The transient transmission variations were monitored at right angles to the excitation in a crossbeam arrangement using a 450W xenon flash lamp, a monochromator, a photomultiplier, and a digitized oscilloscope interfaced with a desktop computer. The power of the incident 355 nm laser pulse in the sample was ~ 5 mJ. The triplet quantum yield Φ_{T} was obtained by comparing the ΔA_{T} of the optically matched sample solution at peak maximum in a 1 cm cuvettes with that of the reference using the equation:²⁰

$$\Phi_{\text{T}} = \Phi_{\text{T}}^{\text{ZnPc}} \cdot \frac{\Delta A_{\text{T}}}{\Delta A_{\text{T}}^{\text{ZnPc}}} \cdot \frac{\Delta \varepsilon_{\text{T}}^{\text{ZnPc}}}{\Delta \varepsilon_{\text{T}}} \quad (2)$$

where the superscript represents the reference, ΔA_{T} is the absorbance of the triplet transient difference absorption spectrum at the selected wavelength, and $\Delta \varepsilon_{\text{T}}$ is the triplet-state molar absorption coefficient, which is obtained by eq 3.

$$\Delta \varepsilon_{\text{T}} = \varepsilon_{\text{s}} \frac{\Delta A_{\text{T}}}{\Delta A_{\text{s}}} \quad (3)$$

where ΔA_{s} and ΔA_{T} are the absorbance change of the triplet transient difference absorption spectrum at the minimum of the

bleaching band and the maximum of the positive band, respectively, and ε_{s} is the ground-state molar absorption coefficient at the UV-vis absorption band maximum. Both ΔA_{s} and ΔA_{T} were obtained from the triplet transient difference absorption spectra.

Singlet Oxygen Generation. Singlet oxygen quantum yield (Φ_{Δ}) determinations were carried out using the chemical trapping method.²¹ Typically, a 3 mL portion of the respective PS solutions that contained diphenylisobenzofuran (DPBF) was irradiated at 510 nm in air-saturated toluene. The Φ_{Δ} value was obtained by the relative method using methylene blue as the reference (eq 4):

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{ref}} \cdot \frac{k}{k^{\text{ref}}} \cdot \frac{I_{\text{a}}^{\text{ref}}}{I_{\text{a}}} \quad (4)$$

where $\Phi_{\Delta}^{\text{ref}}$ is the singlet oxygen quantum yield for the standard (0.79);²² k and k^{ref} are the DPBF photobleaching rate constants in the presence of the respective samples and standard, respectively; and I_{a} and $I_{\text{a}}^{\text{ref}}$ are the rates of light absorption at the irradiation wavelength of 510 nm by the samples and standard, respectively. Their ratio can be obtained by eq 5.

$$\frac{I_{\text{a}}^{\text{ref}}}{I_{\text{a}}} = \frac{1 - 10^{-A_{670}^{\text{ref}}}}{1 - 10^{-A_{670}}} \quad (5)$$

To avoid chain reactions induced by DPBF in the presence of singlet oxygen, we lowered the concentration of DPBF to $\sim 3 \times 10^{-5}$ mol dm⁻³. A solution of sensitizer (absorbance ~ 0.80 at the irradiation wavelength) that contained DPBF was prepared in the dark and irradiated in the 510 nm. DPBF degradation was monitored by UV-vis absorption spectrum. The error in the determination of Φ_{Δ} was $\sim 10\%$ (determined from several Φ_{Δ} values).

RESULTS AND DISCUSSION

The triplet-state properties are summarized in Table 1, together with ground-state absorption and fluorescence parameters.

In the absence of Br substitution, no triplet absorption and singlet oxygen photooxidation was found. Brominated BODIPYS, however, hold remarkable Φ_{T} and Φ_{Δ} values from 39 to 66%. Both the position and number of Br atoms exhibit a significant effect. The heavy atom effect (HAE) does not lead to 100% efficiency for Φ_{T} even after the BODIPY core is fully halogenated by six Br atoms. The details are explained in the following.

Ground-State Absorption Spectra. Figure 2 shows the normalized absorption spectra of brominated BODIPYS in toluene. There are three types of bromine atoms on the BODIPY core π -system (Figure 1): (i) 2,6-Br in **1B** and **2B**, (ii) 3,5-Br in **4B**, and (iii) 1,7-Br in **6B**. The shape of the absorption spectra remains very similar to **0B** upon the addition of more Br atoms at different positions in **1B** to **6B**.

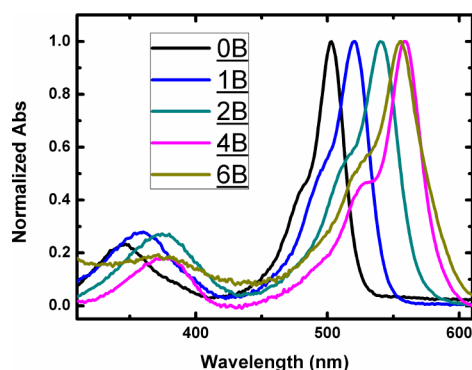


Figure 2. Normalized absorption spectra of brominated BODIPYS in toluene.

The absorption maximum, however, was changed by the Br presence. Br atoms in the 2,6-position have the most remarkable effect, whereas that in the 1,7-position shows the least influence. For example, the occurrence of 2-Br in **1B** caused a 20 nm red shift relative to **0B**, and one more 6-Br in **2B** gave a 19 nm further red shift relative to **1B**; each Br made the same contribution. Two additional Br atoms on the 3,5-position of **4B**, however, exhibited a total of 19 nm further red shift relative to **2B**, that is, 10 nm on average for each Br atom. This 10 nm red shift is consistent with that the Br substitution shows on the electronic absorption of aromatic compounds. 1,7-Br substitutions cause a slight blue shift that is due to their steric effect because the large Br atoms at 1,7-position cause the rotational hindrance of the phenyl and BODIPY core. The similar blue shift was also observed for 2,2',6,6'-tetramethylbiphenyl relative to biphenyl.²³

Triplet–Triplet (T_1 – T_n) Absorption. Upon laser flash photolysis (Nd:YAG; 355 nm; 4 ns), both deaerated and

air-saturated **0B** solutions in toluene produced no observable transient absorption in the visible region. The brominated BODIPYS **1B** to **6B**, however, showed similar transient absorption spectra (TAS). All TAS have a positive band with peak maximum within 420–460 nm and a negative band at 460–550 nm (Figure 3).

The positive band occurred immediately only with the presence of laser excitation of the dyes. It then decayed after the laser excitation was shut off. Therefore, the positive absorption relates to an excited state of BODIPYS. It is T_1 absorption, for several reasons discussed hereafter. It is certainly not S_1 because the decay lifetime of the positive band is on the order of tens of microseconds (Table 1), while the fluorescence lifetime is shorter than 1 ns (Table 1). The shape and position of the negative band for each dye match the corresponding S_0 absorption (Figure 2). The negative band was increased concurrently with the decay of the positive band. The positive bands are separated from the negative bands with well-defined isosbestic points, indicating that a transformation exists between only two species T_1 and S_0 . Therefore, both the rise of the negative bands and the decay of the positive bands are due to: $T_1 \rightarrow S_0$. In other words, the decay of T_1 led to the formation of S_0 .

The following facts also indicate that the positive bands are due to triplet–triplet (T_1 – T_n) absorption.

(1) Efficient molecular oxygen quenching on τ_T . Figure 4 shows the first-order decay kinetics of the transient species for **6B** in the absence of oxygen. From the decay of these dyes, the lifetimes (τ_T^0) were computed to be 43, 39, 36, and 26 μ s for **1B**, **2B**, **4B**, and **6B**, respectively. It can be emphasized that these lifetime values on the microsecond scale also correspond to T_1 – T_n absorption. In the air-saturated solutions (e.g., inset of Figure 4), however, τ_T was dramatically reduced to 0.41, 0.33, 0.32, and 0.40 μ s for **1B**, **2B**, **4B** and **6B**, respectively; in the mean time, the shape of the TAS remained the same. This suggests that a very fast

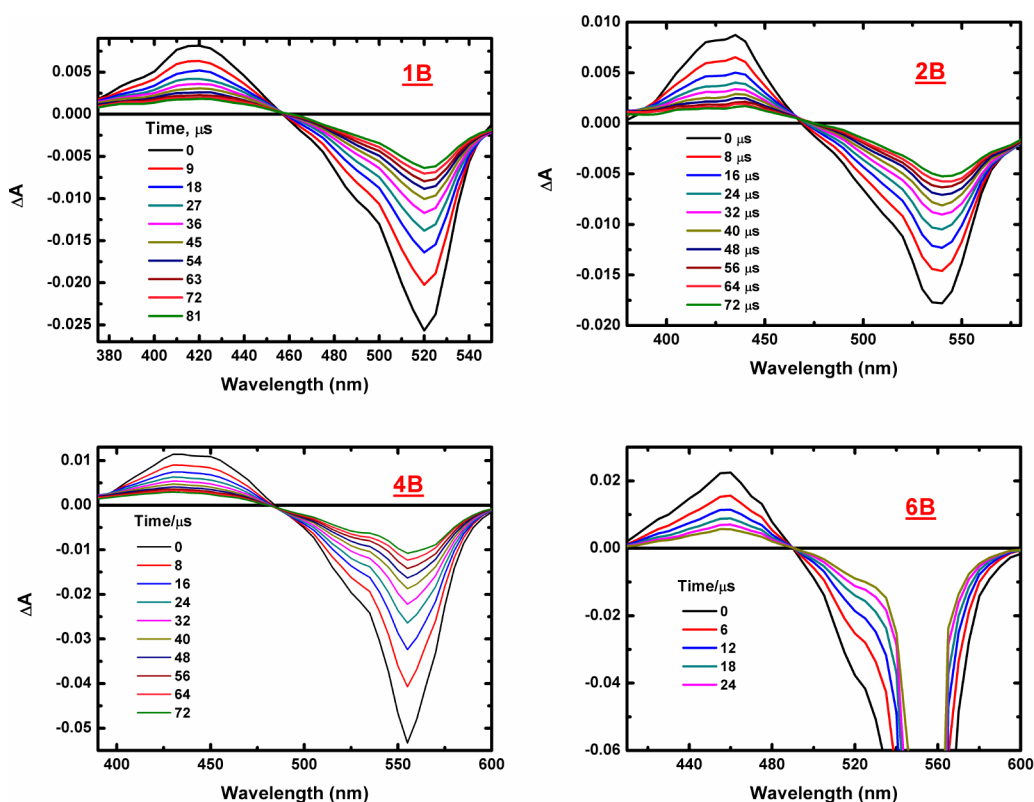


Figure 3. Transient absorption spectra of brominated BODIPYS in degassed toluene with 355 nm laser excitation.

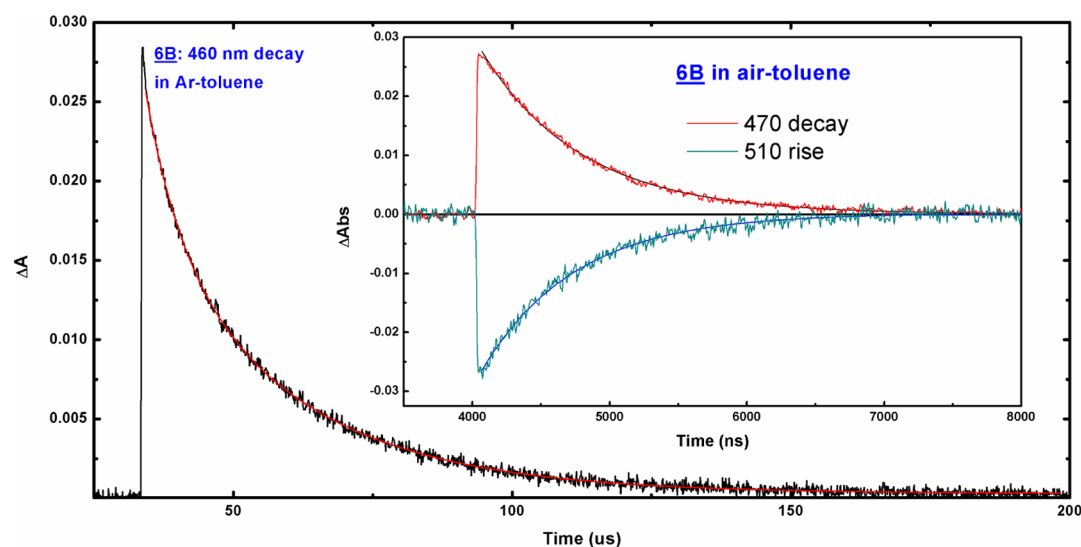


Figure 4. Decay of T_1-T_n absorption at 460 nm in argon-saturated toluene of 6B with excitation by 355 nm laser. Inset: The decay of T_1-T_n absorption at 470 nm and recovery of ground-state absorption at 510 nm in air-saturated toluene of 6B with excitation by 355 nm laser.

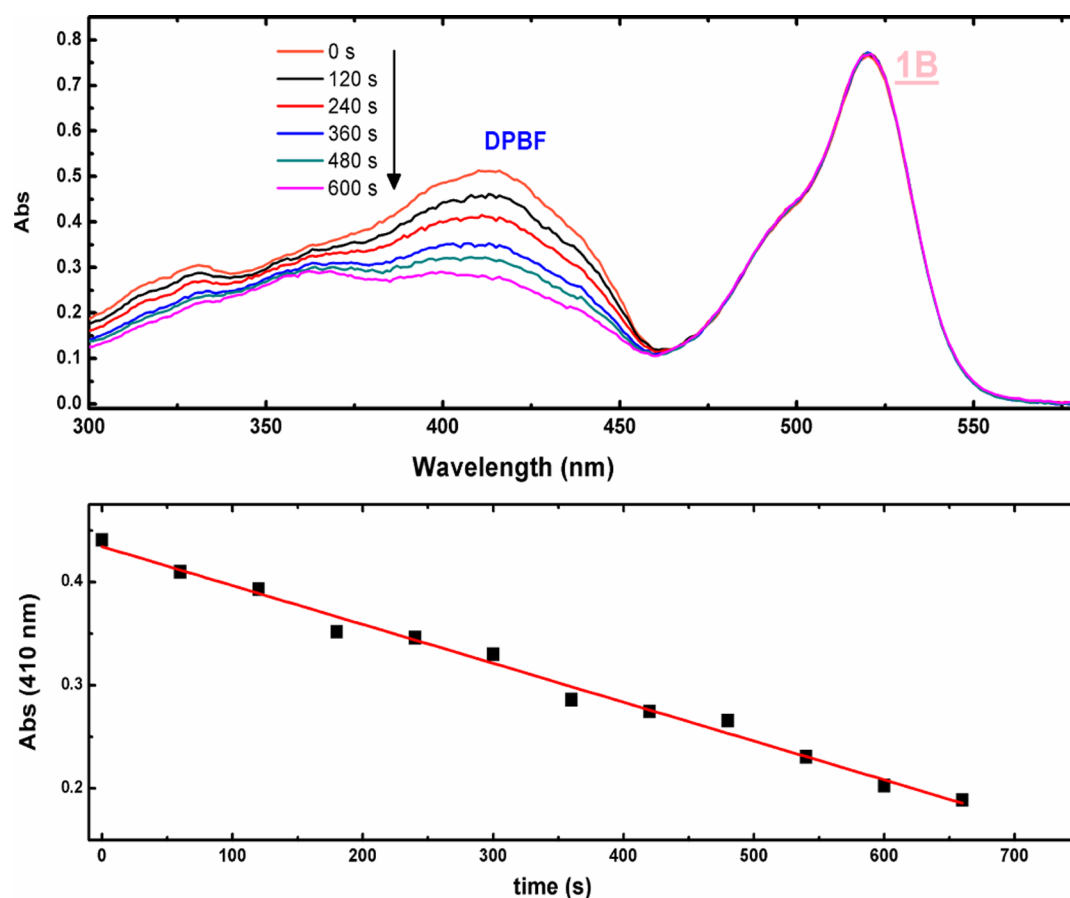


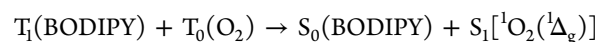
Figure 5. Top: The time evolution of the absorption spectra in **1B** ($15 \mu\text{M}$) photosensitized system containing $22 \mu\text{M}$ DPBF in toluene, with irradiation at 510 nm. Bottom: The plot of DPBF absorbance at 410 nm against time and the linear fitting.

physical quenching process exists. The quenching rate constant k_q can be evaluated by eq 6

$$\tau_T^0/\tau_T = 1 + k_q \tau_T^0 [\text{O}_2] \quad (6)$$

from which the k_q value is $(1.33, 1.67, 1.72, \text{ and } 1.34) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for **1B**, **2B**, **4B**, and **6B**, respectively, taking $[\text{O}_2]$ as 1.8 mmol/L in air-saturated solution.²⁴ The value of k_q is on the order of the

diffusion rate constant; such a fast process means that the quenching is spin-allowed, consistent with the triplet–triplet energy transfer from T_1 of brominated BODIPY to molecular oxygen (also triplet state):



(2) The HAE also indicates that the positive band is due to T_1 absorption. With increasing the number of Br atoms on the

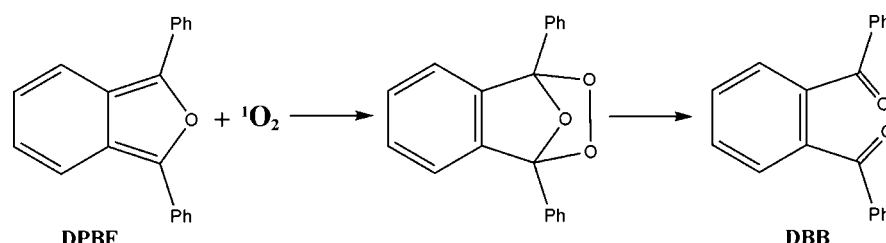
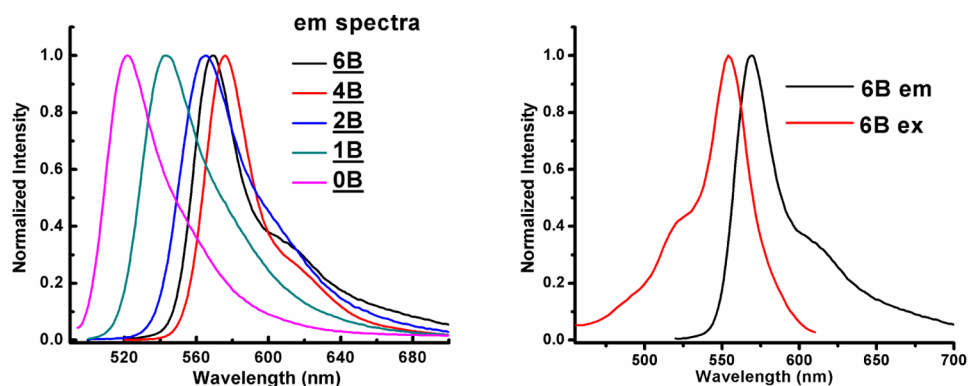


Figure 6. DPBF photooxidation product.

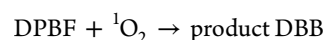
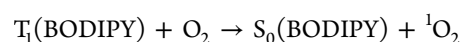
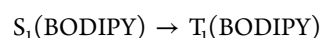
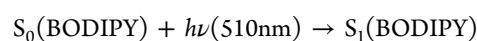
Figure 7. Left: the fluorescence spectra of the brominated BODIPYs (10 μ M) in toluene with excitation at 480 nm. Right: The normalized excitation and emission spectra for 6B.

BODIPY core from **1B** to **6B**, the τ_T value is decreased while Φ_T is increased (Table 1). The more heavy the atoms, the faster the intersystem crossing (ISC) proceeds for both (a) $S_1 \rightarrow T_1$ and (b) $T_1 \rightarrow S_0$. The enhancement of the former process (a) increases Φ_T , while the promotion of process (b) shortens the τ_T .

The increase in Br atom numbers also led to the gradual red shift of the T_1-T_n absorption (Table 1), even in the case of **6B**. For **6B**, its S_0-S_1 absorption is blue-shifted relative to **4B**. This suggests that 3,5-Br substitution exhibits different effects on S_0-S_1 and T_1-T_n electronic transitions, respectively.

Singlet Oxygen Formation. Figure 5 shows the time profiles of the absorption spectra with irradiation at 510 nm in air-saturated toluene, in which **1B** was the photosensitizer while DPBF was the substrate. DPBF absorbs with peak maximum at 410 nm and shows no absorption at 510 nm. The 510 nm light was absorbed only by the brominated BODIPYs.

The absorption bands of the sensitizer **1B** were not changed by the light illumination. The DPBF absorption was decreased with irradiation in the presence of the sensitizer. Without any one of the sensitizer, light, or oxygen, DPBF was not subjected to the change. The results confirm that the degradation of DPBF is indeed due to the oxidation by singlet oxygen through the following mechanism.



(The final step of the mechanism is shown in Figure 6.)

Because the product shows no absorption in the visible range, the concentration decrease in DPBF was monitored using UV-vis spectrometer, and the absorbance at 410 nm of

DPBF (absorption maximum) was recorded and plotted against irradiation time for quantitative kinetic analysis (Figure 5, bottom). The plot can be approximated by a linear fitting, indicating it is pseudo-zero-order kinetics. The slope k of the line is the representative of the reaction rate constants. The singlet oxygen quantum yields (Φ_Δ) were then calculated, as described in the Experimental Section. The Φ_Δ values for the dyes are 0.00, 0.39, 0.45, 0.49, and 0.64, respectively. Φ_Δ is increased with the increase in Br atom number, consistent with the change of Φ_T .

Fluorescence Properties. The steady-state fluorescence spectra and fluorescence quantum yield (Φ_f) in dichloromethane had been reported before.¹⁶ We measured here τ_f (Table 1) in toluene in addition to the steady-state fluorescence spectra (Figure 7) and Φ_f (Table 1). The shape of all fluorescence spectra is similar, but the emission maximum is red-shifted by the increase in Br number except for **6B**. The change tendency is consistent with the effect of Br substitution on the absorption maximum. A mirror symmetry holds between the excitation and emission spectra (e.g., **6B** in Figure 7 bottom) for each compound.

All of these dyes show a small value of Φ_f , mostly consistent with the previous report.¹⁶ Figure 8 shows the fluorescence decay curves. The fluorescence decays are biexponential (Figure 8). An additional long-lived component that appeared in these compounds suggests the presence of complicated photophysical processes. In toluene, both Φ_f and τ_f do not show the monotonical decrease with the increase in Br number due to the presence of several different effects caused by the Br substitution. The bromination causes at least four different effects as follows.

(1) HAE that can enhance ISC and hence decrease Φ_f and shorten τ_f . HAE is solvent-independent. It is generally established that HAE on fluorescence is significant only when Φ_f of the parent compound is sufficiently high. In this case, the Φ_f of the parent compound **0B** is already very low (0.044, 0.036 in toluene and DMF, respectively), and the lifetime (main component) is also

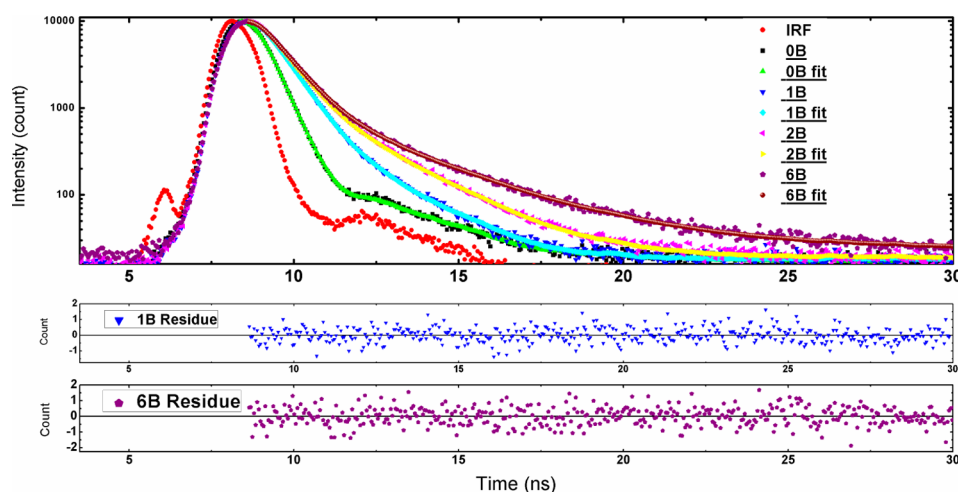


Figure 8. Top: the decay traces of the fluorescence of the brominated BODIPYs (10 μ M) in toluene with excitation by 379 laser (69 ps). The emission was monitored at the emission maximum of each dye. Middle and bottom: The fitting residue for **1B** (monoexponential) and **6B** (biexponential).

short (0.44 ns), so the influence of HAE on Φ_f of the dyes will not be obvious, which is supported by the data in Table 1 measured in toluene. The significant HAE on Φ_T by the bromination occurs because Φ_T of the parent compound **0B** is 0.0.

(2) The bromination significantly increases the mass of BODIPY core so that the vibration and rotation rate of BODIPY core along the σ bond linked to the phenyl moiety is remarkably slowed. Note that the vibration and rotation are the main paths that deactivate the S_1 state of the BODIPY core. In the absence of the phenyl, Φ_f and τ_f are 0.80 and 5.2 ns,² respectively. The value is decreased to 0.044 and 0.44 ns, respectively, when the phenyl is present. Hence k_{ic} (the rate of internal conversion) is increased from 0.38×10^8 to $0.22 \times 10^{10} \text{ s}^{-1}$ by the vibration and rotation of the phenyl. The mass ratio of the phenyl over the BODIPY core (containing n Br atoms) is 77:(167 + 80 n), which shows a big increase from 1:2.17 to 1:3.21, 1:4.24, 1:6.32, and 1:8.4 for **0B**, **1B**, **2B**, **4B**, and **6B**, respectively. The slowing down of the vibration and rotation rate will increase the value of Φ_f and τ_f .

(3) Bromination lowers also the oxidation potential of the linked BODIPY π -system, as we have shown in a previous report,²⁵ so that intramolecular photoinduced electron transfer (PET) can occur from S_1 of the core π -system.²⁵ BF_2 is strongly electron-withdrawing and can act as a good electron acceptor (Figure 9). PET competes with emission and ISC to lower Φ_f

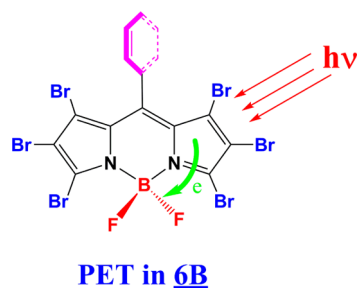


Figure 9. Photoinduced electron transfer in a brominated BODIPY.

and τ_f . However, PET is strongly solvent-dependent and expected to be very slow in toluene, which is a solvent with low polarity. We then measured the Φ_f and τ_f in ethanol and DMF; both are polar solvents. For example, the main component of τ_f

for **1B** is 0.73, 0.51, and 0.42 ns in toluene, ethanol, and DMF, respectively; the main component of τ_f for **2B** is 0.76, 0.60, and 0.46 ns in toluene, ethanol, and DMF, respectively; and the main component of τ_f for **6B** is 0.82, 0.63, and 0.31 ns in toluene, ethanol, and DMF, respectively. Φ_f shows the same solvent effect. In each case, the higher the polarity, the lower the value for Φ_f and τ_f ; this is consistent with that expected for PET. This PET from S_1 has no effect on Φ_T .

(4) Steric effect is particularly important for **6B**, in which the rotation of the phenyl is hindered by the Br atoms at positions 1 and 7. This hindrance also disfavors PET.

Because of the coexistence of four different effects caused by the bromination, the overall result of a specific dye can be different from one another.

CONCLUSIONS

The transient absorption on a microsecond scale for the brominated dyes was shown to be due to T_1 – T_n triplet–triplet absorption, which has rarely been studied. τ_T and Φ_T were then calculated based on the T_1 – T_n absorption. Except for 1,7-Br atoms, the other bromination causes the red shift of S_0 absorption, S_1 fluorescence, and T_1 – T_n absorption. All of the bromination led to the increase in Φ_T and Φ_Δ and shortening of τ_T . τ_T is still fairly long on the order of tens of microseconds, which allow the efficient generation of singlet oxygen with Φ_Δ close to its Φ_T in each case. Φ_T and Φ_Δ of the dyes containing Br atoms are in the range from 40 to 65%, which suggests that the brominated BODIPYs are potential photosensitizers.

In contrast with the remarkable HAE on Φ_T , the bromination has smaller but complexed influence on Φ_f and τ_f due to the very low fluorescence efficiency of the parent compound, the slowing of vibration and rotation rate of BODIPY core, the change of oxidation potential of the BODIPY, and the hindrance to the rotation of the phenyl.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangxianfu@tsinghua.org.cn. Fax: 86 3358357040. Tel: 86 3358357040.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Loudet, A.; Burgess, K. *Chem. Rev.* **2008**, *107*, 4891–4932.
- (2) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2007**, *47*, 1184–1201.
- (3) Alvarez, M.; Costela, A.; Garcia-Moreno, I.; Amat-Guerri, F.; Liras, M.; Sastre, R.; Arbeloa, F. L.; Prieto, J. B.; Arbeloa, I. L. *Photochem. Photobiol. Sci.* **2008**, *7*, 802–813.
- (4) Ortiz, M. J.; Garcia-Moreno, I.; Agarrabeitia, A. R.; Duran-Sampedro, G.; Costela, A.; Sastre, R.; Arbeloa, F. L.; Prieto, J. B.; Arbeloa, I. L. *Phys. Chem. Chem. Phys.* **2012**, *12*, 7804–7811.
- (5) Duran-Sampedro, G.; Agarrabeitia, A. R.; Garcia-Moreno, I.; Costela, A.; Bañuelos, J.; Arbeloa, T.; Arbeloa, I. L.; Chiara, J. L.; Ortiz, M. J. *Eur. J. Org. Chem.* **2012**, *2012*, 6335–6342.
- (6) Gießler, K.; Griesser, H.; Göhringer, D.; Sabirov, T.; Richert, C. *Eur. J. Org. Chem.* **2010**, *2010*, 3611–3620.
- (7) Deniz, E.; Ray, S.; Tomasulo, M.; Impellizzeri, S.; Sortino, S.; Raymo, F. i. M.; Deniz, E.; Ray, S.; Tomasulo, M.; Impellizzeri, S.; Sortino, S.; Raymo, F. i. M. *J. Phys. Chem. A* **2010**, *114*, 11567–11575.
- (8) Boens, N.; Leen, V.; Dehaen, W. *Chem. Soc. Rev.* **2012**, *41*, 1130–1172.
- (9) Laure, B.; Hani, K.; Franck, C.; Pascale, J.; Pascal, R.; Raymond, Z. *Adv. Funct. Mater.* **2008**, *18*, 401–413.
- (10) Kamkaew, A.; Lim, S. H.; Lee, H. B.; Kiew, L. V.; Chung, L. Y.; Burgess, K. *Chem. Soc. Rev.* **2013**, *42*, 77–88.
- (11) Lim, S. H.; Thivierge, C.; Nowak-Sliwinska, P.; Han, J.; Bergh, H. v. d.; Wagniere, G.; Burgess, K.; Lee, H. B. *J. Med. Chem.* **2010**, *53*, 2865–2874.
- (12) Awuahab, S. G.; You, Y. *RSC Adv.* **2012**, *2*, 11169–11183.
- (13) Wu, W.; Guo, H.; Wu, W.; Ji, S.; Zhao, J. *J. Org. Chem.* **2011**, *76*, 7056–7064.
- (14) Chen, Y.; Zhao, J.; Xie, L.; Guo, H.; Li, Q. *RSC Adv.* **2012**, *2*, 3942–3953.
- (15) Singh-Rachford, T. N.; Castellano, F. N. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (16) Jiao, L.; Pang, W.; Zhou, J.; Wei, Y.; Mu, X.; Bai, G.; Hao, E. *J. Org. Chem.* **2011**, *76*, 9988–9996.
- (17) Jiao, L.; Yu, C.; Li, J.; Wang, Z.; Wu, M.; Hao, E. *J. Org. Chem.* **2009**, *74*, 7525–7528.
- (18) Jiao, L.; Yu, C.; Uppal, T.; Liu, M.; Li, Y.; Zhou, Y.; Hao, E.; Hu, X.; Vicente, M. G. H. *Org. Biomol. Chem.* **2010**, *8*, 2517–2519.
- (19) Magde, D.; Wong, R.; Seybold, P. G. *Photochem. Photobiol.* **2002**, *75*, 327–334.
- (20) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1–250.
- (21) Lagorio, M. G.; Dico, L. E.; Roman, E. A. S.; Braslavsky, S. E. *J. Photochem. Photobiol., B* **1989**, *3*, 615–624.
- (22) DeRosa, M. C.; Crutchley, R. J. *Coord. Chem. Rev.* **2002**, *233*, 351–371.
- (23) Pretsch, E.; Buehlmann, P.; Affolter, C. *Structure Determination of Organic Compounds: Tables of Spectral Data*; Springer-Verlag: Berlin, 2000.
- (24) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; Taylor & Francis: New York, 2006.
- (25) Zhang, X. F.; Zhang, I.; Liu, L. *Photochem. Photobiol.* **2010**, *86*, 492–498.