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BODIPY-based photosensitizers with intense visible light harvesting ability and high $^1O_2$ quantum yield in aqueous solution

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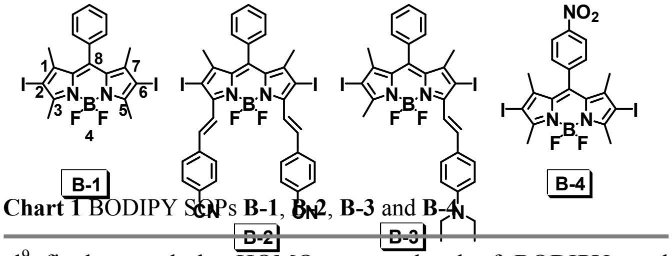
A novel method to enhance the singlet oxygen quantum yield of photosensitizers in aqueous solution has been developed by introducing electron-withdrawing group into BODIPY. B-2 were prepared based on this method and shows intense light harvesting ability (ε = 6.8×10^4 M^{-1}cm^{-1} at 643 nm) and high $^1O_2$ quantum yield in aqueous solution (Φ = 0.21). B-2 has been successfully used as $^1O_2$ sensitizers for the photo-oxidation of 1,5-dihydroxynaphthalene. This method substantially improves the photooxidation capability and photostability of $^1O_2$ sensitizers in aqueous solution.

Singlet state oxygen ($^1O_2$) is a potent oxidation reagent, which can be produced by triplet-triplet energy transfer between ground state oxygen (triplet state, $^3O_2$) and singlet oxygen photosensitizers (SOP).[1] Now much attention has been paid to the production of $^1O_2$ and its application for photooxidation and photodynamics therapy.[2-5] However, the conventional SOPs have many limitations, such as short wavelength absorption, and a limited usable range of solvent conditions. For example, the molar extinction coefficients of Ir(III) complexes as SOP are usually less than 5000 M^{-1} cm^{-1} beyond 400 nm and their absorption maxima are located in the UV range.[6] Organic SOPs, such as BODIPY covalent dimmer, are always in the off state of the photosensitizers and unable to generate $^1O_2$ in polar solvents.[7] It is well known that aqueous phase system is more economical and environmentally friendly for organic reactions. However, solvents with strong polarity are detrimental to triplet-triplet energy transfer, and the further generation of $^1O_2$. Therefore, it is highly desired to develop a methodology to enhance the $^1O_2$ quantum yield and light harvesting ability of SOPs in various conditions, especially in aqueous phase system.

After excitation of photosensitizers, electron transfer process and energy transfer process could happen between photosensitizers and $^3O_2$. These two processes always compete with each other. Increasing the polarity of the solvents always causes electron transfer to dominate, which unfortunately results in the off state of SOPs.[8-10] By introducing the electron-donating substituents into meso benzene moiety of BODIPY, Nagano et al[9] finely tuned the HOMO energy level of BODIPY, and selectively controlled the generation of $^1O_2$ through photoinduced electron transfer (PET) process so as to be sensitive to environment polarity. Other groups also make great achievements in tuning photoinduced energy and electron transfer process in dyads.[7,8,10,11]



B-1 B-2 B-3 B-4

Chart 1 BODIPY SOPs **B-1**, **B-2**, **B-3** and **B-4**

Inspired by these pioneering works, we propose that inhabitation of PET process is a key factor to enhance $^1O_2$ quantum yield of SOPs for photooxidation in wide range of solvent conditions, which could be achieved by finely tuning SOPs' photoredox properties through rational design and synthesis.[12,13] Herein, to develop the photosensitizer with intense visible-light harvesting ability and high singlet oxygen quantum yield in aqueous phase system, the boron dipyrromethene (BODIPY) fluorophores attracted our attentions. After Knovengel condensation reaction at C3 and C5 (Chart 1), the π-conjugation could be effectively enlarged, and the absorption could be extended to near infrared region (NIR) with intensive absorption. The generation of $^1O_2$ through energy transfer process could be enhanced by incorporating electron-withdrawing group (−CN) at the C3 and C5 instead of electron-donating group (−NEt$_2$).

B-1 and **B-4** were prepared according to the literature.[14,15] **B-2** and **B-3** were prepared by Knoevenagel condensation reaction (see Scheme 1, Figure S1–S4 of ESI†). **B-1** has high extinction coefficient (ε = 8×10^4 M^{-1} cm^{-1} at λ_{max} = 535 nm, Figure 1a). After derivation at C3 and C5 position by Knoevenagel condensation reaction, the absorption spectra of the derivatives show obvious red shifts, extending from visible light to NIR. For example, the maximum absorption wavelength of **B-2** is at 643 nm (ε = 6.8×10^4

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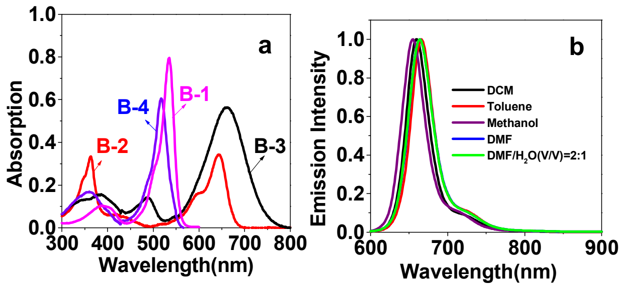

Figure 1 a) UV-Vis absorption spectra of **B-1**, **B-2**, **B-3** and **B-4** in mixed solvent of DMF/H_2O=5:1(V/V); b) fluorescence emission spectra of **B-2** in different solvents (DCM, Toluene, Methanol, DMF, DMF/H_2O (V/V) =5:1). (c = 1.0×10^{-5} M, 20 °C).

Table 1 Redox potential and photocatalysis properties of SOPs

	$\Phi_\Delta{}^a$	E_{ox}/V ^{b}	E_{red}/V ^{b}	k_{obs} ^{c}	Yield/%^{d}	ΔG_0 ^{e}
B-1	0.30	1.41	−1.03	371.5	74.7	−0.09
B-2	0.21	1.25	−0.63, −1.28	135.0	70.9	−0.08
B-3	0.006	0.87, 1.28	−1.17	40.2	47.9	−0.18
B-4	0.01	1.58	−0.77, −1.04	49.1	52.1	−0.05

[a] Singlet oxygen quantum yield in aqueous solution (DMF/H_2O (V/V)=5:1). With **B-1** as standard (Φ_Δ=0.69 in CH_2Cl_2). [b] Redox potential (vs. NHE, CH_2Cl_2). [c] Photoreaction rate constants of photoxidative reaction of 1,5-DHN, catalyzed by the SOPs; 10^{-4}min^{-1}. [d] The yield of photoxidative reaction of 1,5-DHN. [e] free energy changes of the potential PET effect with Rehm–Weller Equation (see Table S2 of ESI†).

M^{-1}cm^{-1}, Figure 1a). Compared with the other SOPs, **B-2** shows a new absorption at 361 nm, which could be attributed to styryl absorption. This result indicates that there is no significant electronic coupling between the distyryl and fluorophore.[17] The fluorescence properties of SOPs were also measured in various solvents (see Figure 1b, Table S1 and Figure S5 of ESI†). **B-2** with electron-withdrawing group (−CN) shows maximum fluorescence emission at 664 nm, and there is no obvious wavelength shifts with the increase of solvents' polarity, which suggest that no charge separate state has formed and to some extent, improve the efficiency of energy transfer. It is note that the $^1O_2$ quantum yield of **B-2** is up to 0.21 in the mixed solvent of DMF and H_2O, which is obviously higher than that of the SOPs based BODIPY previously reported (Φ_Δ = 0.05).[17] The emission wavelengths of **B-1** and **B-4** are also not sensitive to the polarity of solvents, the $^1O_2$ quantum yield of **B-1** comes to 0.30, which is in agreement with **B-2**. Conversely, introducing electron-donating group (−NEt_2) to the C3 position makes **B-3** more sensitive to the polarity of solvents than C8 derivatives.[9] **B-3** shows almost 80 nm red shifts, from 716 nm in toluene to 796 nm in aqueous solution, which indicates that there exists obvious PET process to form charge separate state. As consequence, energy transfer is hindered. The $^1O_2$ quantum yield of **B-3** is only 0.006, which is subsequently decreased after introducing the electron-donating group.

The cyclic voltammetry (CV) were performed in dichloromethane solution (10^{-3} M) with tetrabutylammonium hexafluorophosphate (0.05 M) as supporting electrolyte, glassy carbon as the working electrode and platinum wires as the counter and pseudo-reference electrode. Based on redox potential of BODIPY unit (**B-1**), the oxidation potential greater than 1.0 can be ascribed to the oxidations of BODIPY unit in each SOP. Interestingly, two reductions are observed for **B-2** (−0.63, −1.28 vs NHE) and **B-4** (−0.77, −1.04 vs NHE), of which the more negative one can be ascribed to the reduction of –CN (−1.28 vs NHE) and –NO_2 (−1.04 vs NHE) respectively, which means –CN and –NO_2 can grab electrons in redox reactions. However, no oxdidation potentials of −CN and −NO_2 exist, so there is no such a process for –CN and –NO_2 to release electrons, resulting in the inhibition of the PET. Furthermore, the thermodynamic driving forces for PET process (ΔG_0, free energy change of the potential PET effect) were calculated based on the redox potential values, by employing the Rehm-Weller Equation (see Table 1 and Table S2 of ESI†).[18,19] For **B-3**, amino group acts as electron donor and O_2 acts as electron acceptor in the PET process. **B-3** shows more negative ΔG_0

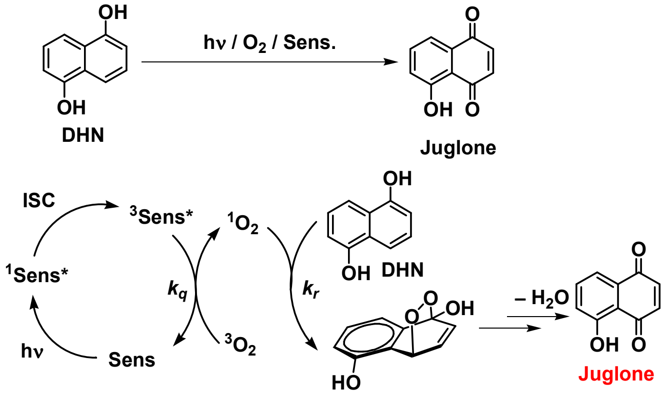

Chart 2 Mechanism for the photooxidation of DHN with singlet oxygen ($^1O_2$) photosensitizer.

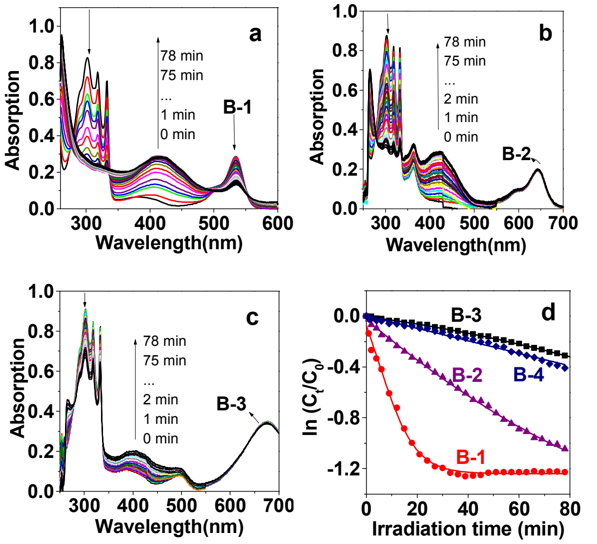

Figure 2 UV/Vis absorption spectral changes for the photooxidation of 1,5-DHN (1.0×10^{-4} M) using SOPs (a) **B-1**, (b) **B-2** and (c) **B-3** in DMF/H_2O (5:1, v/v) mixed solvent, [SOP]= 5.0×10^{-6} M (5% mol), 20 ºC. Irradiated with 35 W xenon lamp (25 mW·cm^{-2}). Light with wavelength shorter than 385 nm was blocked by 0.72 M $NaNO_2$ solution. (d) Absorption changes in the photoxidation of 1,5-DHN and plots of ln (C_t/C_0) vs irradiation time.

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than others, indicating that PET process is enhanced while energy transfer process is inhibited. Therefore, **B-3** has the lowest $^1O_2$ quantum yield among these SOPs ($\Phi_\Delta = 0.006$). The electron-withdrawing group conjugated to the BODIPY fragment contributes to the increase of ΔG_0, as **B-2** shows significantly higher ΔG_0 than that of **B-3**, which means much weaker ability to undergo PET process thermodynamically. Thus, the $^1O_2$ quantum yield of **B-3** is enhanced ($\Phi_\Delta = 0.21$). However, ΔG_0 (or redox potential) is not the sole determinal factor for $^1O_2$ quantum yield. Relative researches need to be further explored in the future.

In order to further investigate the performance of SOPs in aqueous solution, the photooxidation of 1,5-dihydroxynaphthalene (1,5-DHN) with different SOPs were conducted in aqueous solvent (Figure 2). The mechanism for the photooxidation of 1,5-DHN with singlet oxygen photosensitizer is presented in Chart 2. $^1O_2$ is produced upon photoexcitation of the aerated solution of the SOP. In this process, an energy transfer process from the triplet excited state of a sensitizer to triplet oxygen ($^3O_2$) contributes to singlet oxygen ($^1O_2$) production. Then, 1,5-DHN can be oxidized by the $^1O_2$ and Juglone are produced in further, which could be monitored by the decrease of the absorption of 1,5-DHN at 301 nm and the increase of that of Juglone, the product at 427 nm (Figure 2).[4] The photooxidation velocity with SOPs were quantitatively compared by plots of $\ln(C_t/C_0)$ vs t curves (Figure 2d). There are clear differences between the photoreaction rate constants (k_{obs}) of the photooxidation with different SOPs. For example, the photoreaction rate constant of **B-2** ($k_{obs} = 135.0 \times 10^{-4}$ min^{-1}) is much larger than that of **B-3** ($k_{obs} = 40.2 \times 10^{-4}$ min^{-1}), but less than that of **B-1** (Figure 2d and Table 1). Although **B-1** has the highest singlet oxygen quantum yield (Φ_Δ=0.30) compared with the other prepared SOPs, there is an obvious photobleaching phenomenon for **B-1** at 533 nm, indicating that the photostability of **B-1** is not as good as those of **B-2** and **B-4**. The introduced electron-withdrawing group (−CN, $-NO_3$) could improve the photostability of SOPs.[17]

Conclusions

In conclusion, we prepared a series of 2,6-diiodo-BODIPY derivatives with intense light harvesting ability. For the applications in enhancing singlet oxygen production in aqueous solution, **B-2** with electron-withdrawing group shows intense ability of sensitizing $^1O_2$ ($\Phi_\Delta = 0.21$) which is much higher than those of **B-3** (Φ_Δ=0.006) and **B-4** (Φ_Δ=0.01). Compared with **B-1**, **B-2** with electron-withdrawing group shows better photostability. The enhanced $^1O_2$ sensitization properties, intense light harvesting ability and significant photostability of SOPs in aqueous solution, will benefit for the development of green chemistry in a broad stage.

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Notes and references

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1. (a) J. Z. Zhao, W. H. Wu, J. F. Sun, and S. Guo, *Chem. Soc. Rev.* 2013, **42**, 5323; (b) W. Wu, L. Zhan, W. Fan, X. Wu, Q. Pan, L. Huang, Z. Li, J. Zheng, Y. Wang and M. Wu, *Macromol. Chem. Phys*., 2014, **215**, 280; (c) W. Wu, P. Yang, L. Ma, J. Lalevée and J. Zhao, *Eur. J. Inorg. Chem.*, 2012, **2**, 228.
2. J. F. Lovell, T. W. B. Liu, J. Chen and G. Zheng, *Chem. Rev.* 2010, **110**, 2839.
3. (a) N. Adarsh, R. R. Avirah and D. Ramaiah, *Org. Lett.* 2010, **12**, 5720; (b) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher and D. F. O'Shea, *J. Am. Chem. Soc.*, 2004, **126**, 10619; (c) Y. Zhang, K. Aslan, M. J. R. Previte and C. D. Geddes, *J. Fluoresc.*, 2007, **17**, 345; (d) Y. You and W. Nam, *Chem. Soc. Rev.*, 2012, **41**, 7061.
4. J. F. Sun, J. Z. Zhao, H. M. Guo and W. H. Wu, *Chem. Commun.* 2012, **48**, 4169.
5. (a) L. Huang and J. Z. Zhao, *Chem. Commun.* 2013, **49**, 3751; (b) Y. Cakmak, S. Kolemen, S. Duman, Y. Dede, Y. Dolen, B. Kilic, Z. Kostereli, L. T. Yildirim, A. L. Dogan, D. Guc and E. U. Akkaya, *Angew. Chem., Int. Ed.*, 2011, **50**, 11937; (c) M.-R. Ke, S.-L. Yeung, W.-P. Fong, D. K. P. Ng and P.-C. Lo, *Chem. –Eur. J.*, 2012, **18**, 4225; (d) F. Schmitt, J. Freudenreich, N. P. E. Barry, L. Juillerat-Jeanneret, G. Süss-Fink and B. Therrien, *J. Am. Chem. Soc.*, 2012, **134**, 754.
6. S. Takizawa, R. Aboshi and S. Murata, *Photochem. Photobiol. Sci.* 2011, **10**, 895.
7. (a) X. F. Zhang and X. Yang, *J. Phys. Chem. B* 2013, **117**, 9050; (b) S. Duman, Y. Cakmak, S. Kolemen, E. U. Akkaya and Y. Dede, *J. Org. Chem.*, 2012, **77**, 4516; (c) W. Pang, X.-F. Zhang, J. Zhou, C. Yu, E. Hao and L. Jiao, *Chem. Commun.*, 2012, **48**, 5437.
8. D. G. Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. A. Herranz and L. Echegoyen, *J. Am. Chem. Soc.* 2004, **126**, 6301.
9. T. Yogo, Y. Urano, A. Mizushima, H. Sunahara, T. Inoue, K. Hirose, M. Lino, K. Kikuchi and T. Nagano, *Proc. Natl Acad. Sci. USA* 2008, **105,** 28.
10. D. G. Rodríguez, C. G. Claessens, T. Torres, S. Liu, L. Echegoyen and N. Vila, *Chem. Eur. J.* 2005, **11**, 3881.
11. R. Ziessel, B. D. Allen, D. B. Rewinska and A. Hariman, *Chem. Eur. J.* 2009, **30**, 7382.
12. D. Ravelli, D. Dondi, M. Fagnoni and A. Albini, *Chem. Soc. Rev.* 2009, **38**, 1999.
13. S. Fukuzumi and K. Ohkubo, *Chem. Sci.* 2013, **4**, 561.
14. X. Fang, Y. C. Liu and C. Li, *J. Org. Chem.* 2007, **72**, 8608.
15. L. Huang, J. Z. Zhao, S. Guo, C. Zhang and J. Ma, *J. Org. Chem.* 2013, **78**, 5627.
16. H. Sunahara, Y. Urano, H. Kojima and T. Nagano, *J. Am. Chem. Soc.* 2007, **129**, 5597.

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DOI: 10.1039/C4RA08654F

17. T. Yogo, Y. Urano, Y. Ishisuka, F. Maniwa and T. Nagano, *J. Am. Chem. Soc*. 2005, **127**, 12162.
18. X. Zhang, L. Chi, S. Ji, Y. Wu, P. Song, K. Han, H. Guo, T. D. James, J. Zhao. 2009, **131**, 17452.
19. D. Rehm, A. Weller. *Isr. J. Chem.* 1970, **8**, 259.

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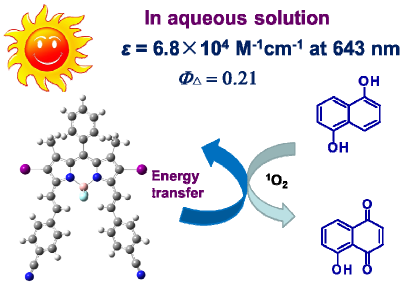

Introducing electron-withdrawing group into BODIPY enhanced $^1O_2$ sensitization properties, intense light-harvesting ability and significant photostability of SOPs in aqueous solution.