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Synthesis di-bromo substituted BOPHY dye for the singlet oxygen generation

Q1 Tian-Fang Cui^a, Jing Zhang^a, Xin-Dong Jiang^{a,*}, Ya-Jun Su^a, Chang-Liang Sun^b, Jiu-Li Zhao^a

^a College of Applied Chemistry, Key Laboratory of Rare-earth Chemistry and Applying Liaoning Province, Shenyang University of Chemical Technology, Shenyang 110142, China

^b Center of Physical and Chemistry Test, Shenyang University of Chemical Technology, Shenyang 110142, China

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ABSTRACT

A dibromo substituted BOPHY derivative (2) was prepared and found to exhibit photo-sensitization capability. *Rapid* oxidation of 80% DPBF *at* the first 6 min was observed suggesting that 2 is a superior photo-sensitizer than methylene blue. The HOMO–LUMO band gap for the lowest energy absorption bands of the BOPHY 1 is smaller than that of PS 2, which is in good agreement with the red shift in the absorption observed between 1 and 2.

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transition with attached heavy atoms [32].

have been widely investigated (Fig. 1) [18-31]. Recently, BODIPY

based photosensitizers were reported by promoting $S_1 \rightarrow T_1$

fluorophore bis(difluoroboron)1,2-bis((1H-pyrrol-2-yl)methy-

lene)-hydrazine (BOPHY) was independently reported by Ziegler

and Hao et al. (Fig. 1) [33,34]. The new fluorescent BOPHY dye can

be smoothly obtained by the reaction of pyrrole-2-carboxalde-

hvde with hvdrazine, and followed by complexation with Et₃N-

BF₃·Et₂O. The symmetric structure is composed of four rings at the

same plane, including two BF₂ units in six-membered chelate

rings in the center and two pyrrole units on the periphery (Fig. 1)

[33,34]. The fluorescence quantum yield for the unmodified

BOPHY is near 100% [33,34]. Since the new BOPHY dye has a rigid

structure, excellent optical properties promote us to use the

BOPHY scaffold as a template for further functionalizations. Our

recent research interest lies in the novel BODIPY/aza-BODIPY

family of fluorescent dyes and their application [35–43]. Very

recently, our group reported the study on a (p-dimethylamino)-

styryl-containing BOPHY as a turn-on fluorescent probe for pH

[44], and Ziessel et al. subsequently also reported the BOPHY dye

with the intramolecular cascade energy transfer [45]. However,

no other modifications on BOPHY dyes were reported. Herein, we

report our studies on the modifications on BOPHY dyes by attaching heavy atoms as a photosensitizer for singlet oxygen

Very recently, another type of unique pyrrole-BF₂-based

1. Introduction

Singlet oxygen $({}^{1}O_{2})$ is of great importance to various applications of cycloaddition reactions, photodynamic therapy (PDT) and so forth [1-3]. Especially, PDT is a noninvasive technique for the treatment of a variety of tumors by the combined use of visible or near-infrared light with a photosensitizing drug [4-7]. The tumor is selectively irradiated with low-energy light of wavelength [8–11], resulting in excitation of the photosensitizer (PS). Since the singlet oxygen is the key cytotoxic agent in the PDT therapeutic process, the singlet oxygen generation from a photosensitizer is regulated by the efficiency of a spin-forbidden electronic transition from a singlet to a triplet state upon irradiation [12]. Comparing to several types of directly linked BODIPY dimmers without the use of heavy atoms as a PS [13,14], the heavy atom effect was still advocated and has been a popular and applicable chemical approach to improve intersystem crossing (ISC) to generate the singlet oxygen in several molecules by attaching heavy atoms [15–17].

Due to the excellent photochemical properties of boron dipyrromethenes (BODIPY), such as high fluorescence quantum yields, high absorption coefficients and so on, such derivatives

E-mail address: xdjiang@syuct.edu.cn (X.-D. Jiang).

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generation.

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^{*} Corresponding author.

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Fig. 1. The core structure of BODIPY and BOPHY.

57 Singlet oxygen generation was studied with 1,3-diphenyliso-58 benzofuran (DPBF), a well-known singlet oxygen scavenger, whose 59 maximum absorption at 416 nm diminishes upon reacting with 60 singlet oxygen [46]. However, the reported BOPHY dyes are not 61 suitable as a photosensitizer, due to the overlap of the absorption 62 between BOPHY and DPBF or the no site to attach heavy atoms in 63 the BOPHY structure [33,34]. To avoid the defect, a tetraphenyl-64 containing BOPHY dye as a PS was herein designed and found to be 65 highly effective to generate the singlet oxygen.

66 2. Experimental

67 ¹H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. ¹H NMR chemical shifts (δ) are given in ppm 68 69 downfield from Me₄Si, determined by chloroform (δ 7.26). ¹³C 70 NMR spectra were recorded on a Bruker AVANCE III 125 MHz 71 spectrometer. ¹³C NMR chemical shifts (δ) are reported in ppm 72 with the internal CDCl₃ at δ 77.0 as standard. Toluene solvents 73 were distilled over CaH₂. Merck silica gel 60 was used for the 74 column chromatography.

Fluorescence spectra were recorded on a FluoroSENS spectrophotometer. UV/vis spectra were recorded on UV-2550 spectrophotometer at room temperature. The refractive index of the medium was measured by 2 W Abbe's refractometer at 20 °C. The fluorescence quantum yield (Φ_f) of the BOPHY system was calculated using the following relationship (Eq. (1) [47]):

$$\Phi_{\rm f} = \Phi_{\rm ref} F_{\rm sampl} A_{\rm ref} n_{\rm sampl}^2 / F_{\rm ref} A_{\rm sampl} n_{\rm ref}^2 \tag{1}$$

82 Here *F* denotes the integral of the corrected fluorescence spectrum, *A* is the absorbance at the excitation wavelength. Rhodamine 6G in 84 methanol was used as the standard ($\Phi_f = 0.95$ [48], in air 85 equilibrated water and deaerated solutions) for BOPHY 1.

The MO calculations were performed at the DFT level, and the frontier molecular orbitals of BOPHY **1** and **2** at the MP2/6-31G* level with Gaussian 03.

89 2.1. Synthesis of BOPHY 1

90 3,5-Diphenyl-1*H*-pyrrole-2-carbaldehyde (45 mg, 0.18 mmol) 91 and hydrazine hydrate (5.0 mg, 0.09 mmol) were dissolved in 92 20 mL of ethanol. Three drops of acetic acid were added, the 93 solution became yellow. After few seconds, a yellow precipitate 94 formed and the reaction mixture was left to stir at room 95 temperature for an hour. The yellow precipitate was collected 96 by filtration and rinsed with cold ethanol (2×10 mL) and dried under vacuum to afford a yellow solid. Then, Et₃N (0.5 mL) was 97 added to a solution of this yellow solid in CH₂Cl₂ (10.0 mL). 98 BF₃·Et₂O (1.0 mL) was then added dropwise. The reaction mixture 99 was stirred at room temperature overnight. The reaction was 100 quenched with crushed ice, extracted with CH₂Cl₂, and purified by 101 chromatography on silica gel followed by recrystallization from 102 CH_2Cl_2/n -hexane to afford BOPHY **1** (25.1 mg, 47%) as red solids. 103 Mp: 287.0–288.0 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.21 (s, 2H), 7.84 104 (d, 4H, ${}^{3}I$ = 7.5 Hz), 7.42–7.51 (m, 16H), 6.82 (s, 2H). ${}^{13}C$ NMR 105 (125 MHz, CDCl₃): δ 152.2, 145.2, 138.3, 132.2, 131.4, 129.8, 129.2, 106 129.0, 128.9, 128.8, 128.4, 123.4, 117.1. HRMS-MALDI (m/z): 107 [M+Na]⁺ calcd. for C₃₄H₂₄B₂F₄N₄Na: 609.2021; found 609.2069. 108

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2.2. Synthesis of BOPHY **2**

BOPHY 1 (21.5 mg, 0.036 mmol) was treated with bromine 110 (7.6 mg, 0.095 mmol) in dry CCl₄ (15 mL) at 30 °C under nitrogen 111 for 12 h. The reaction was quenched with water, extracted with 112 CH₂Cl₂, and purified by chromatography on silica gel followed by 113 recrystallization from CH_2Cl_2/n -hexane to afford dye 2 (17.2 mg, 114 64%) as yellowish red solids. Mp: 291.0-292.0 °C. ¹H NMR 115 (500 MHz, CDCl₃): δ 7.98 (s, 2H), 7.69 (s, 3H), 7.47-7.55 (m, 116 17H). ¹³C NMR (125 MHz, CDCl₃): δ 149.6, 142.9, 139.1, 130.1, 117 129.9, 129.5, 129.4, 129.1, 128.9, 128.1, 126.7, 123.0, 106.3. HRMS-118 MALDI (m/z): $[M+Na]^+$ calcd. for $C_{34}H_{22}B_2Br_2F_4N_4Na$: 767.0211; 119 found 767.0356. 120

2.3. Detection of singlet oxygen by DPBF oxidation

Singlet oxygen generation experiment was set up, using a 122 150 W xenon lamp at 0.5 mW/cm². A toluene solution of 123 photosensitizer $(5 \times 10^{-6} \text{ mol/L})$ and 1,3-diphenylisobenzofuran 124 $(6 \times 10^{-5} \text{ mol/L})$ was exposed to the monochromatic light by the 125 optical filter at the peak absorption wavelength (500 nm) for 1-126 2 min at 25 °C. The absorbance was measured several times after 127 each irradiation. Reaction of 1,3-diphenylisobenzofuran with 128 singlet oxygen was monitored by the reduction in intensity of 129 the absorption band at 416 nm over 32 min. 130

3. Results and discussion

Synthesis of the BOPHYs were outlined in Scheme 1. Utilizing1323,5-diphenyl-1H-pyrrole-2-carbaldehyde as the starting material,
a centrosymmetric tetraphenyl-containing BOPHY 1 was smoothly1330btained in a 47% yield based on the reported literatures135[33,34]. The PS 2 was prepared in a 64% yield by bromination of
BOPHY 1 with Br2.137

The BOPHY **1** absorbs maximally at 508 nm and emits at 138 524 nm in CHCl₃ (Fig. 2), with the high extinction coefficients ($\varepsilon = 60,000 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$), the narrow full width at half maximum (Fwhm = 78 nm) and the high fluorescence quantum yield 141 ($\Phi_{\rm f} = 0.96$), which optical properties are comparable to those of the reported BOPHY dyes [33,34,44,45]. Due to remarkable absorption difference between BOPHY **2** (506 nm) and DPBF 144



Scheme 1. Synthesis of the tetraphenyl-containing BOPHY 1 and the PS 2.

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Fig. 2. (a) Normalized absorption and (b) fluorescence spectra of 1 in CH₂Cl₂ at 293 K.

(416 nm), the detection of generating singlet-oxygen becomepossible and was carried out in the following experiments.

147 A comparative study of singlet oxygen generation in toluene was performed to assess the ability of the PS 2 to generate singlet 148 149 oxygen. The solutions were irradiated with monochromatic light 150 [49] at the peak absorption wavelength (500 nm) in the visible 151 region by using a 150 W xenon lamp at 0.5 mW/cm². Singlet 152 oxygen generation was estimated experimentally by DPBF. The 153 decrease of the absorbance band at 416 nm was monitored. caused by the oxidation of DPBF with reactive oxygen species, the singlet 154 155 oxygen [46]. The experiments were performed at initial concentrations of 5×10^{-6} mol/L of PS **2** and 6×10^{-5} mol/L of DPBF over 156 a period of 32 min. The absorption intensity of DPBF was rapidly 157 decreased 80% at the first 6 min (Fig. 3). A high rate (20.2-fold) of 158 159 oxygenation of DPBF by 2 was recorded, compared to that of the 160 reference methylene blue (Fig. 4) [26]. Finally, the absorption 161 intensity of DPBF completely disappeared in the following 26 min 162 (Fig. 3). Moreover, in H₂O-DMSO (v/v: 9/1) system, the PS **2** also 163 generated the singlet oxygen when the solutions were irradiated with the light (Fig. S1 in Supporting information). 164

165 Interestingly, the experimental results showed that PS **2** had 166 high the singlet oxygen production over the 6 min time period 167 (Fig. 3). In addition, no photobleaching of PS **2** was observed during 168 this experiment, based on the absorption intensity (λ_{abs} = 506 nm) 169 in toluene (Fig. 3). These are evidences that the PS **2** bearing



Fig. 3. DPBF (initial concentration at 6×10^{-5} mol/L) degradation profile in toluene by BOPHY **2** (5×10^{-6} mol/L), and the absorption (the bottom curve: λ_{abs} = 506 nm) of BOPHY **2** in toluene. Monochromatic light (500 nm at 0.5 mW/cm²) was used. The curves display time-dependent decrease (0, 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30 and 32 min) of absorbance at 416 nm by oxidation of DPBF with BOPHY **2**.

dibromo substituted groups could be thought to be an excellent PS 170 to be potentially used for the singlet oxygen generation. 171

The molecular geometries of BOPHYs **1** and **2** were optimized 172 using density functional theory (DFT) at the B3LYP/6-31G(d) level 173



Fig. 4. Comparative DPBF (initial concentration at 6×10^{-5} mol/L) degradation profiles over a period of 6 min in toluene by BOPHY 2.



Fig. 5. Frontier molecular orbitals of BOPHYs **1** and **2** at the B3LYP/6-31G(d) level with Gaussian 03. HOMO/LUMO (eV) = -5.58/ - 2.63 for **1**; HOMO/LUMO (eV) = -5.80/ - 2.82 for **2**.

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174 [50]. The calculated HOMO and LUMO orbital energy levels were 175 summarized in Fig. 5. As shown in Fig. 5, for BOPHY 1 and 2, the 176 HOMO are distributed at the BOPHY core, and the LUMO are localized at the BOPHY core and two phenyl groups of the adjacent 177 178 Br atoms. In addition, the BOPHY core is almost coplanar. 179 Furthermore, the energy gap between the HOMO and LUMO of 180 the BOPHY 1 (2.95 eV) is slightly smaller than that of PS 2 (2.98 eV) 181 (Fig. 5), which is in good agreement with the red shift in the absorption observed between 1 and 2. 182

183 4. Conclusion

184 In summary, dibromo substituted BOPHY dye 2 was success-185 fully obtained in 64% yield by the reaction of BOPHY 1 with 186 Br₂. BOPHY **2** as a photosensitizer was able to high-efficiently generate the singlet oxygen. Singlet oxygen generation by 2 can 187 188 rapidly accomplish the oxidation of 80% DPBF at the first 6 min. No 189 photobleaching of PS 2 was observed based on the absorption 190 intensity (λ_{abs} = 506 nm) in toluene. PS **2** having dibromo 191 substituted group can be thought to be a PS to be potentially 192 used for the singlet oxygen generation. By MO calculations the 193 HOMO-LUMO band gap for the lowest energy absorption bands of 194 the BOPHY 1 is smaller than that of PS 2, which is in good 195 agreement with the red shift in the absorption observed between 1 196 and **2**.

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207 Appendix A. Supplementary data

Supplementary data associated with this article can be found, in
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