The photophysical characteristics of 2-butylamino-2-demethoxy-hypocrellin B

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Abstract

2- Butylamino-2-demethoxy-hypocrellin B (BAHB), is an efficient photodynamic sensitizer, excited singlet-state energies are determined from the overlap of the normalized from absorption and emission spectra to be 176.4 kJ mol^{-1} ($E_{S_{CT}}$) and 202.8 kJ mol^{-1} (E_{S_1}), respectively. The quantum yields of BAHB fluorescence are 0.0098 (Φ_{f1}) and 0.0076 (Φ_{f2}), respectively. The energies and quantum yields of excited triplet states of BAHB are examined from the external effect of heavy atom on its florescence emission in the mixture of n-propyl iodide and benzene. The energies of excited triplet states of BAHB are 134.4 ± 10.5 kJ mol^{-1} ($E_{T_{CT}}$) and 158.6 ± 10.5 kJ mol^{-1} (E_{T_1}), respectively. The quantum yields of excited triplet states of BAHB are 0.73 ± 0.04 ($\Phi_{T_{CT}}$) and 0.56 ± 0.04 (Φ_{T_1}), respectively. Meanwhile, the kinetic constants of fluorescence emission, intersystem crossing and internal conversion are also calculated from relative equations.
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Keywords: 2- Butylamino-2-demethoxy-hypocrellin B; External heavy-atom effect; Singlet state; Triplet state

1. Introduction

Amino-substituted hypocrellins are new kinds of efficient photodynamic sensitizers. Especially, 2- butylamino-2-demethoxy-hypocrellin B (BAHB) has shown the prefect photoinduced anticancer ability to tumor cells, such as Hela cancer cell, murine ascitic hepatoma cells, human pancreatic cancer cell and line Capan-1 cells [1–4]. Wu et al. [1,3] has reported the photopotentiation factor of BAHB for killing Hela cancer cell is 200–400-fold and much higher than that of HB (only 10-fold for HB). The quantum yield of O$_2$ ($^1\Delta_g$) generatied by BAHB is only 56% of HB and the ability of O$_2^-$ generation by BAHB is 2.7 times stronger than that of HB. Although the investigation of the mechanism of the excellent photodynamic action of BAHB is undergoing, it is believed that both O$_2$ ($^1\Delta_g$) and O$_2^-$ are involved in the photodynamic action of BAHB. It is well known that the generation of O$_2$ ($^1\Delta_g$) by BAHB is through the energy transfer process from the excited triplet state of BAHB to ground state of oxygen and the generation of O$_2^-$ by BAHB is originated from the electron transfer between semiquinone anion radical and ground state of oxygen (the semiquinone anion radical is also produced from its excited state). The electron and energy transfer abilities of BAHB in its photodynamic mechanism have intimate relationship with its energies and quantum yields of excited state [3].

However, so far, little has been reported about the photophysical characteristics of excited states of BAHB, especially, excited triplet states, since BAHB does not exhibit appreciable phosphorescence even at low temperature. Hu and Jiang reported an efficient method for determination of triplet state energy and quantum yield of HB by the effect of external heavy atom on its fluorescence and singlet oxygen quantum yields [8]. In the present work, using this method along with the examination of absorption and fluorescence spectra, for the first time, we reported the energies and quantum yields of the excited states of BAHB and the kinetic constant of fluorescence emission, intersystem crossing and internal conversion.

2. Materials and methods

2.1. Chemicals

2- Butylamino-2-demethoxy-hypocrellin B was synthesized by the amination of HB (Scheme 1) and characterized

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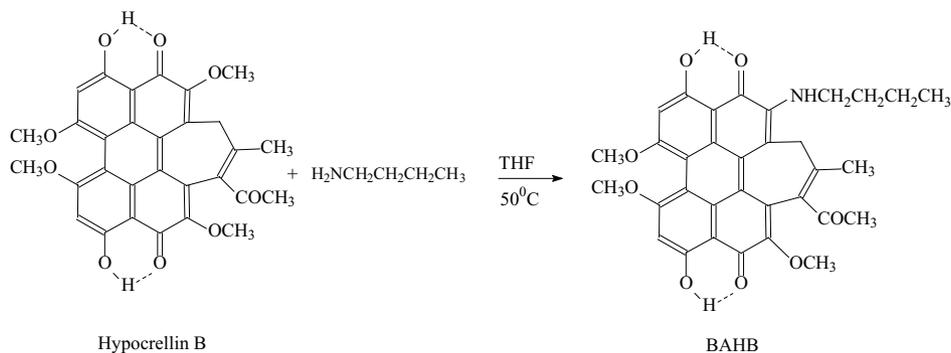
Scheme 1. Synthesis of 2-butylamino-2-demethoxy-hypocrellin B (BAHB).

by IR, ^{1}H-NMR, ^{13}C-NMR, FAB-MS, and UV-Vis spectrometers [1,5]. 9,10-Diphenyl-anthracene (DPA, A.R.) was purchased from Aldrich, USA. *n*-Propyl iodide (C.P.), benzene (A.R.) and other solvents were purchased from Beijing Chemical Plant China, and further purified before use.

2.2. Measurements

2.2.1. Spectrometer measurement

Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-160-A spectrometer; fluorescence emission spectra were measured on HITACHI-F4500 spectrometer, and lifetime of fluorescence was determined on HORIBA NAES-1100 time-resolved fluorescence spectrometer.

2.2.2. Determination of the quantum yield of singlet oxygen

The photooxidation of 9,10-DPA to its endoperoxide derivative by singlet oxygen (Scheme 2) is usually used to detect singlet oxygen generated from photosensitizers [6]. In order to determine the quantum yield of O_2 ($^1\Delta_g$) generated by BAHB, we used 9,10-DPA bleaching method with HB in benzene solution as standard. Samples were placed in the series of Pyrex glass cells of the same specification, and irradiated with a 500 W tungsten–halogen lamp on a marry-go-around apparatus. Filters are combined to select wavelengths around 460 and 600 nm, respectively, in which only the sensitizers absorb significantly. The concentration of samples was adjusted to give the same optical density at the selected wavelength (460 or 600 nm). The reaction was followed spectrometrically via observing the decrease in
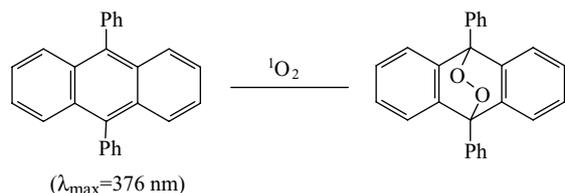
374 nm absorption peak of DPA (where BAHB and *n*-propyl iodide have the smallest absorption) as a function of irradiation time. The irradiation time was controlled so that the conversion rate for the BAHB-sensitized photo-oxidation of DPA was within 5–10%.

2.2.3. Determination of the energy and quantum yield of excited state

The energies and quantum yields of excited singlet state of BAHB were investigated through the measurements of its absorption and fluorescence spectra in benzene solution. Based on the Stoke's shift, the energy gap of zero vibration energy level, E_{0-0} between S_{CT} and S_0 was measured by the curve crossing point of absorption and emission spectrum (exited wavelength is 620 nm), and also the energy gap of zero vibration energy level of E_{0-0} between S_1 and S_0, was measured by the curve crossing point of excitation spectra (detected wavelength is 625 nm) and fluorescence emission spectra (excited wavelength is 460 nm) [7]. The fluorescence quantum yield of BAHB was measured and calculated according to the standard of HB ($\Phi = 0.058$ in benzene) [6], The concentration of BAHB and standard solution was adjusted to the same absorbance at excited wavelength (460 nm). The dissolved oxygen was removed by bubbling with high purity nitrogen for 30 min before measurement.

The energies and quantum yields of excited triplet-state of BAHB were estimated through the heavy atom effect on its fluorescence emission and quantum yields of singlet oxygen generation in benzene solution, and the DPA bleaching method [6,8] was used to examine the generation quantum yields of singlet oxygen.

A set of solutions consisting of BAHB and $CH_3CH_2CH_2I$ (BAHB 1×10^{-5} M, $CH_3CH_2CH_2I$ $0.5x$ M, x is the multiple of 0.5) in benzene were used to determine the relative quantum yields of fluorescence at 611 and 732 nm, respectively. A set of solution consisting of BAHB (0.8×10^{-4} M), DPA (1.2×10^{-3} M) and $CH_3CH_2CH_2I$ ($0.5x$ M, x is the multiple of 0.5) in benzene was carefully prepared to ensure the apparent external heavy atom effect could be observed, the relative quantum yields of singlet oxygen generated by the sensitizer were determined at two different wavelength bands: around 460 nm or around 600 nm by the

(λ_{max}=376 nm)

Scheme 2. The photooxidation of 9,10-DPA to its endoperoxide derivative by singlet oxygen.

DPA-bleaching method. The energies of BAHB triplet states (T_{CT} and T_1) were estimated via the rate constant of BABH fluorescence quenching by $CH_3CH_2CH_2I$ in benzene solution [9]. The quantum yield of triplet states of BAHB was measured by the relationship between the relative fluorescence quantum yield of BAHB and the relative quantum yield of singlet oxygen generated by BAHB in the different $CH_3CH_2CH_2I$ concentration of benzene solutions [8].

3. Results and discussions

3.1. Characteristics of the excited singlet state

The absorption spectrum of BAHB is shown in Fig. 1A (Curve a). Base on the study of absorption spectrum of HB (Fig. 1A (Curve c)) [2,5]. The absorption of shorter wavelength at 463 nm (log ε = 4.06) is assigned to the $\pi–\pi^*$ transition and the absorption of the longer wavelength at 583 nm (log ε = 4.10) was in relation to intramolecular proton transfer between peri-hydroxyl and quinone groups, which may take on some active role in the photodynamic activity. Compared with HB, the absorption of BAHB at the longer wavelength is enhanced obviously, and raises a new absorption at 621 nm (log ε = 4.09), which resulted from the introduction of a butylamino group into the perylenequinone ring. Its curve shapes of fluorescence emission excited respectively at 460 and 620 nm are apparently different: when excited at 460 nm, the fluorescence spectrum shows double emission peaks with maxima at 613 and 733 nm (Fig. 1B (Curve d)), respectively, when excited at 620 nm, there is only one emission peak with maximum at 733 nm (Fig. 1A (Curve b)). Compared with the fluorescence spectrum of HB [10,11], the shorter wavelength emission of BAHB is similar to the emission of peri-hydroxyl perylenequinone group

in HB caused by intramolecular proton transfer, while the longer wavelength emission of BAHB is a new peak caused apparently by the introduction of a butylamino group into perylenequinone ring Fig. 1A and 1B (Curves c and d)). The excitation spectra at different detecting wavelengths, 625 and 725 nm, respectively, are shown in Fig. 1B (Curves e and f). Two different excitation spectra belong to different fluorescence excited states of BAHB. When excited at 460 nm, the dual fluorescence emission is related to two excited fluorescence states, S_{CT} and S_1 [12,13]. The energy level of S_{CT} and S_1 can be estimated by the crossing points of absorption (or excitation) and fluorescence spectra. They are listed in Table 1. The fluorescence quantum yields of S_1 and S_2 are determined using the standard HB in benzene via Eq. (1) and listed in Table 1.

$$\frac{\Phi_f^X}{\Phi_f^S} = \frac{F_X}{F_S} \frac{A_S}{A_X} \tag{1}$$

Φ_f^X and Φ_f^S are the fluorescence quantum yields of BAHB and the standard HB, respectively. A_X and A_S are the absorptions at the excitation wavelength (460 and 620 nm) of the BAHB and standard HB, respectively. F_X and F_S are the area of the fluorescence peaks of the BAHB and the standard HB, respectively, at the same sensitivity scale. The photophysical characteristics of singlet state of BAHB along with those of HB [7,8,10] are listed in Table 1.

Judged from Table 1, in contrasted with HB, the fluorescence quantum yields of BAHB reduced obviously. It is known that the fluorescence of HB mainly results from the intramolecular proton transfer between peri-hydroxyl and perylenequinoid carbonyl groups. When a butylamino group was introduced into perylenequinone structure, it reduces the intramolecular proton transfer between quinone and perihydroxyl group, and in the consequence, reduces the
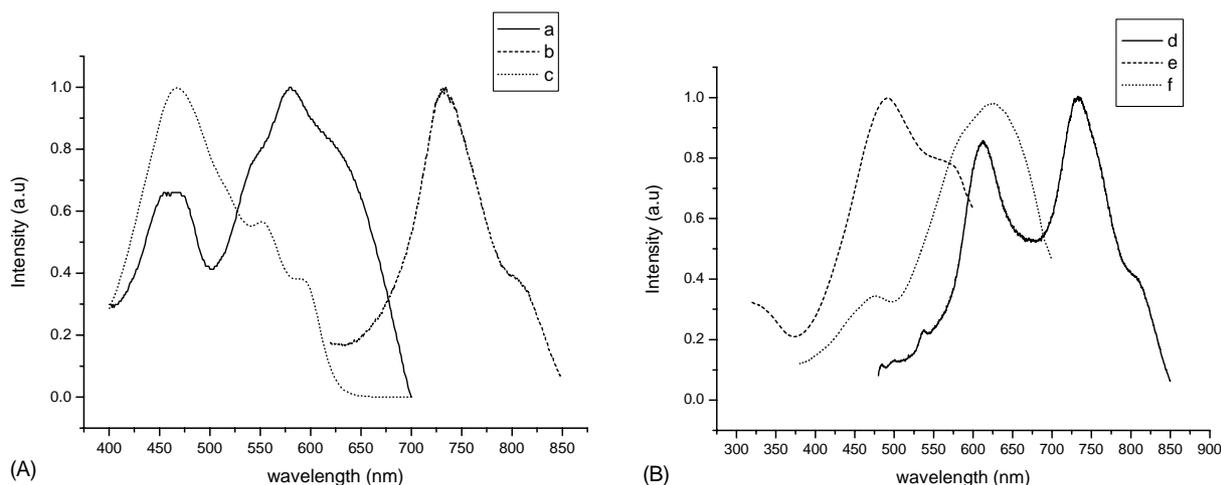
Fig. 1. The normalized absorption and fluorescence emission and excitation spectra of BAHB and HB in benzene. (A) (Curve a) The absorption spectrum of BAHB; (Curve b) the emission spectrum of BAHB, excited wavelength at 620 nm; (Curve c) the absorption spectrum of HB. (B) (Curve d) The emission spectrum of BAHB, excited wavelength at 460 nm; (Curve e) the excitation spectrum of BAHB, detecting wavelength at 625 nm; (Curve f) the excitation spectrum of BAHB, detecting wavelength at 725 nm.

Table 1
The photophysical characteristics of BAHB singlet state

Photophysical characteristics	BAHB	HB[a]
Absorption spectrum		
λ_{max} (nm) (log ε)	463 (4.06); 583 (4.10); 621 (4.09)	466 (4.35); 548 (4.08); 580 (3.96)
Fluorescence emission		
λ_{max} (nm) ($\lambda_{exc} = 460$ nm)	613; 733	628
Φ_f	0.0098 (S$_1$); 0.0076 (S$_2$)	0.058 (S$_1$)
τ_S (ns)	1.51 (S$_{CT}$); 1.33 (S$_1$)	1.0 (S$_1$)
Energy level (kJ mol^{-1})	176.4 (S$_{CT}$); 202.8 (S$_1$)	199.4 (S$_1$)

[a] Ref. [7,8]. *Notes*: Φ_f is the quantum yield of fluorescence; τ_S is the lifetime of fluorescence.

florescence quantum yield. Moreover, the electron donating properties of amino group may cause some extent of intramolecular charge transfer (ICT) between the butylamino and quinonoid carbonyl groups, which provides a pathway for fluorescence quenching via radiationless transition that also reduces the fluorescence quantum yields of BAHB.

3.2. Determination of the energy of triplet state

Intersystem crossing process will be accelerated in presence of heavy atoms in solution system such as iodine and bromine [6]. This leads to the fluorescence quenching of fluorephore by heavy atom and the increase of quantum yield of triplet state. When adding $CH_3CH_2CH_2I$ gradually to BAHB in benzene solution (1.07×10^{-5} M), the fluorescence quantum yield of BAHB varied with the concentration of $CH_3CH_2CH_2I$ that satisfied the Stern–Volmer behavior. The typical Stern–Volmer curve is shown in Fig. 2. From Fig. 2, two Stern–Volmer constants can be calculated to be $K_{sv1} = 1.17 \pm 0.05$ and $K_{sv2} = 0.139 \pm 0.005$. As the fluorescence lifetime of S$_{CT}$ and S$_1$ are 1.51 and 1.33 ns, respectively, therefore, two bimolecular kinetic con-
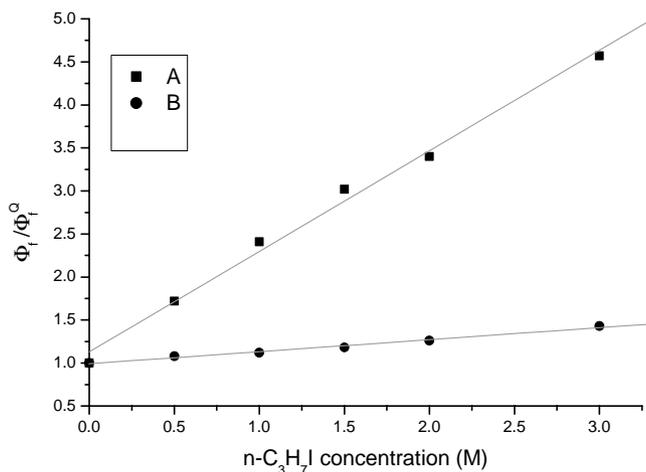
Fig. 2. The Stern–Volmer curves of fluorescence quenching of BAHB by $CH_3CH_2CH_2I$ in benzene solution. Φ_f/Φ_f^Q is the relative fluorescence quantum yield. (Curve A) S$_1$ state ($\lambda_{max} = 613$ nm); (Curve B) S$_{CT}$ state ($\lambda_{max} = 733$ nm).

stants of BAHB are $1.77 \pm 0.05 \times 10^9$ and $1.84 \pm 0.05 \times 10^8$ M^{-1} s^{-1}.

As shown in Fig. 2, the external heavy atom effects on S$_{CT}$ and S$_1$ are different: S$_1$ was much more influenced by $CH_3CH_2CH_2I$ than S$_{CT}$, and $CH_3CH_2CH_2I$ affected the S$_1$ so little that its Stern–Volmer curves of fluorescence quenching was nearly a level line against the concentration of $CH_3CH_2CH_2I$. As the energy levels of excited singlet and triplet states of $CH_3CH_2CH_2I$ are all greatly higher than those of excited singlet states of BAHB, so that it is impossible that $CH_3CH_2CH_2I$ quenched the fluorescence of the BAHB via intermolecular energy transfer mechanism from BAHB to $CH_3CH_2CH_2I$. We realized that heavy atom accelerated the intersystem crossing processes of S$_{CT} \rightarrow$ T$_{CT}$ and S$_1 \rightarrow$ T$_1$, which lead to quenching of the fluorescence BAHB. Von Dreeskamp et al. [9] has researched the fluorescence quenching behavior of $CH_3CH_2CH_2I$ influencing on a series of aromatic compounds, and proved that the bimolecular kinetic constant log K_q have linear relationship with ΔE_{ts} (i.e. ΔE_{ts} is the energy gap of triplet and singlet state).

Based on the relationship mentioned above, we can determinate the ΔE_{ts} of BAHB to be 42.0 ± 10.5 kJ mol^{-1} for S$_{CT} \rightarrow$ T$_{CT}$ and 44.21 kJ mol^{-1} for S$_1 \rightarrow$ T$_1$. Since the S$_{CT}$ and S$_1$ energy level of BAHB are 176.43 and 202.8 kJ mol^{-1}, the T$_{CT}$ and T$_1$ energy levels of BAHB are 134.4 ± 10.5 and 158.6 ± 10.5 kJ mol^{-1}, respectively.

3.3. Estimation quantum yields of the triplet state

BAHB is a good photosensitizer of singlet oxygen [1]. In addition, since the fluorescence of BAHB is not quenched by ground oxygen in benzene solution, singlet oxygen is formed only by the energy transfer from triplet state of BAHB to ground oxygen [3]. We can probe the heavy atom influence on the triplet state of BAHB via measuring the quantum yields of singlet oxygen by varying the concentration of external heavy atom. We use 9,10-DPA bleaching method to detect the influence of external heavy atom on generation of singlet oxygen. A set of solutions, consisted of BAHB (0.8×10^{-4}) M, DPA (a singlet oxygen acceptor, 1.2×10^{-3} M) and $CH_3CH_2CH_2I$ ($0.5x$ M, x is the multiple of 0.5, saturated by the oxygen), were irradiated at two
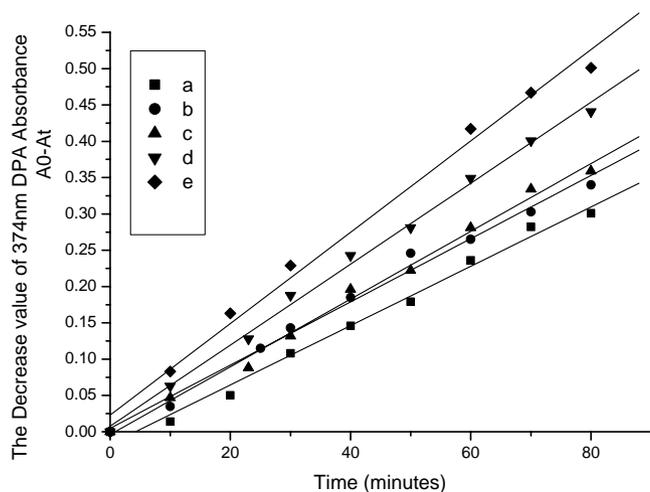
Fig. 3. Photosensitized DPA bleaching by measuring the absorbance decrease at 374 nm as a function of irradiation time in aerobic benzene solution irradiated at 460 nm, BAHB (0.8×10^{-4} M); DPA (1.2×10^{-3} M); $CH_3CH_2CH_2I$ (a: 0 M, b: 0.5 M, c: 1 M, d: 1.5 M, e: 2 M).

selected irradiation wavelength (460 or 600 nm), respectively, which were absorbed only by the BAHB; the reaction was followed spectrometrically by observing the decrease in the 374 nm absorption peak of DPA as a function of irradiation time (Scheme 2), where the samples have the smallest absorption. Figs. 3 and 4 indicate that the quantum yields of singlet oxygen generated by BAHB increase obviously in the presence of heavy atom. The relative quantum yields against the BAHB solution without $CH_3CH_2CH_2I$ were measured from the ratio of the line slope.

Those results furthermore demonstrate that $CH_3CH_2CH_2I$ accelerated the intersystem crossing procedures of $S_{CT} \rightarrow T_{CT}$, $S_1 \rightarrow T_1$ resulting in quenching of the fluorescence of BAHB. In our experimental conditions, a reasonable assumption is that the efficiency of the energy transferring
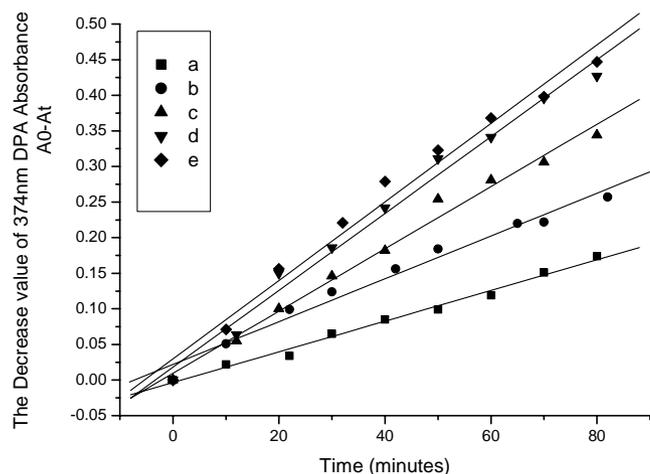
Fig. 4. Photosensitized DPA bleaching by measuring the absorbance decrease at 374 nm as a function of irradiation time in aerobic benzene solution irradiated at 600 nm, BAHB (0.8×10^{-4} M); DPA (1.2×10^{-3} M); $CH_3CH_2CH_2I$ (a: 0 M, b: 0.5 M, c: 1 M, d: 1.5 M, e: 2 M).

Table 2
Φ_T^Q/Φ_T in different concentration of $CH_3CH_2CH_2I$ excited at different wavelength

λ_{ex} (nm)	The concentration of heavy atom (mol l^{-1})				
	0	0.5	1	1.5	2.0
460	1	1.08	1.15	1.39	1.56
600	1	1.42	2.08	2.58	3.34

Notes: Φ_T^Q and Φ_T are the quantum yields of triplet state in the presence of heavy atom and in the absence of it, respectively. The values of Φ_T^Q/Φ_T can be repeated within 3–5%.

from the BAHB triplet state to ground oxygen that produces singlet oxygen, does not vary with the adding heavy atom (Eq. (2)). The quantum yield of singlet oxygen generated by BAHB only depends on the quantum yields of BAHB triplet states. Eq. (2) was used to estimate the quantum yields of triplet states of BAHB.

$$\frac{\Phi_O^Q}{\Phi_O} = \frac{n\Phi_T^Q}{n\Phi_T} = \frac{\Phi_T^Q}{\Phi_T} \tag{2}$$

Here, Φ_O^Q and Φ_O are the quantum yields of singlet oxygen in the presence and absence of heavy atom, respectively. Φ_T^Q and Φ_T are the quantum yield of triplet state in the presence and absence of heavy atom, respectively.

When the concentration of $CH_3CH_2CH_2I$ was altered gradually in the sample solutions irradiated with selected excited wavelength, a series of Φ_T^Q/Φ_T can be calculated which are listed in the Table 2.

In order to estimate the quantum yields of two triplet states of BAHB, we make use of the relationship between relative fluorescence quantum yield and relative triplet quantum yield of BAHB in benzene solution of different heavy atom concentrations irradiated at 460 nm and 600 nm, respectively (Table 3). Medinger has deduced the following formula [14]:

$$\Phi_T = \frac{(\Phi_f/\Phi_f^Q) - 1}{\{([T]^Q/[T])(\Phi_f/\Phi_f^Q)\} - 1} \tag{3}$$

Here, $[T]^Q/[T]$ is the concentration ratio of triplet state with or without heavy atom effect. In our experimental condition, the absorbance of BAHB at select wavelength are all the same, therefore, equation $([T]^Q/[T]) = (\Phi_T^Q/\Phi_T)$ can exist and Eq. (3) is changed to Eq. (4).

$$\Phi_T = \frac{(\Phi_f/\Phi_f^Q) - 1}{\{(\Phi_T^Q/\Phi_T)(\Phi_f/\Phi_f^Q)\} - 1} \tag{4}$$

Table 3
The photophysical characteristics of BAHB triplet state

	Φ_T	Energy level (kJ mol^{-1})
BAHB	0.73 ± 0.04 (T_{CT})	134.4 ± 10.5 (T_{CT})
	0.56 ± 0.04 (T_1)	158.6 ± 10.5 (T_1)
HB[a]	0.76 (T_1)	168.0 (T_1)

Notes: Φ_T is the quantum yield of triplet state.
[a] [7,8].
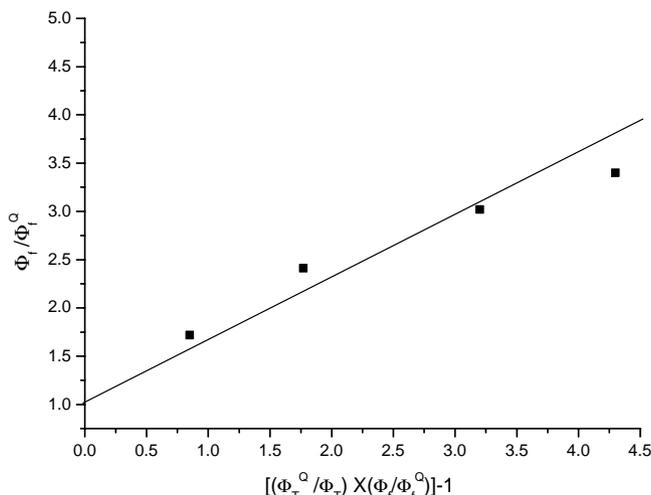
Fig. 5. The relationship between relative fluorescence quantum yield and relative triplet quantum yield of BAHB in benzene solution of different heavy atom concentrations irradiated at 460 nm.

According to Eq. (4), measuring (Φ_f/Φ_f^Q) at different concentrations of $CH_3CH_2CH_2I$ irradiated at 460 or 600 nm in benzene as a function of the numerator of Eq. (4) will give the consequences of the quantum yields of two triplet states of BAHB from the slopes of line (Figs. 5 and 6). The quantum yield of T_1 0.73 ± 0.04 and T_2 0.55 ± 0.04 are shown in Figs. 5 and 6, respectively.

3.4. Calculating the kinetic constants of fluorescence emission, intersystem transition and internal conversion

Based on the data of research described above, we can estimate kinetic constants of fluorescence emission, intersystem crossing and internal conversion with following
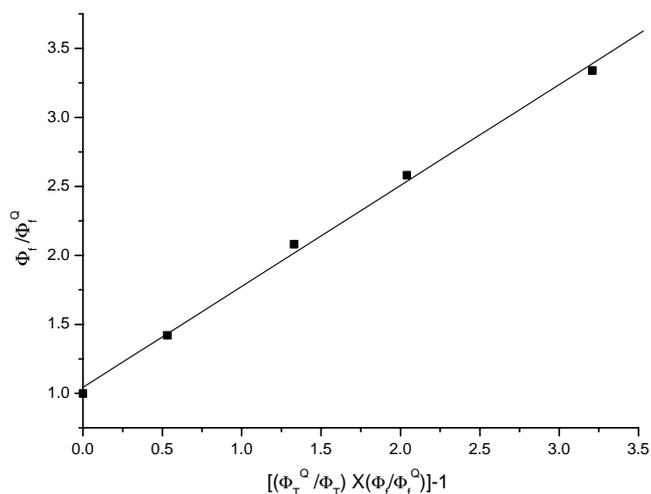
Fig. 6. The relationship between relative fluorescence quantum yield and relative triplet quantum yield of BAHB in benzene solution of different heavy atom concentrations irradiated at 600 nm.

Table 4
Calculation of the kinetic constants and Φ_{IC}

	Kinetic constant (s^{-1})			Φ_{IC}[d]
	κ_f[a]	κ_{ST}[b]	κ_{IC}[c]	
S_{CT}	6.49×10^6	4.77×10^8	1.72×10^8	0.26
S_1	5.71×10^6	4.21×10^8	3.23×10^8	0.43

Notes: Φ_{IC} is the quantum yield of internal conversion; κ_f, κ_{ST} and κ_{IC} are kinetic constants of fluorescence emission, intersystem crossing and internal conversion, respectively.

[a] ±0.02.
[b] ±0.03.
[c] ±0.04.
[d] ±0.05.
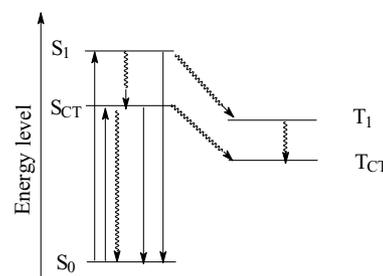
Fig. 7. State diagram for BAHB. *Notes*: ⌇⌇➤ represents the radiationless transitions and → the radiative transitions.

formula [6,7]:

$$\Phi_{IC} = 1 - \Phi_f - \Phi_T \tag{5}$$

$$\Phi_f = \kappa_f \tau_S \tag{6}$$

$$\Phi_T = \kappa_{ST} \tau_S \tag{7}$$

$$\Phi_{IC} = \kappa_{IC} \tau_S \tag{8}$$

Here, Φ_{IC} is the quantum yield of internal conversion; Φ_f is the quantum yield of fluorescence; Φ_T is the quantum yield of triplet state; κ_f, κ_{ST} and κ_{IC} are kinetic constants of fluorescence emission, intersystem crossing and internal conversion, respectively, τ_S is the lifetime of fluorescence. The calculated results are listed in Table 4 and the energy level and photophysical transitions are summarized in Fig. 7.

4. Conclusions

In our work, by the measurement of absorption and fluorescence spectra of BAHB under the external heavy atom effect of $CH_3CH_2CH_2I$, we determined a series of physical characteristics of BAHB excited singlet and triplet states. It will be important for understanding the mechanism of photodynamic action of BAHB.

Acknowledgements

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