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The effect of heavy atom to two photon absorption properties and intersystem crossing mechanism in aza-boron-dipyrromethene compounds

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ABSTRACT

New aza-boron-dipyrromethene compounds containing bromine atoms at various positions were designed and synthesized to enhance the triplet state population and two photon absorption properties for applications such as two-photon photodynamic therapy, triplet–triplet annihilation up-conversion. Steady state fluorescence and ultrafast pump probe spectroscopy techniques revealed that only 2, 6 positions of aza-boron-dipyrromethene core contribute to triplet state population significantly. Density function theory calculations showed that when bromine atoms introduced to 2, 6 position of aza-boron-dipyrromethene core, singlet and triplet energy levels get closer therefore probability of intersystem crossing increases. Z-scan experiments at 800 nm wavelengths revealed considerably large (610 GM) two photon absorption cross section value with respect to literature for compounds showing intersystem crossing mechanism. The efficient intersystem crossing and enhanced two-photon absorption properties make the investigated aza-boron-dipyrromethene compounds good candidates for two-photon photodynamic therapy application.

1. Introduction

There has been a great deal of interest on intersystem crossing (ISC) process of novel materials due to their related applications in photochemical and photophysical processes, such as photodynamic therapy (PDT) [1–5], photocatalytic organic reactions [6–11], triplet–triplet annihilation (TTA), upconversion (UC), and singlet oxygen generation [12,13]. ISC process is an efficient way to generate singlet oxygen especially for PDT application. The spin–orbit perturbation of electronic states plays an important role on the photophysical properties of organic molecules. Introducing heavy atoms to molecular systems increases ISC process and therefore, changes photophysical properties, which is known as heavy atom effect [14]. Enhanced spin–orbit perturbations can be achieved by introducing a heavy atom directly onto the absorbing core of the molecule (internal heavy atom effect) [15,16] or by positioning heavy atoms to the peripheral positions (external heavy atom effect) [13,17,18]. Internal heavy atom effect is the most efficient way to enhance ISC process. Therefore, the effects of heavy atom on the photoinduced electron transfer mechanism to the triplet state have been extensively studied [1,19].

On the other hand, organic molecules with large two photon absorption (TPA) properties have attracted increasing attention due to a wide range of potential applications including optical limiting [20,21], TPA imaging microscopy [22], three-dimensional microfabrication [23,24], optical data storage [25,26], TPA upconversion lasing [27], and especially for two-photon PDT [28]. Therefore, design and synthesis of molecules with large

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TPA cross-sections (TPCS) become a popular research field [29,30]. Two-photon PDT application requires efficient ISC mechanism and high TPCS at near-IR region due to its low energy, deep penetration and negligible damage to the normal biological tissue. However, near-IR TPA photodynamic therapy is limited due to lack of TPA photosensitizer with high intersystem crossing rate and large TPCS.

There have been several studies about the application of aza-boron-dipyrromethene (aza-BODIPY) compounds to one photon PDT in the literature [1,31]. Our previous research on aza-BODIPY compounds show that these compounds exhibit TPA properties [32,33]. In this work, we designed and synthesized new aza-BODIPY compounds (see Scheme 1) possessing both ISC and TPA properties for PDT applications.

In literature, heavy atom effect on photophysical properties of organic molecules and complexes of various types of molecules such as meso-tetraaryl porphyrins for selenium atoms [34,35], poly halogenated *meso*-tetraaryl porphyrins and bacteriochlorins molecules [36,37], BODIPY [38,39], and aza-BODIPY [40–42] compounds were studied. Heavy atoms introduced to 2,6 position of aza-BODIPY core are known to enhance the probability of ISC due to internal heavy atom effect (i.e. spin orbit coupling) [14–16]. This effect was investigated by monitoring fluorescence, phosphorescence and singlet oxygen quantum yields [1,39,43,44]. It is known that number of heavy atoms introduced to BODIPY core other than 2,6 positions do not affect ISC [43]. However, it is not clear, how do heavy atoms on the peripheral positions effect ISC in the literature for aza-BODIPY compound. Therefore, our designed and synthesized new aza-BODIPY compounds contain Br atoms at various positions. Previous works investigating the heavy atom effects on the triplet population used indirect methods such as singlet oxygen quantum yields. We investigated their triplet level populations by using ultrafast pump probe spectroscopy technique. This technique is a very sensitive tool to investigate directly the transition of triplet to levels with fs time resolution. In order to clarify our experimental results and reveal the mechanism causing ISC, we performed density functional theory (DFT) calculations for our investigated compounds.

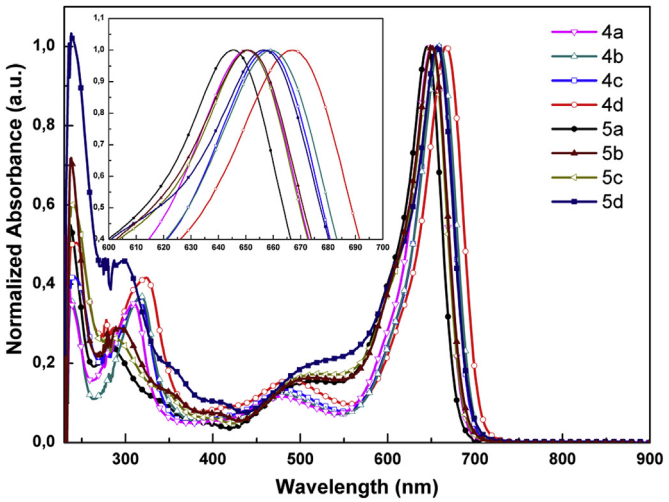
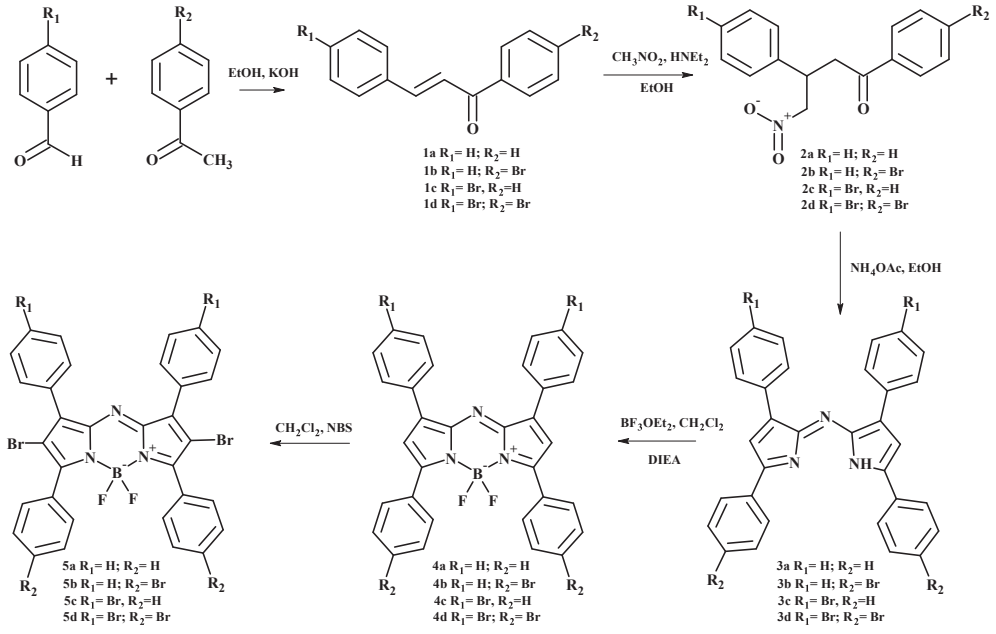


Fig. 1. Normalized absorption spectra of studied compounds in THF (1×10^{-5} M). The inset shows the shifts of maximum absorption wavelengths.

2. Result and discussion

2.1. Absorption and fluorescence measurement

UV–Vis absorption and emission spectra of **4a–d** and **5a–d** are shown in Figs. 1 and 2, respectively. Absorption spectrum of **4a** compound reveals $S_0 \rightarrow S_1$ transition with maximum absorbance wavelength at 650 nm in Fig. 1. However, $S_0 \rightarrow S_1$ transition of Br containing compounds is between 645 nm and 667 nm. This spectral shift depends on the position of Br atoms on aza-BODIPY core. Bathochromic shifts were observed when Br atoms on the para positions of the phenyl ring on the any of 1,7 and 3,5 positions (**4b–d**, **5b–d**) as seen in Table 1. On the contrary, directly introducing of Br atoms to 2,6 position of aza-BODIPY core leads to hypsochromic shifts (**5a–d**). Interestingly, the amounts of spectral shift per binding position, whether it is bathochromic or



Scheme 1. Synthesis of the aza-BODIPY Compounds (**4a–d**, **5a–d**).