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Preparation of BODIPY- fullerene and monostyryl BODIPY-fullerene dyads as heavy atom free singlet oxygen generators

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ABSTRACT

Unsubstituted and monostyryl BODIPY- C_{60} dyads that show absorption in the visible region have been prepared via Bingel Cyclopropanation between BODIPY derivatives and C_{60} and characterized via mass, ^{1}H and ^{13}C NMR spectroscopy as novel heavy atom free triplet photosensitizers to generate singlet oxygen. The new photosensitizers contain one and two light-harvesting antennas as well as associated different absorption wavelengths, resulting in high singlet oxygen generation. The panchromatic excitation energy harvested by the BODIPY moieties is funneled into a spin converter (C_{60}), thus ensuring intersystem crossing and population of the triplet state. We found that the BODIPY- C_{60} dyads can be used as photocatalysts that is singlet oxygen ($^{1}O_2$). In the photooxidation of DPBF the $^{1}O_2$ photosensitizing abilities of the C_{60} dyads are greater than the conventional triplet sensitizer methylene blue.

1. Introduction

Triplet photosensitizers are widely used in photocatalytic organic reactions [1,2], photovoltaics [3], photodynamic therapy [4–6], and triplet–triplet annihilation (TTA) upconversion [7,8]. Regarding these demand, design of efficient triplet photosensitizers showing strong absorption of visible light with long-lived triplet excited states is crucial [9]. Generally, transition metal complexes such as Pt^{II}, Ru^{II} Ir^{III} or bromine, iodine substituted chromophores are used as triplet photosensitizers owing to their heavy atom effect that facilitates intersystem crossing (ISC), upon photoexcitation [10,11]. Even though derivatization of a known fluorophore is a commonly used strategy for preparing new fluorescent molecules, it is not applicable to design new organic triplet photosensitizers because there are no established relationships between the ISC and molecular structures that even subtle derivatizations of a known photosensitizer may annihilate the ISC completely [12,13]. Recently, a new generation of BODIPY-based photosensitizers has been emerged that undergo efficient ISC not demanding the presence of heavy atoms on the fluorophore structure [6,14].

However, it is difficult to attract the triplet state of organic chromophores without heavy atoms besides it is not always convenient to prepare brominated/iodated organic chromophore, since the ISC property of the chromophore cannot be guaranteed [15–17]. Thus, it is a genuine challenge to design a heavy- atom-free organic triplet photosensitizer with the preconcerted ISC [18]. In order to avoid aforementioned conflicts, an intramolecular spin converter can be used, which undertake efficient ISC, but does not necessarily have strong absorption of visible light. The principle is to modify a visible light-harvesting unit with a spin converter. Thus, upon photoexcitation of the light- harvesting antenna, the energy transfer to the spin converter will occur, ensued the triplet excited state via the ISC of the spin converter [13].

Fullerenes have drawn attention due to their remarkable electron acceptor properties that was predicted theoretically and confirmed experimentally [19,20]. Due to the small reorganization energy of fullerenes in electron transfer chemistry a variety of electron donor (such as BODIPY, porphyrin, phthalocyanine, etc.) and fullerene have been prepared in the areas of heavy atom free triplet photosensitizers [13,21–24].

Recently, a well-known fluorophore, BF_2-chelated dipyrromethanes (BODIPY), has attracted increasing attention, because of their high extinction coefficients and large fluorescence quantum yields, intense and tunable absorption in the 450–750 nm regions, and good solubility in most organic solvents [25]. Thus, they have

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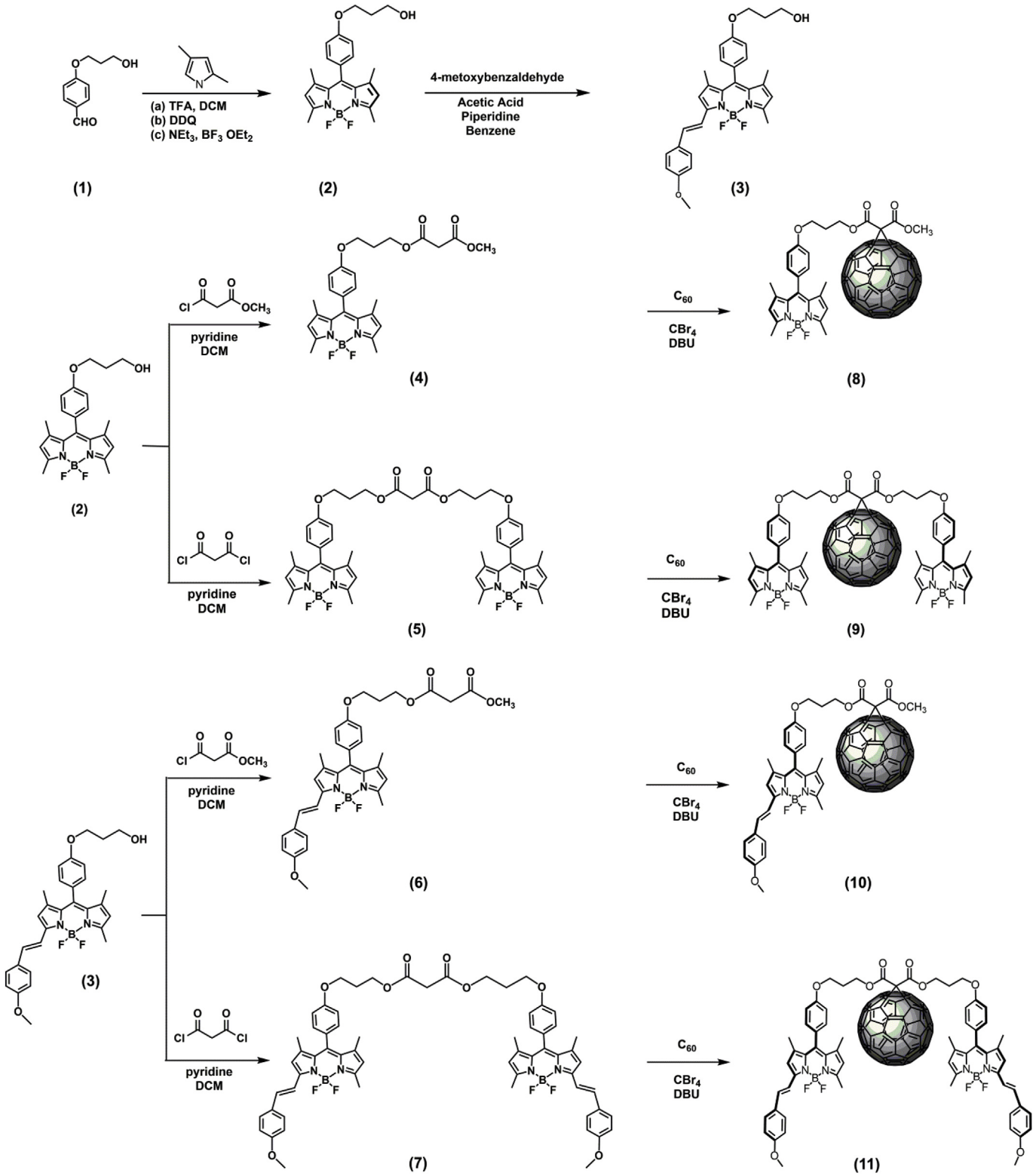
been used in applications ranging from sensors and photodynamic therapy agents [26–29].

The aim of this feature article is the design, synthesis and characterization of heavy atom free novel BODIPY- fullerene dyads whose structures contain one and two antennae with different wavelength absorption that focused on the investigation of their singlet oxygen generation capacities, considering their molecular structures that ensures ISC property. Herein, we devised visible light-harvesting BODIPY-C_{60} (**8**, **9**) and monostyryl BODIPY- C_{60} (**10**, **11**) dyads as molecular structure motifs for the heavy atom free organic triplet photosensitizers (Scheme 1). BODIPYs and monostyryl-BODIPYs were used as the light harvesting antennae,



Scheme 1. Synthesis of the BODIPY- C_{60} and Monostyryl-BODIPY- C_{60} Dyads.