



Tetrahedron report number 939

## 4,4'-Difluoro-4-bora-3a,4a-diaza-s-indacenes (BODIPYs) as components of novel light active materials

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### ARTICLE INFO

#### Article history:

Received 1 March 2011

Available online 17 March 2011

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### 1. Introduction

4,4'-Difluoro-4-bora-3a,4a-diaza-s-indacenes (hereafter referred to as BODIPYs) are a class of fluorescent dyes that are finding

an increasing number of applications in both the materials and optical imaging fields. BODIPYs have a sharp fluorescence profile, high degree of photostability and can have fluorescence quantum yields approaching unity, depending on the attached substituents.

**Abbreviations:** ANT, Anthracene; BHJ, bulk-heterojunction solar cell; BODIPY/BDP, 4,4'-Difluoro-4-bora-3a,4a-diaza-s-indacene, 4; CDB, Cumyl dithiobenzoate; Col<sub>h</sub>, hexagonal columnar; CS, charge-separated state; DABCO, 1,4-Diazabicyclo[2.2.2]octane; DMAEMA, 2-(Dimethylamino)ethyl methacrylate; DSSC, dye-sensitised solar cell; EDOT, 3,4-Ethylenedioxythiophene; EGDMA, Ethylene glycol dimethylacrylate; FRET, fluorescence/förster resonance energy transfer; FTO, fluorinated tin oxide; HEMA, hydroxyethyl methacrylate; HFMA, 2,2,3,3,4,4,4-Heptafluorobutyl methacrylate; HOMO, highest occupied molecular orbital; ITO, Indium-tin oxide; LUMO, lowest occupied molecular orbital; MeTMOS, Methyltrimethoxysilane; MLCTtransfer, metal-to-ligand charge; MMA, Methyl methacrylate; OLED, organic light emitting diode; PCBM, [6,6]-Phenyl-C<sub>61</sub>-butyric acid methyl ester; PCE, power conversion efficiency; PDI, polydispersity index; PEDOT-PSS, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate); PEG, poly(ethylene glycol); PETA, Pentaerythritol triacrylate; PETRA, Pentaerythritol tetraacrylate; PFMA, 2,2,3,3,3-Pentafluoropropyl methacrylate; PM, Pyrromethene; PMMA, poly(methyl methacrylate); POLICRYPS, polymer liquid crystal polymer slice; RE, relative efficiency; TEOS, Tetraethyl orthosilicate; TFMA, 2,2,2-Trifluoromethyl methacrylate; TMSPMA, 3-(Trimethoxysilyl)propyl methacrylate.

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BODIPYs and their dipyrin precursors have been recently reviewed<sup>1–3</sup> with emphasis placed on their syntheses, reactions and applications as fluorescent chemosensors. These reviews outlined the relatively straightforward synthetic routes to the BODIPY fluorophore (Fig. 1), as well as a variety of reliable reactions that can be carried out to produce a shift in the absorption and emission wavelengths. BODIPYs have been used to detect metal cations,<sup>4–12</sup> anions,<sup>13–16</sup> reactive oxygen species<sup>17</sup> and even changes in viscosity<sup>18</sup> by alterations in either the fluorescence intensity or wavelength. Marked changes in the fluorescence intensity as a means of detection are more common and occur because of an ON/OFF switching of photoinduced electron transfer, generally between the BODIPY core and an 8-phenyl substituent. More recently, BODIPY derivatives have been functionalised with groups promoting singlet oxygen generation (e.g., iodide groups), allowing their use as photodynamic therapy agents, an application more commonly associated with porphyrins and phthalocyanines.<sup>19–23</sup> This review, however, focuses on BODIPYs as fluorescent components in materials, and their applications. There is an increasing interest in photonic organic based materials, and BODIPYs are emerging as a unique sub-set of this class of compound,

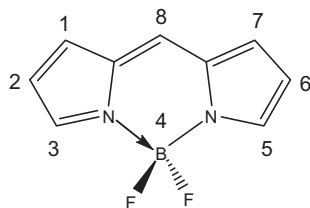


Fig. 1. Core unsubstituted BODIPY.

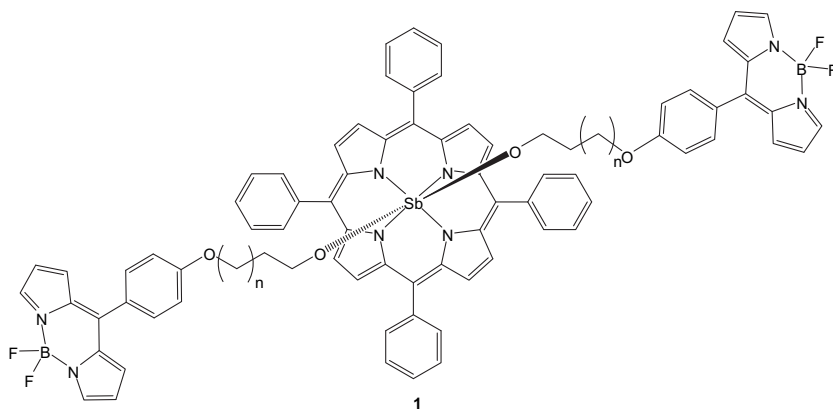


Fig. 2. Antimony-porphyrin-BODIPY array.

which exhibit novel self-assembly, laser behaviour and highly efficient through-bond and through-space energy transfer.

## 2. Energy-transfer cassettes

### 2.1. Through-space energy-transfer cassettes

An energy-transfer cassette consists of two or more fluorescent units attached to the same molecule. The reason for this is that one of these units acts as a donor and the other as an acceptor. The donor absorbs light and this energy is then passed to the acceptor, which emits the light at a longer wavelength. The energy can be transferred to the acceptor via through-space or through-bond energy transfer.

The efficiency of through-space energy transfer depends on the spectral overlap of the donor emission with the acceptor absorbance, the distance between the donor and the acceptor, the relative orientation of donor and acceptor, and the effectiveness of other de-excitation modes (e.g., emission from donor, non-radiative

processes). Through-space energy transfer has the effect of artificially enhancing the Stokes' shift of the molecule by causing emission from the acceptor in place of the absorbing (donor) fluorophore. Due to their intense fluorescence, BODIPYs have found uses in the synthesis of new energy-transfer cassettes.

Due to the similarity of their structures, energy-transfer cassettes containing BODIPY and porphyrin units have received a lot of attention for their through-bond energy-transfer processes and subsequent applications as molecular wires. Through-space energy transfer involving porphyrinic units has been less thoroughly investigated. A simple 8-(4-hydroxyphenyl)-BODIPY has been coordinated to an antimony tetraphenylporphyrin (Sb(TPP)) via an alkyl chain to form a through-space energy-transfer cassette. The efficiency of the energy transfer varied between 13 and 40%. By increasing the length of the alkyl chain spacer unit, the efficiency was found to decrease. It was found that the BODIPY acted as the donor and, therefore, no quenching of the excited state of the porphyrin by donation of energy to the BODIPY was found. It was found that quenching did occur when a phenoxy group was coordinated to the other side of the antimony in conjunction with the BODIPY (1) (Fig. 2).<sup>24</sup>

A similar compound based on a silicon phthalocyanine has been synthesised, which exhibits competitive energy and electron transfer. Analogous to the antimony-porphyrin-BODIPY array (1), when excited at the BODIPY absorption maximum, emission was observed from the phthalocyanine core (2) (Fig. 3). The phthalocyanine emission was also observed when the compound was excited at the phthalocyanine core wavelength. However, when a styryl-BODIPY was attached to the silicon centre in the same way, i.e., (3), different energy transfer behaviour was observed. When excited at the styryl-BODIPY absorption wavelength, very weak emission from the BODIPY

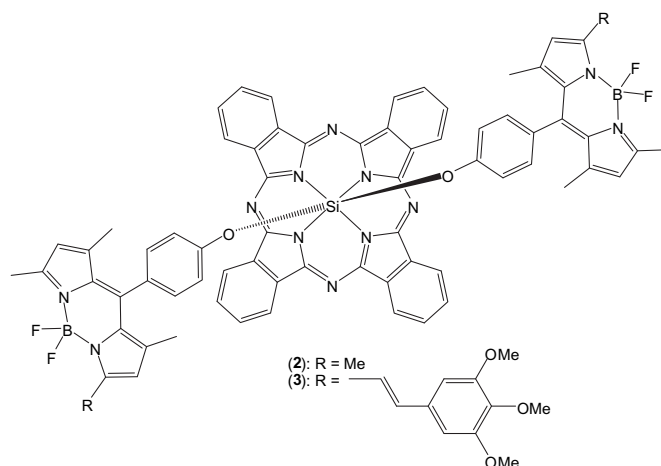


Fig. 3. Di-BODIPY-phthalocyanine array.

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