



# Photophysical studies of 2,6-dibrominated BODIPY dyes substituted with 4-benzyloxystyryl substituents

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Dedicated to Professor Claudio Ercolani on the occasion of his 80th birthday.

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**ABSTRACT:** A series of novel 2,6-dibrominated BODIPY dyes with styryl groups at the 3,5-positions has been prepared, and their photophysical properties have been analyzed to assess their potential utility for use as photosensitizers in photodynamic therapy and in bioimaging.

**KEYWORDS:** BODIPYs, singlet oxygen, Knoevenagel condensation, photophysics, fluorescence, TD-DFT calculations

## INTRODUCTION

Photosensitization is the most important photochemical reaction in the context of singlet oxygen applications such as photodynamic therapy (PDT) [1], antimicrobial photodynamic therapy (PACT) [2, 3], and the photodegradation of organic pollutants [4]. The first singlet excited state of molecular oxygen lies at a relatively low energy and hence can be readily accessed through energy transfer from the triplet manifold of a photoexcited organic dye [5]. Singlet oxygen is cytotoxic and is hence useful for laser related biomedical applications. Photosensitizers such as porphyrins, phthalocyanines, naphthalocyanines, chlorins, bacteriochlorins, and texaphyrins [6–9] are among the most widely used dyes in PDT research. Structurally modified boron dipyrromethene (BODIPY) dyes [10–13] can also be used in this context. This family of dyes was first reported by Treibs and Kreuzer [14], and their derivatives have since been studied for a wide range of applications, such as use as laser dyes [15], as fluorescent switches [16] and as chemosensors [17]. Halogenation of BODIPY dyes enables a heavy atom effect which enhances the rate of intersystem crossing and hence the singlet oxygen quantum yield [18–20]. In

recent years there has been a strong research focus on the synthesis and physicochemical studies of structurally modified BODIPY dyes that absorb the near infrared (NIR) region [18–22] which is most useful for biomedical applications. In this paper, we report the photophysical properties of BODIPY dyes functionalized with *p*-hydroxybenzaldehyde and *p*-benzyloxybenzaldehyde to form styryl groups at the 3,5-positions through Knoevenagel condensation reactions and we make use of TD-DFT calculations to analyze trends in their electronic structures and optical properties.

## EXPERIMENTAL

### Materials

2,4-Dimethylpyrrole, 4-bromobenzaldehyde, 4-formylbenzoic acid, 4-nitrobenzaldehyde, 4-hydroxybenzaldehyde, trifluoroacetic acid, *p*-chloranil, triethylamine, boron trifluoride diethyl etherate, *N*-bromosuccinimide, diphenylisobenzofuran, acetic acid, and piperidine were obtained from Sigma-Aldrich and were used without further purification unless otherwise noted. Dried solvents (supplied by Merck or Minema) were used for spectroscopic measurements, and 2,4-dimethylpyrrole was distilled before use.

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