

# IMPROVED SINGLET OXYGEN GENERATION BY A NOVEL BODIPY DYE AND A STUDY OF UPCONVERSION NANOPARTICLES MIXED WITH A FUNCTIONALIZED BODIPY COMPOUND

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## ABSTRACT

This research explores the use of the versatile 4,4-difluoro-4-boro-3a,4a-diaza-s-indacene (BODIPY) dyes and the modification of their spectroscopic properties. The synthesis of a tetramethyl-BODIPY bearing a sterically hindered meso-phenyl ring with an ethynyl functional group at the para-position was compared to that of its freely rotating counterpart with no methyl substituents on the BODIPY core, with the fluorescence properties in particular proving to be markedly different. These phenyl-ethynyl-substituted BODIPYs were used as the starting materials for the synthesis of novel BODIPY dyes for sensor applications via Sonogashira coupling reactions at the ethynyl position, but this resulted instead in the serendipitous synthesis of a novel BODIPY dimer in which the para-positions of the meso-phenyl rings are linked by a diethynyl bridge. Following iodination at the 2, 6-positions, the dimer was found to have a singlet oxygen quantum yield of 0.88, compared to the value of 0.86 that was obtained for the analogous monomer. Since the  $\epsilon_{\text{max}}$  values for the main spectral bands of the dimers are significantly higher, the compounds may be of interest for singlet oxygen generation applications. A second study was carried out on the interaction between methyl ester functionalized BODIPY dyes and upconversion nanoparticles (UCNPs) to explore the possible use of BODIPY-UCNP conjugates in biomedical applications. The singlet oxygen generation properties of the BODIPY were tested following iodination at the 2, 6-positions, a singlet oxygen quantum yield value of 0.86 was obtained. Three sets of oleate capped UCNPs were synthesized with different diameters and were rendered water dispersible with the addition of a silica shell. The necessary scaffolding for conjugation to the BODIPY was provided by amine groups following functionalization of this shell. v All of the sets of oleate capped and silica coated UCNPs were characterized by transmission electron microscopy (TEM) and X-ray diffractometry (XRD) and their emission properties were studied upon excitation at 978 nm with a diode laser with a Picoquant Fluotime 300 spectrophotometer that enables the measurement of anti-Stokes emission. The potential utility of UCNP-BODIPY conjugates for singlet oxygen applications, such as PDT, was then assessed.