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# ACCEPTED MANUSCRIPT

### Optical limiting properties of 3,5-dipyrenylvinyleneBODIPY dyes at 532 nm

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#### **ABSTRACT**

The optical limiting (OL) properties of 3,5-dipyrenylvinyleneBODIPY dyes that contain both electron withdrawing and donating moieties have been investigated by using the z-scan technique at 532 nm in the nanosecond pulse range. The extension of the  $\pi$ -conjugation at the 3,5-positions with pyrenylvinylene groups results in a ca. 200 nm red shift of the main BODIPY spectral band to ca. 700 nm so there is relatively weak absorbance at 532 nm under ambient light conditions. Reverse saturable absorbance (RSA) profiles are observed in response to incident pulsed laser light that is consistent with a two photon absorption-assisted excited state absorption (ESA) mechanism in  $CH_2CI_2$  solution and when the dyes are embedded in poly(bisphenol carbonate A) (PBC) polymer thin films. This demonstrates that 3,5-divinyleneBODIPY dyes are potentially suitable for use in OL applications, since limiting threshold fluence ( $I_{lim}$ ) values of below 0.95 J cm<sup>-2</sup> are observed when thin films are prepared.

KEYWORDS: BODIPY dyes, Knoevenagel condensation, Optical limiting, z-scan.

#### 1. Introduction

Optical limiting (OL) materials are useful in applications, since they can protect the human eye and sensitive optical devices from intense incident laser beams [1-3]. The second harmonic of Nd/YAG laser systems at 532 nm is particularly important in this regard [4-7]. Ideally there should be high transmittance of low-intensity light, along with the attenuation of the incident laser beam, in manner that limits the output fluence [1-3]. There has been a strong focus on the OL properties of phthalocyanines [8-10], porphyrins [8,11], fullerenes [1], carbon nanotubes [12], nanoparticles [13], metal nanowires [14], and other organic chromophores [15-20].

The main mechanisms involved in achieving optical limiting are nonlinear absorption (NLA), nonlinear refraction and nonlinear light scattering [21,22]. The focus in this study was on the optical limiting that results from NLA processes when molecular dyes are used. Materials with a positive NLA coefficient exhibit reverse saturable absorption (RSA) with a decrease in transmittance at high-intensity levels, and so function as optical limiters. Two photon absorption (2PA) is a resonant third-order nonlinear optical (NLO) process in which an excited state is formed by the simultaneous

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