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Effect of bromination on the optical limiting properties at 532 nm of BODIPY dyes with *p*-benzyloxystyryl groups at the 3,5-positions

Bokolombe P. Ngoy [1], Aviwe K. May [1], John Mack*, Tebello Nyokong

[uaff] *Centre for Nanotechnology Innovation, Department of Chemistry, Rhodes University, Makhanda, 6140, South Africa*

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ABSTRACT

The optical limiting (OL) properties of 3,5-di-*p*-benzyloxystyrylBODIPY dyes that contain both protons and bromine atoms at the 2,6-positions have been investigated by using the Z-scan technique at 532 nm on the nanosecond timescale. There is relatively weak absorbance at 532 nm under ambient light conditions, because the incorporation of *p*-benzyloxystyryl groups at the 3,5-positions results in a ca. 140 nm red shift of the main BODIPY spectral band to the 640–670 nm range. Reverse saturable absorbance (RSA) profiles that are consistent with an excited state absorption (ESA) mechanism involving the T_1 and/or S_1 states are observed in CH_2Cl_2 solution. Second order hyperpolarizability values of ca. 8×10^{-30} esu are obtained and this demonstrates that the dyes are potentially suitable for use in OL applications at 532 nm. There is a slight enhancement of the OL properties upon bromination, due to increased intersystem crossing to the triplet manifold, but the enhancement of the OL properties is less significant than has been observed with metal phthalocyanine complexes.

1. Introduction

Optical limiting (OL) materials can protect the human eye and sensitive optical devices from intense incident laser beams [1–3]. An ability to effectively absorb intense pulses of laser light at 532 nm is particularly important in this regard [4–7], since it is the second harmonic of Nd:YAG laser systems that are widely used in laser pointers. Ideally, there should be high transmittance of low-intensity light, along with the attenuation of the incident laser beam, in a manner that limits the output fluence [1–3]. Optical limiting can be achieved through nonlinear absorption (NLA), nonlinear refraction and nonlinear light scattering [8,9]. The focus of this study is on the use of the NLA processes of molecular dyes in OL applications. Materials with positive NLA coefficients result in a reverse saturable absorption (RSA) response during Z-scan measurements with a strong decrease in transmittance at high-intensity levels at the focal point for the laser beam. Two-photon absorption (2PA) is a resonant third-order nonlinear optical (NLO) process in which an excited state is formed by the simultaneous absorption of two photons of half-energy. The 2PA process can be described by the imaginary part of the third order susceptibility (Im $[\chi^{(3)}]$) and second-order hyperpolarizabilities (γ) [10,11].

There has been a strong focus on the OL properties of phthalocyanines [12–14] and porphyrins [12,15], but until recently there were very few studies reported on the use of boron dipyrromethene (BODIPY) dyes as optical limiters for 532 nm laser excitation pulses [16–18] and for those at other wavelengths [19–21]. In recent decades, BODIPYs have been considered for a wide range of applications such as their widespread use as fluorescent sensor and laser dyes [22–29], as a result of (i) their easy structural modification and synthesis, (ii) their favorable spectroscopic properties with intense narrow spectral bands ($\varepsilon > 80\,000\ M^{-1}\ cm^{-1}$ and $\Phi_F > 0.50$) that can be readily shifted from the green region of the visible region into the near infrared, negligible triplet-state formation, (iii) their high solubility in most organic solvents, and (iv) their high photostability. Over the past year, we have demonstrated that BODIPY dyes that have extended π-systems at the 3,5-positions are more suitable for OL applications at 532 nm [30–35], since the extension of the π-conjugation system shifts the main BODIPY spectral bands to longer wavelength, and this leads to relatively weak absorption at 532 nm, making the dyes potentially suitable for OL where the second harmonic of Nd:YAG lasers is concerned.

It has been demonstrated that extended π-conjugation systems possess large electronic polarizabilities, and hence it is reasonable

* Corresponding author.
E-mail address: j.mack@ru.ac.za (J. Mack).
[1] These authors contributed equally to this study.

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