

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

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ABSTRACT: The synthesis and characterization of a series of 3,5-di-*p*-benzyloxystyrylBODIPY dyes with different substituents at the *meso*-aryl position is reported. The photophysical and nonlinear optical properties are described. BODIPYs of this type are found to be suitable for optical limiting at 532 nm on the nanosecond timescale. An enhancement of the population of the T_1 state through the incorporation of bromine atoms at the 2,6-positions does not result in an enhancement of the optical limiting properties on a nanosecond timescale. This suggests that, in contrast with phthalocyanines, access to excited state absorption (ESA) from the T_1 state through the introduction of a heavy atom effect does not provide a significantly improved reverse saturable absorbance response compared to ESA from the S_1 state.

KEYWORDS: BODIPYs, Knoevenagel condensation, singlet oxygen, optical limiting, photophysics, z-scan.

INTRODUCTION

The nonlinear optical properties of organic and inorganic materials have attracted considerable attention in recent years because of their use in applications such as optical data storage, fluorescence imaging, and photochromic switches [1-7]. The organic materials that are studied in this context usually consist of π -conjugated systems since they provide rapid nonlinear optical responses [8–12], while interest in inorganic materials has focused on crystals of salts such as lithium niobate or potassium dihydrogen phosphate [13-15]. Over the last two decades, there has been a strong focus on organic chromophores such as phthalocyanines [16] and metallophthalocyanines [17] in this context, and recently BODIPY dyes [18–21] have started to be investigated in this context. BODIPY dyes have found widespread application due to their photochemical and thermal stability as well as their high molar extinction coefficients [22]. The structure of this chromophore can be easily manipulated synthetically [23], and the main spectral band can be shifted from the green portion of the visible region to the near infrared region that is useful as a photosensitizer for photodynamic antimicrobial chemotherapy, and photodynamic therapy [22-25]. This also opens up possibilities for their use as optical limiters at 532 nm, since there is only weak absorption at this wavelength for most 3,5-distyrylBODIPY compounds. It has recently been demonstrated that the long π -conjugation system of these compounds result in promising reverse saturable absorbance (RSA) responses during z-scan measurements and hence have promising optical limiting (OL) properties [26–30]. When electron donating benzyloxyphenyl rings are attached at either end of the π -electron deficient BODIPY core, structures are formed that are analogs to those of push-pull olefins that have been found to form unusually efficient two-photon dyes [31]. In this study, a series of spectroscopic, photophysical, and nonlinear z-scan measurements are reported, along with TD-DFT calculations studies for brominated and non-brominated p-benzyloxystyryl-substituted BODIPY dyes in order

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to assess their potential utility in OL applications and to explore the effect of introducing heavy atoms at the 2,6-positions on the BODIPY core.

EXPERIMENTAL

Materials

4-Carbomethoxybenzaldehyde, 4-hydroxybenzaldehyde, 2,4-dimethylpyrrole, *N*-bromosuccinimide (NBS), trifluoroacetic acid, *p*-chloranil, triethylamine, boron trifluoride diethyl etherate, diphenylisobenzofuran, acetic acid, and piperidine were purchased from Sigma-Aldrich and were used without further purification, with the exception of 2,4-dimethylpyrrole which was distilled prior to use. Spectroscopic grade dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were used for the spectroscopic and non-linear optical (NLO) measurements.

Instrumentation

Fluorescence excitation and emission spectra, and UV-visible absorption spectra were measured on a Varian Eclipse spectrofluorimeter and a Shimadzu UV-2550 spectrophotometer respectively, while ¹H and ¹³C NMR spectra were recorded on a Bruker 600 MHz spectrometer in CDCl₃. A Bruker AutoFLEX III Smartbeam MALDI-TOF mass spectrometer was used to perform mass spectrometry in a dithranol matrix in positive ion mode. A Picoquant GmbH time-correlated single photon counting (TCSPC) set-up equipped with LDH-P-670 diode laser with a 44 ps pulse width and 20 MHz rate repetition was used to determine the fluorescence lifetimes of compounds. The fitting of the exponential decay curves were carried out by using the Fluofit software package. NLO studies were conducted by using a Nd:YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source operating in a near Gaussian transverse mode at 532 nm as shown before [32]. A low pulse repetition rate of 10 Hz was used to avoid cumulative thermal nonlinearities. The beam was filtered spatially before being focused with a lens (focal length = 15 cm), so that higher order modes could be eliminated. DMSO solutions and a 2 mm quartz cuvette were used for the z-scan measurements.

Photophysics

The fluorescence and singlet oxygen quantum yields of BODIPY dyes **1a**, **2a**, **1b**, and **2b** were determined in DMF and DMSO solutions using comparative methods with zinc phthalocyanine as the standard [33, 34] and 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen scavenger [35, 36]. The sample and the standard solutions were excited at crossover wavelength with the same absorbance values. An Ekspla NT 342B-20-AW laser with a tunable optical parametric oscillator unit (20 mJ/5 ns, 20 Hz) was used in this context during the singlet oxygen quantum yield measurements. All measurements were carried out at least three times to ensure the accuracy of the reported values.

Synthesis

The 4-benzyloxybenzaldehyde (BBzA) precursor for the Knoevenagel condensation reactions (Scheme 1) was prepared and characterized according to the literature procedure [37]. 1,7-Methyl-4-methoxycarboxyphenyl-BODIPY or 1,7-methyl-4-hydroxyphenyl-BODIPY core compounds with methyl ester and hydroxy groups at the *para*-positions of the *meso*-phenyl rings $(A_1 \text{ and } B_1)$ were prepared according to literature procedures [38, 39]. 1b and 2b were obtained after the synthesis of the corresponding BODIPY core followed by Knoevenagel condensation reactions with 4-benzyloxybenzaldehyde (Scheme 1). 1a and 2a were synthesized with an initial bromination reaction to form 2,6-dibromo core intermediates $(A_2 \text{ and } B_2)$ immediately prior to the Knoevenagel condensation reactions (Scheme 1). The synthesis procedures that were used have been reported previously [40, 41] and the presence or absence of the 2,6-position peak in the ¹H NMR spectrum was used to monitor that bromination was complete in a similar manner to what we described in a previous study [37].

The brominated A_2 and B_2 intermediates were prepared from the non-brominated A_1 and B_1 precursors by adding 2.4 eq of NBS in DCM, and the mixture was left to stir for 2 h. Glacial acetic acid (1 mL) and piperidine (1.2 mL) in benzene (70 mL) was added dropwise to solutions of the A_2 or B_2 precursors (1 eq) and 4-benzyloxybenzaldehyde (3 eq). The mixture was refluxed for 2 h using a Dean–Stark apparatus. The crude products were concentrated, diluted with dichloromethane, and washed with hydrochloric acid. Magnesium sulfate was used to remove trace water. The **1a** and **1b** target compounds were obtained in 32% and 25% yields, respectively, as dark green solids after purification by column chromatography using petroleum ether-ethylacetate (4:1 v/v) as the eluent.

1a: ¹H NMR (600 MHz, CDCl₃) δ, ppm 8.23 (s, 2H), 8.13 (d, J = 16.3 Hz, 2H), 7.64 (s, 6H), 7.44 (d, J = 24.0 Hz, 10H), 7.36 (s, 3H), 7.05 (s, 4H), 5.15 (s, 4H), 4.01 (s, 3H), 1.60 (s, 6H). UV-vis (DMSO) λ, nm (log ε) 677 (5.06). MALDI-TOF m/z calc. for C₄₉H₃₉B₁Br₂F₂N₂O₄: 928.48; Found: 929.1 amu [M]⁺.

1b: ¹H NMR (600 MHz, CDCl₃) δ, ppm 8.15 (d, J = 16.6 Hz, 2H), 7.63 (t, J = 13.7 Hz, 6H), 7.48 (d, J = 7.2 Hz, 4H), 7.46 (s, 2H), 7.44 (t, J = 7.5 Hz, 5H), 7.38 (t, J = 7.1 Hz, 3H), 7.05 (d, J = 8.5 Hz, 4H), 5.15 (s, 4H), 1.54 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ, ppm 160.06, 150.51, 148.85, 140.44, 139.29, 136.66, 134.26, 132.14, 132.05, 129.89, 129.44, 128.70, 128.18, 127.51, 116.15, 115.17 (m), 111.08, 70.22, 53.79, 33.52, 32.29, 29.74, 29.12, 24.65, 22.76, 14.48. UV-vis (DMSO) λ , nm (log ε) 671 (4.60). MALDI-TOF m/z calc. for C₄₇H₃₈B₁Br₂F₂N₂O₃: 887.45 amu; Found: 888.1 amu [M + H]⁺.



Scheme 1. Synthesis of BODIPY dyes 1a, 1b, 2a and 2b

To solutions of the A_1 or B_1 precursors (1 eq) and 4-benzyloxybenzaldehyde (3 eq) in benzene (50 mL) glacial acetic acid (1 mL) was added dropwise followed by piperidine (1.5 mL). The mixtures were refluxed overnight using Dean–Stark set up. The crude mixture was concentrated *in vacuo* and washed with hydrochloridric acid (2 M), water, and dried with magnesium sulfate then concentrated. Petroleum ether-ethylacetate (4:1 v/v) was used for purification. **2a** and **2b** were obtained in 38% and 35% yields, respectively, as dark blue-green solids.

2a: ¹H NMR (600 MHz, CDCl₃) δ, ppm 8.22 (s, 2H), 7.63 (d, *J* = 16.6 Hz, 6H), 7.45 (d, *J* = 25.2 Hz, 10H), 7.38 (s, 2H), 7.24 (d, *J* = 16.2 Hz, 2H), 7.02 (s, 4H), 6.64 (s, 2H), 5.14 (s, 4H), 4.00 (s, 3H), 1.60 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ, ppm 166.62, 159.65, 153.10, 141.43, 140.23, 136.66, 136.44, 136.07, 132.68, 130.67, 130.28, 129.74, 129.14, 129.02, 128.68, 128.15, 127.55, 117.77, 117.21, 115.08, 70.09, 31.23, 14.21. UV-vis (DMSO) λ, nm (log ε) 653 (5.11). MALDI-TOF m/z calc. for C₄₉H₄₁BF₂N₂O₄: 770.69 amu; Found: 771.3 amu [M]⁺.

2b: ¹H NMR (600 MHz, CDCl₃) δ, ppm 7.58 (d, *J* = 7.7 Hz, 5H), 7.46 (s, 4H), 7.42 (s, 5H), 7.36 (s, 3H), 7.22 (s, 1H), 7.19 (s, 1H), 7.14 (s, 2H), 7.01 (s, 4H), 6.96 (s, 2H), 6.61 (s, 2H), 5.12 (s, 4H), 1.49 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ, ppm 159.51, 152.56, 141.88, 136.66, 135.65, 133.57, 129.90, 129.76, 129.07, 128.70, 128.14, 127.59, 117.37, 116.04, 115.15, 70.07, 29.65, 14.91. UV-vis (DMSO) λ , nm (log ε) 646 (4.97). MALDI-TOF m/z calc. for C₄₇H₃₉BF₂N₂O₃: 728.65 amu; Found: 729.3 amu [M+H]⁺.

Polymer thin film

Polystyrene (200 mg) was dissolved in 4 ml of chloroform and the mixture was sonicated for 30 min, and 1×10^{-2} moles each of **2b** was first dissolved in 1 ml of chloroform and then added with stirring for 24 h. The BODIPY-polystyrene mixture was added onto a thin glass slide with a Pasteur pipette, which was air dried to remove the chloroform to form a thin film (**2b**_TF). The thickness of the film was determined to be 0.024 mm with the knife edge attachment of a Bruker D8 Discover X-ray diffraction (XRD) system.

Theoretical calculations

Optimized structures of the synthesized BODIPYs **1a**, **1b**, **2a** and **2b** and the A_1 and A_2 precursors were

obtained using the B3LYP functional of the Gaussian 09 software package with 6-31G(d) basis sets [42]. TD-DFT calculations were carried out using the CAM-B3LYP functional with 6-31G(d) basis sets.

RESULTS AND DISCUSSION

Synthesis and characterization

As has been reported previously, the protons on the methyl groups at the 3,5-positions of the 1,3,5,7tetramethyl BODIPY precursor dyes are sufficiently acidic to enable Knoevenagel condensation reactions with aryl aldehydes [43, 44]. This approach was used to prepare the **1a**, **2a**, **1b**, and **2b** target compounds from the A₁, A₂, B₁ and B₂ BODIPY core precursor compounds (Scheme 1). The number of equivalents of 4-benzyloxybenzaldehyde was increased compared to our previous work [37] in order to improve the yield and to allow for easier purification.

Optical spectroscopy

The normalized absorption spectra of **1a**, **1b**, **2a**, and **2b** in DMSO and their BODIPY core precursors are provided in Fig. 1 and spectroscopic data in DMSO and DMF are provided in Table 1. The absorption maxima for **1a/b** and **2a/b** lie in the 675–677 and 649–653 and nm range, respectively. The large bathochromic shifts of the main spectral bands that are observed in Fig. 1 relative to those of the BODIPY core precursors (Fig. 2) have been reported previously for BODIPY dyes [23] and result from a relative destabilization of the HOMO upon styrylation (Fig. 3), since there are larger MO coefficients at the 3,5-positions where the electron donating styryl groups are attached. There is also a smaller red shift due to bromination at the



Fig. 1. Normalized UV-visible absorption spectra of 1a, 1b, 2a and 2b in DMSO



Fig. 2. The TD-DFT calculations of the A_2 and A_1 precursor compounds and **1a**, **1b**, **2a** and **2b** at the CAM-B3LYP/6-31G(d) level of theory. Black diamonds are used to highlight the main visible region spectral bands that are associated with the HOMO \rightarrow LUMO transition (Table 2). Simulated spectra were calculated using the Chemcraft program by using bandwidths of 30 nm [61]



Fig. 3. The energies of the frontier MOs of the A_2 and A_1 precursor compounds and **1a**, **1b**, **2a** and **2b** at the CAM-B3LYP/6-31G(d) level of theory. Small black squares are used to highlight the occupied MOs. Wider gray lines with gray circles and wider gray lines with no extra symbols denote MOs that are localized on the styryl and *meso*-phenyl moieties, respectively. The HOMO–LUMO gap values are highlighted with gray diamonds and are plotted against a secondary axis

2,6-positions due to the mesomeric interaction between the lone pairs on the bromine atom and the π -system [45, 46]. The shift of the main absorption band of the BODIPY chromophore to the therapeutic window

	Solvent	λ_{max} [nm]	$\lambda_{em} [nm]$	τ_1 [ns]	$\Phi_{ m f}$	Φ_{Δ}
1a	DMF	675	707	3.67 ± 0.03	0.18 ± 0.02	0.20 ± 0.02
	DMSO	677	707	3.42 ± 0.02	0.14 ± 0.01	0.26 ± 0.01
1b	DMF	670	694	2.65 ± 0.02	0.08 ± 0.02	0.33 ± 0.03
	DMSO	671	698	2.34 ± 0.01	0.07 ± 0.01	0.38 ± 0.01
2a	DMF	649	666	4.01 ± 0.01	0.50 ± 0.03	0.06 ± 0.02
	DMSO	653	672	3.72 ± 0.02	0.49 ± 0.02	0.06 ± 0.03
2b	DMF	642	659	3.85 ± 0.02	0.56 ± 0.02	0.07 ± 0.02
	DMSO	646	663	3.87 ± 0.01	0.53 ± 0.01	0.08 ± 0.01

Table 1. Spectroscopic properties of compounds 1a, 2a, 1b and 2b in DMSO and DMF

makes the compounds potentially useful for biomedical applications and this could be further enhanced through conjugation with or encapsulation in nanoparticles [47, 48]. The emission bands of brominated compounds 1a and 1b lie at 707 and 694-698 nm, respectively, in DMF and DMSO (Table 1), while those of **2a** and **2b** lie in the 666–672 and 659–663 nm. The fluorescence lifetime ($\tau_{\rm F}$) values for **1a** and **1b** lie between 2.3–3.6 ns, while those for 2a and 2b are significantly longer as would be anticipated based on a lower intersystem rate in the absence of a heavy atom effect [49] and lie in the 3.7-4.0 range. The fluorescence quantum yield $(\Phi_{\rm F})$ values are also consistent with this, since for **1a** and 1b lie in the 0.07-0.18 range, while significantly larger values in the 0.49–0.56 range are obtained for 2a and **2b**. The singlet oxygen quantum yield (Φ_{Δ}) values listed in Table 1 are also higher for compounds 1a and 1b (0.20–0.38) than those for 2a and 2b (0.06–0.08) because of the heavy bromine atoms at the 2,6-positions of the BODIPY core.

Optical limiting properties

The marked red shift of the main spectral bands of **1a**, **1b**, **2a** and **2b** beyond 600 nm means that there is relatively weak absorbance at 532 nm, making these dyes potentially suitable for OL at this wavelength, which is the second harmonic of Nd:YAG lasers and hence is one of the most problematic wavelengths from a laser safety standpoint. A relatively large energy gap is predicted between the S₁ and S₂ excited states in the theoretical calculations (Fig. 2 and Table 2), since there is a relatively large gap between the HOMO and LUMO of the BODIPY chromophore and MOs that are largely localized on the styryl substituents (Fig. 3).

The z-scan technique was used to analyze the NLO properties of **1a**, **1b**, **2a** and **2b** in DMSO solution (Table 3), since these compounds are highly soluble in this solvent. The z-scan profiles of all four compounds exhibit downward dipping RSA behavior, similar to that obtained for **2b**, which is shown in Fig. 4. The normalized

transmittance of the open aperture measurement for a Gaussian laser pulse time profile can be derived from Equation 1 [50, 51]:

$$\mathbf{T}(z) = \frac{1}{\sqrt{\pi}q_0(z)} \int_{-\infty}^{\infty} \ln[1 + q_0(z)e^{-\tau^2}] d\tau$$
(1)

where $q_0(z)$ provides an indicator of the strength of the nonlinearity. For a circular shaped beam in spatial terms, $q_0(z)$ is given by Equation 2:

$$q_0(z) = \frac{2\beta_{\rm eff} P_0 l_{\rm eff}}{\pi \omega(z)^2}$$
(2)

where β is the effective nonlinear absorption coefficient of the material, P_0 is the peak power of the laser pulse and l_{eff} is the effective pathlength, given by Equation 3:

$$l_{\rm eff} = \frac{1 - e^{(-\alpha L)}}{\alpha} \tag{3}$$

where α is the linear absorption coefficient and *l* is the pathlength of the material. The beam width as a function of sample position ω (*z*) in Equation 2 can be obtained from Equation 4 [52]:

$$\omega(z) = \omega_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2} \tag{4}$$

where ω_0 is the beam waist at the focus (z = 0), which is defined as the distance from the center of beam to the point in which the intensity reduces to $1/e^2$ of its axis value, and z and z_0 are the translation distance of the sample relative to the focus, and Rayleigh length, respectively. The Rayleigh length (z_0) is defined as $\pi\omega_0^2/\lambda$ where λ is the wavelength of the laser. The effective nonlinear absorption coefficient (β_{eff}) can be extracted from the experimentally measured transmittance using Equations 1–4. An analytical version of this formula

₿	Calculated ^b			Experimental ^c		Wave function= ^d			
	v/cm ⁻¹	λ/nm	f	v/cm ⁻¹	λ/nm	_			
					1a				
1	17.8	561	1.01	14.8	677	$96\% \text{ H} \rightarrow \text{L}; \dots$			
2	27.1	369	0.96	_	—	$93\% \text{ H-1}^{\text{Sty}} \rightarrow \text{L}; \dots$			
4	30.7	326	0.16	_	—	$92\% \text{ H}-4 \rightarrow \text{L}; \dots$			
7	33.1	302	1.34	_	—	91% H-1 ^{Sty} \rightarrow L+2 ^{Sty} ; 6% H-2 ^{Sty} \rightarrow L+3 ^{Sty} ;			
1b									
1	17.9	557	1.01	14.9	671	96% $H \rightarrow L; \dots$			
2	27.4	365	0.91			$93\% \text{ H-1}^{\text{Sty}} \rightarrow \text{L}; \dots$			
4	30.8	325	0.15			$93\% \text{ H}-4 \rightarrow \text{L}; \dots$			
7	33.1	302	1.30	_	—	91% H-1 ^{Sty} \rightarrow L+2 ^{Sty} ; 6% H-2 ^{Sty} \rightarrow L+3 ^{Sty} ;			
					2a				
1	18.4	544	1.06	15.3	653	96% $H \rightarrow L; \dots$			
2	28.7	348	0.99	—	—	$93\% \text{ H-1}^{\text{Sty}} \rightarrow \text{L}; \dots$			
5	32.5	308	1.45	—	—	$89\% \text{ H-1}^{\text{Sty}} \rightarrow \text{L+2}^{\text{Sty}}; 5\% \text{ H-2}^{\text{Sty}} \rightarrow \text{L+3}^{\text{Sty}}; \ldots$			
2b									
1	18.5	541	1.05	15.5	646	$96\% \text{ H} \rightarrow \text{L}; \dots$			
2	29.0	345	0.92	—	—	$93\% \text{ H-1}^{\text{Sty}} \rightarrow \text{L}; \dots$			
5	32.5	308	1.37			91% H-1 ^{Sty} \rightarrow L+2 ^{Sty} ; 5% H-2 ^{Sty} \rightarrow L+3 ^{Sty} ;			

Table 2. The TD-DFT calculations at the CAM-B3LYP/6-31G(d) basis sets for the B3LYP optimized structures of **1a**, **1b**, **2a** and **2b**

^aThe number of the state assigned in terms of ascending energy within the TD-DFT calculation. ^bCalculated band energies (10³ cm⁻¹), wavelengths (nm) and oscillator strengths (c) in parentheses. ^cObserved energies (10³ cm⁻¹) and wavelengths (nm) in DMSO. ^dThe wave functions based on the eigenvectors predicted by TD-DFT. Only one-electron transitions of 5% or more are included. H and L are used to denote the HOMO and LUMO.

(Equation 5) can be used to derive $q_0(z)$ directly from the normalized transmittance:

$$T(z) = 0.363e^{\left(\frac{-q_0(z)}{5.60}\right)} + 0.286e^{\left(\frac{-q_0(z)}{1.21}\right)} + 0.213e^{\left(\frac{-q_0(z)}{24.62}\right)} + 0.096e^{\left(\frac{-q_0(z)}{115.95}\right)} + 0.038e^{\left(\frac{-q_0(z)}{965.08}\right)}$$
(5)

On substituting Equation 4 into Equation 2, $q_0(z)$ can be defined by Equation 6:

$$q_0(z) = \frac{Q_0}{1 + \frac{z^2}{z_0^2}} \tag{6}$$

where Q_0 is given as:

$$Q_0 = \frac{2\beta P_0 l_{\text{eff}}}{\pi \omega_b^2} \tag{7}$$

A Gaussian-shaped curve having Q_0 as the maximum value at the beam waist (z = 0) can be obtained from

Equation 5. The peak value and the FWHM of the plot provide the values of Q_0 and z_0 respectively. Equation 8 can then be used to calculate the value of β , which provides an important indicator for assessing the suitability of materials as OL materials, since it is dependent on the population of molecules in the excited state:

$$\beta = \frac{\lambda z_0 Q_0}{2P_0 l_{\text{eff}}} \tag{8}$$

When femtosecond laser pulses are used, the β value depends only on the two photon absorption (2PA) or other multiphoton process [53, 54]. When a material acts as an optical limiter, a positive nonlinear absorption coefficient is obtained, since there is decreased transmittance as the z-scan measurement approaches the focal point of the laser light [55]. For molecules that have zero linear absorption at the laser wavelength of 532 nm, all of the observed absorption at that wavelength is initially due to a multi-photon absorption process. However, when nanosecond pulses are used, as is the case in this study, an RSA response can arise from a 2PA pumped state, if

	Conc. [µM]	α [cm ⁻¹]	$\beta_{eff} [cm \cdot GW^{-1}]$	$Im[\chi^{(3)}]$ [esu]	γ[esu]	$I_{\rm lim} \left[{ m J} \cdot { m cm}^{-2} \right]$	$I_{00} [{ m MW} \cdot { m cm}^{-2}]$
1a	21.6	0.72	120	3.24×10^{-10}	4.8×10^{-30}	0.87	355
1b	21.6	1.02	202	4.74×10^{-10}	9.6×10^{-30}	0.97	355
2a	21.6	0.77	170	3.99×10^{-10}	8.1×10^{-30}	1.09	355
2b	21.6	2.08	280	6.57×10^{-10}	1.3×10^{-29}	0.76	355

Table 3. The nonlinear optical parameters of the synthesized BODIPYs in DMSO



Fig. 4. Open-aperture *z*-scans for **2b** in DMSO, which is typical of those measured for the entire **1a**, **1b**, **2a** and **2b** series. Detailed NLO parameters are provided in Tables 3 and 4

the ESA is more intense than absorption by the ground state, as is likely when there is relatively weak ground state absorption [28]. Therefore, the intrinsic value for β that is associated with 2PA alone cannot be determined, and only an effective value (β_{eff}) is determined instead. RSA behavior consistent with 2PA-assisted ESA has been reported previously for styryl-substituted BODIPYs due to their relatively long-lived S_1 excited states [27, 56]. The β_{eff} values for BODIPYs **1a**, **1b**, **2a** and **2b** were found to be 120, 202, 170 and 280 cm.GW⁻¹, respectively (Table 3), which lie in the range of values that used to be reported as being consistent with promising OL properties [57]. The β_{eff} values for **1a** and **1b**, which 2,6-brominated structures, are not as high as those for the analogous non-brominated structures, 2a and 2b, when solutions of the same concentration are used at a constant incident beam intensity. This means that in contrast with phthalocyanines, the introduction of a heavy atom effect to enhance the rate of intersystem crossing does not significantly enhance the optical limiting properties [58]. This is not unexpected given the strong RSA response that was observed previously for

J. Porphyrins Phthalocyanines Downloaded from www.worldscientific.com by UNIVERSITY OF TORONTO on 01/30/18. For personal use only. 3.5-diphenyldibenzo-azaBODIPY even in the absence of a significant linear absorption coefficient and intersystem crossing to the T_1 state, because ESA from the S_1 state results in efficient optical limiting [28]. Although iodination at the 2,6-positions would further enhance the population of the T_1 state, the broadly comparable results obtained for the main OL parameters of 1a/2a and 1b/2b suggest that this is unlikely to make a large difference and that other structural modification strategies will have to be identified to obtain a further improvement in the OL properties. It should be noted that direct comparisons of the OL properties of 1a, 1b, 2a and 2b are complicated by the differences in the significant linear absorption coefficients that are associated with the solutions of equal concentration (Table 3), since this also helps to determine the population of the S_1 and T_1 states. The effect of the ester and hydroxyl groups at the para-positions of the meso-aryl substituents of 1a/1b and 2a/2b is relatively small (Table 3), since the meso-phenyl rings lie orthogonal to the plane of the BODIPY core due to steric interactions with the methyls at the 1,7-positions.

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The value of the imaginary component of the third-order nonlinear susceptibility $(\text{Im}[\chi^{(3)}])$ provides a measure of the speed of the response by OL materials to the perturbation initiated by an intense laser beam [52]. The imaginary component of the third order susceptibility, $\text{Im}[\chi^{(3)}]$, has a direct relationship with β as given in Equation 9:

$$\operatorname{Im}\left[\chi^{(3)}\right] = \frac{n^2 \varepsilon_0 c \lambda \beta_{\text{eff}}}{2\pi} \tag{9}$$

where η and *c* are the linear refractive index and speed of light, respectively, and ε_0 is the permittivity of free space. The values of (Im[$\chi^{(3)}$]) observed in this work (Table 3) are consistent with what has been reported previously for other organic chromophores [52, 58], given that values in the 10⁻¹²–10⁻¹⁰ esu range have been reported to provide an indication that compounds are promising candidates for use as OL materials. The interaction of the permanent dipole of the molecules with intense laser radiation causes a bias in the average orientation of the molecules, which results in induced hyperpolarizability. The second order hyperpolarizability (γ) value is related to the Im[$\chi^{(3)}$] value as shown in Equation 10:

$$\gamma = \frac{\mathrm{Im}\left[\chi^{(3)}\right]}{f^4 C_{\mathrm{mol}} N_{\mathrm{A}}} \tag{10}$$



Fig. 5. Output fluence (I_{out}) vs. input fluence (I_0) curves for **1a**, **1b**, **2a** and **2b** in DMSO solutions of the same concentration and for **2b** in a polystyrene thin film at a lower incident light intensity. Detailed NLO parameters are provided in Tables 3 and 4

where N_A is Avogadro's constant, C_{mol} is the concentration of the active species in the excited state per mole, and *f* is the Lorentz local field factor, $f = (\eta^2 + 2)/3$. In 2003, the optimal range of hyperpolarizability values was reported to be as low as the $10^{-34}-10^{-29}$ esu range for organic dyes in solution [58], so the values reported in Table 3 imply that these complexes possess superior nonlinear optical properties.

Markedly reduced transmittance at increased incident fluence values (Fig. 5) is a prerequisite for a good OL material. The threshold limit intensity (I_{lim}), is defined as the input fluence at which the nonlinear transmittance is reduced to 50% of the linear transmittance value (Fig. 6). The International Commission on Non-Ionizing Radiation Protection has published a guideline [59] for exposure limits to a variety of lasers. The use of 10 ns laser light pulses at 532 nm results in an exposure limit (lim) that can be determined from Equation 11:

$$\lim = 2.7 C_{\rm A} t^{0.75} J \cdot {\rm cm}^{-2}$$
(11)

where C_A is a correction factor (= 1 for 400–700 nm) and *t* is the exposure time. This equation provides an exposure limit of 0.95 J·cm⁻² for a 0.25 s exposure time, which is the average human blink reflex [60]. Values of I_{lim} can be extracted from a plot of transmittance against input fluence (Fig. 6) and were determined to be 0.87, 0.97, 1.09 and 0.76 J·cm⁻², respectively, for **1a**, **1b**, **2a** and **2b** in DMSO (Fig. 6 and Table 3), which in each case is close to or below the recommended limit and hence provides further evidence for the suitability of these compounds for OL applications. The I_{lim} values are considerably lower than those reported recently for 3,5-dithienylvinylene



Fig. 6. Transmittance *vs.* input fluence (I_0) curves **1a**, **1b**, **2a** and **2b** in DMSO solutions of the same concentration and for **2b** in a polystyrene thin film at a lower incident light intensity. The calculation for the I_{lim} values are highlighted with dashed lines. Detailed NLO parameters are provided in Tables 3 and 4



Fig. 7. The UV-visible absorption spectrum of 2b in the polystyrene thin film used for z-scan measurements

(and 3,5-dipyrenylvinylene BODIPYs [29, 30]), and are comparable to those obtained for 2,6-dibromo-3,5-distyrylBODIPYs with two hydroxyl groups on each styryl ring, which have similar donor- π -acceptor type structures [27]. A strong enhancement in the I_{lim} value was observed when **2a**, which provided the strongest nonlinear response in solution (Table 3), was embedded

Table 4. The nonlinear optical parameters of 2b embedded in a polystyrene thin film

	Thickness [µm]	Conc. [mM]	α [cm ⁻¹]	$\beta_{eff}[cm\cdot MW^{\!-\!1}]$	$Im[\chi^{\scriptscriptstyle (3)}] \; [esu]$	γ[esu]	$I_{\rm lim} \left[{ m J} \cdot { m cm}^{-2} \right]$	$I_{00} [{ m MW} \cdot { m cm}^{-2}]$
2b_TF	24	≈11	165	180	4.76×10^{-7}	$\approx 1.5 \times 10^{-29}$	0.094	47

no evidence for aggregation in the UV-visible absorption spectrum of the **2b**_TF polystyrene thin film (Fig. 7), since there is only limited band broadening. The I_{lim} value of 0.094 J·cm⁻² for **2b**_TF (Fig. 6 and Table 4) demonstrates that BODIPY dyes of this type are suitable for use as OL materials. Since the concentration of **2b** was three orders of magnitude higher when **2b** was embedded into the thin film, the β_{eff} and third order susceptibility values are significantly higher than those obtained in DMSO solution (Tables 3 and 4), but the second order hyperpolarizability value is estimated to be similar since the concentration of the dye molecule is taken into consideration in this context.

into a polystyrene thin film (Fig. 6 and Table 4). There is

CONCLUSIONS

BODIPY dyes with *p*-benzyloxystyryl groups introduced at the 3,5-positions and bromine atoms both present and absent at the 2,6-positions are found to have promising optical limiting properties. The I_{lim} value for a polystyrene thin film of **2a** is well below the exposure limit of 0.95 J·cm⁻² for nanosecond laser pulses at 532 nm, thus demonstrating the potential utility of these dyes for this application. The use of the heavy atom effect to enhance the population of the T₁ state through the incorporation of bromine atoms at the 2,6-positions does not result in an enhancement of the OL properties on a nanosecond timescale. This suggests that, in contrast with phthalocyanines, ESA from the T₁ state does not provide a significantly enhanced RSA response when compared to ESA from the S₁ state.

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