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Nonlinear optical measurements of BF₂-aza dipyrromethene fluorophoresFryad Z. Henari^{a,*}, Donal F. O'Shea^b, Dan Wu^b^a Department of Medical Sciences, Royal College of Surgeons in Ireland, Medical University of Bahrain, P.O. Box 15503, Busaiteen 228, Bahrain^b Department of Chemistry, RCSI, 123 St Stephen's Green, Dublin 2, Ireland

HIGHLIGHTS

- Nonlinear absorption coefficient and refractive index of BF₂-aza dipyrromethene complexes.
- Excited state absorption cross-section higher than the ground state absorption cross-section.
- Nonlinear absorption is Reverse saturation absorption and the nonlinear refractive index is of thermal origin.
- Pump and probe used to record triplet state spectrum.
- The optical limiting process demonstrated.

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ABSTRACT

Nonlinear absorption coefficient and the nonlinear refractive index of a series of BF₂ aza dipyrromethene chromophores in tetrahydrofuran (THF) solutions were measured using the Z-scan technique with a low power continuous wave laser at 633 nm. Acquired data illustrated that the process involved in nonlinear absorption is reverse saturation absorption. The excited state absorption cross sections for all complexes were calculated and a pump and probe technique was used to record the triplet absorption spectrum. The band gap of the triplet state was estimated from this spectral data and the optical limiting behavior was demonstrated for each derivative.

1. Introduction

Studies of materials with large nonlinear optical properties continue to attract considerable research interest due to their applications in various fields such as photonic devices and modern medicine [1–8]. Polyaromatic organic compounds and organometallic complexes are characterized by their delocalized pi-electron system and intramolecular charge transfer (ICT) properties, which are widely investigated for their optical nonlinearities [9,10]. Nonlinear optical materials which exhibit intensity induced refractive index change $\Delta n = n_2 I$ and absorption change $\Delta \alpha = \beta I$; where n_2 and β are the nonlinear refractive index coefficient and the nonlinear absorption coefficient respectively. The nonlinear absorption coefficient comprises of Excited State Absorption (ESA), Saturation Absorption (SA) which is described by an increase in transmission with increase of input intensity, Reverse Saturation Absorption (RSA) is described by a decrease in transmission with increase of input intensity and two-photon absorption (TPA) is characterized by the simultaneous absorption of two photons of identical or different frequencies in order to excite a molecule from one state (usually the ground state) to a higher energy

electronic state [1,11,12]. Materials possessing RSA and TPA are of considerable value for optical limiting devices [8], medical imaging [13] and PDT [14].

BF₂-aza-boron dipyrromethene compounds containing bromine atoms in various positions have been synthesized and used to investigate the enhancement of TPA properties and triplet state population through an intersystem crossing (ISC) process with a pulsed laser [15–17]. Due to high photostability as well as ease of syntheses, these class of fluorophores have been studied for imaging but have not been considered yet for applications in organic electronic devices and little is known about their (NLO) nonlinear optical properties.

In this work, we report measurements of the nonlinear absorption coefficient and nonlinear refractive index for four samples of BF₂ aza dipyrromethene complexes in THF solutions with a low power continuous wave (CW) laser at 633 nm, using the Z-scan technique [18]. The RSA process was observed and a negative nonlinear refractive index was observed for all samples. Using the pump and probe technique the triplet state absorption spectrum was recorded and used to estimate the band gap energy of the triplet state. The optical limiting properties of the chromophores were explored.

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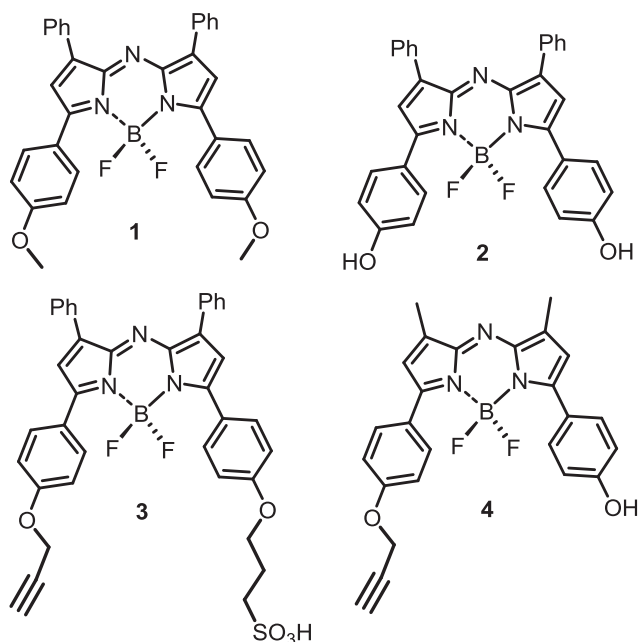


Fig. 1. Molecular structures of the BF_2 -aza dipyrromethenes investigated in this study. (1) 5,5-Difluoro-3,7-bis(4-methoxyphenyl)-1,9-diphenyl-5H-4,14,5,14-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinine. (2) 4,4'-(5,5-Difluoro-1,9-diphenyl-5H-4,14,5,14-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinine-3,7-diyl)diphenol. (3) 3-(4-(5,5-Difluoro-1,9-diphenyl-7-(4-(prop-2-yn-1-yloxy)phenyl)-5H-5,6,14-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)phenoxy)propane-1-sulfonic acid. (4) 4-(5,5-Difluoro-1,9-dimethyl-7-(4-(prop-2-yn-1-yloxy)phenyl)-5H-5,6,14-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)phenol.

2. Experiments

BF_2 -aza dipyrromethene 1–4 were synthesized following the previously reported synthetic routes [19]. The synthesis molecular structures of compounds are shown in Fig. 1.

A solution of 0.1 g/L of each compound was prepared in THF and placed in a 10 mm cuvette. The linear absorption spectrum of the compounds was recorded using a UV–Vis spectrophotometer (SHIMADZU-UV-1800). Fig. 2 shows the absorption spectra of the chromophores. From the absorption spectra, it can be seen that spectra are characterized by their longest wavelength bands at 684, 698, 690 and 652 nm for samples 1–4 respectively. These absorption bands are

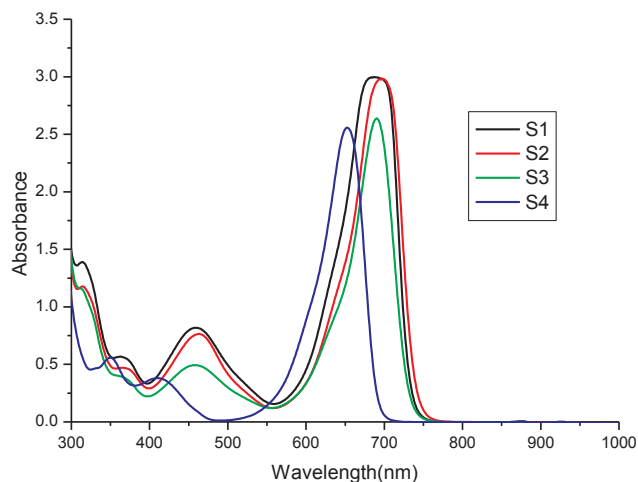


Fig. 2. Absorption spectra of the BF_2 azadipyrromethenes compounds 1–4 in THF in 1 mm cell.

related to the ground state to first excited state transition (S_0 to S_1). The absorption band of chromophore 4 is blue shifted by 32–46 nm with respect to absorption peaks of the other samples. This hypsochromic shift can be attributed to a reduction of electron donation into the core of the fluorophore [20–23].

Measurement of the nonlinear absorption coefficient and the nonlinear refractive index of compounds 1–4 was achieved using the Z-scan technique. This technique relies on the fact that the intensity varies along the axis of the convex lens and it is maximum at the focus. By shifting the sample through the focus, the intensity-dependency can be measured as a change of transmission. The nonlinear refraction can be measured by observing the spot size variation at the plane of finite aperture/detector combination. In the Z-scan procedure, the transmission of the sample was measured with and without an aperture in the far-field of the lens, as the sample moved through the focal point. This enables the nonlinear refractive index (closed aperture) to be separated from that of the nonlinear absorption (open aperture).

The experiment was performed with a He-Ne laser beam operating at 633 nm with an average power of 10 mW. The beam was focused with a lens of 5 cm focal length to a beam waist of 20 μm , giving a power density around of $7.96 \times 10^6 \text{ W/m}^2$ at the focus. As the sample solution was moved through the focal point, the transmission from the samples was measured with and without an aperture in the far-field of the lens. The nonlinear refractive index was measured via a closed aperture while the nonlinear absorption coefficient was measured via an open aperture.

3. Results and discussion

Fig. 3 shows the normalizing transmission for an open aperture case as a function of the distance along the lens axis, z , for a 1 mm thick cuvette of sample 1 solution at 633 nm. The decrease of transmission with intensity is inductive of reverse saturation absorption (RSA) processes. Similar characteristics were observed with other studied compounds. RSA occurs when an absorption cross-section of excited states σ_{ex} is larger than that of an absorption cross-section of ground state σ_g . The RSA processes can be explained using five energy level systems, involving singlet and triplet states S_0 , S_1 , S_2 , T_1 , and T_2 . Briefly, the laser light excites molecules from the ground state S_0 to the first excited singlet state S_1 with an absorption cross section σ_g . From this state, the molecule can relax to the state S_0 , or be excited to the state S_2 , or undergo an intersystem crossing relaxation to the state T_1 . The relaxation from S_2 to S_1 would be unresolvable due to the nature of the laser used

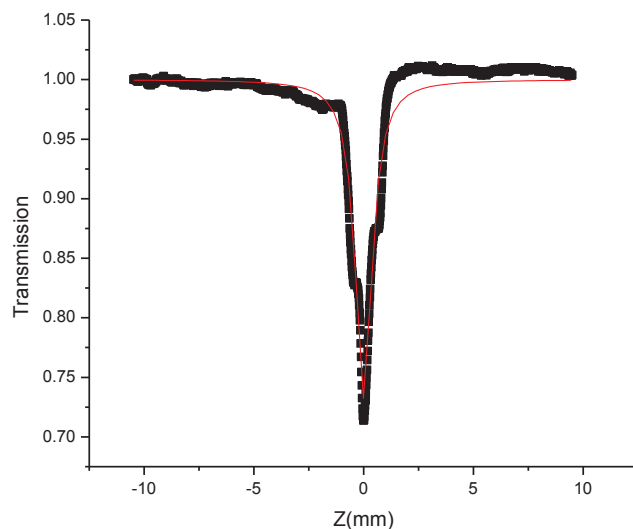


Fig. 3. Normalized transmittance (open aperture) of sample 1 at 10 mW. The solid line is a fit of the data to Eq. (1).

in the experiment (CW mode). From T_1 , the molecule can return to S_0 or, may be promoted to the T_2 state by absorbing another excitation photon. If sufficient population is transferred to S_2 or T_2 and the excited state absorption cross-sections of these states are larger than the ground ones, then RSA arises. As the Z scan was performed with a CW laser one would expect the existence of triplet excited state absorption and the $T_1 \rightarrow T_2$ transition to be at the origin of RSA. Also a pump and probe experiment was performed to observe the triplet state absorption spectrum.

As negative control an open aperture Z-scan was performed with a pure solvent for which no nonlinear absorption was observed within the limit of the intensity used in the experiment. We conclude no nonlinear contribution from the solvent and that the effects recorded are due to the BF_2 -azadipyromethene sample.

The normalized transmittance for the open aperture is given by [18].

$$T(z) = 1 - \frac{\Delta\phi}{(1 + x^2)} \quad (1)$$

where $x = z/z_0$ (with $z_0 = \pi w_0^2/\lambda$) is the diffraction length of the Gaussian beam, w_0 is the beam and $\Delta\phi$ is the nonlinear phase change. The nonlinear absorption β is then related to $\Delta\phi$ by [18]

$$\beta = \frac{2\sqrt{2}\Delta\phi\alpha}{I_0(1 - e^{-\alpha l})} \quad (2)$$

where α is the linear absorption coefficient at $\lambda = 633 \text{ nm}$ and l is the thickness of the sample and I_0 is the peak intensity at the focus. A fit of Eq. (1) to the experimental data is shown in Fig. 3. It can be seen from the figure that the fit of Eq. (1) to the data is not optimal in the shoulder region, this may be due to residual nonlinear refractive index or the astigmatic nature of the laser beam during transmission through the sample. Eqs. (1) and (2) were used for calculation of the nonlinear absorption coefficient, β , the calculated nonlinear absorption coefficient for the samples are shown in Table 1.

As stated above, the RSA occurs when excited absorption cross-section σ_{ex} is larger than absorption cross-section of ground state σ_g . The excited state absorption cross-section can be calculated from the differential transition given from Z scan results using the following equation [23].

$$1 - T_0 = \exp(-(\sigma_{\text{ex}} - \sigma_g)N_0 l) \quad (3)$$

where T_0 is the minimum transmission from Z scan, N_0 is the number of molecules per cm^3 and l is the sample thickness. The ground state absorption cross section was calculated from $\sigma_g = \alpha_0/N_0$ and using Eq. (3). The excited state absorption cross sections for all samples were calculated and the values are given in Table 1. These values are higher by one order than the ground state absorption cross section for all studied samples, which is in agreement with the conditions for observing RSA and indicates that the observed nonlinear absorption is associated with RSA. RSA has been previously observed for azadipyromethene and BODIPY systems at 532 nm using a ns pulsed laser and Z scan technique [24].

A pump and probe experiment was utilized to observe the absorption spectrum of triplet T_1 for sample 1 in THF through the following procedure: He-Ne CW laser beam of wavelength 633 nm (close to resonance) was used as a pump (excitation source) and was focused by a

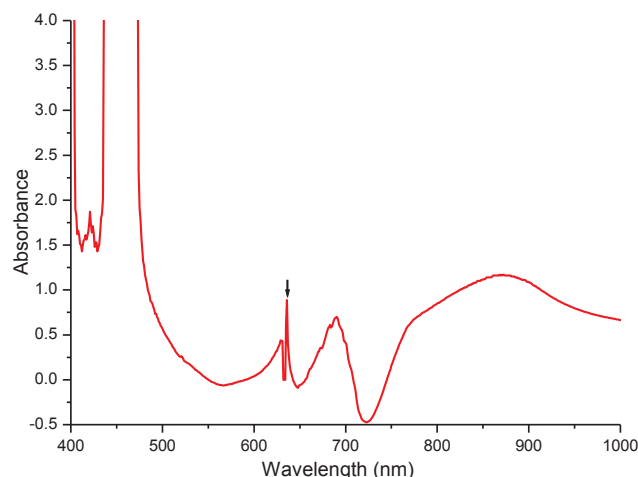


Fig. 4. Pump and probe absorption spectrum of sample 1 in THF solution.

lens of 5 cm focal length to the beam waist of $30 \mu\text{m}$. A halogen lamp was used as a probe beam and focused on the sample by the same lens.

The sample was moved to a post-focusing position (minimum transmission position in open Z scan experiment (see Fig. 3)). The transmitted change of the probe beam was recorded by a CCD spectrometer (Model BRC112E-USB-Vis NIR) and transferred to a computer. The population of triplet excitation achieved by the population of the S_1 state through excitation of the S_0 - S_1 transition by CW excitation beam of wavelength 633 nm, where the S_1 states undergo intersystem crossing, producing a population in T_1 states with the rate of ns. Because of the relatively long lifetime of T_1 state, its population dominates that of other excited states. Fig. 4 shows the absorption spectrum excited at 633 nm (arrow in the figure). The three main features observed in the spectrum are (i) a singlet absorption peak at 689 nm; (ii) a bleaching at 721 nm and (iii) a broad triplet state absorption centered at 870 nm. The ground state absorption decreases at 721 nm and contains contributions of both ground state bleaching and stimulated emission. The remainder of the absorption peak at 689 nm is an indication that the ground state has not completely refilled, therefore some singlets may have undergone intersystem crossing to triplet state. Therefore, it is plausible that the populated triplet may be the contributor to the nonlinear processes. It can be seen from the graph that the absorption peak for triplet state occurs around 1.425 eV (870 nm). The band gap was calculated from the graph and found to be $149.5 \text{ kJ mol}^{-1}$. This value is higher than the singlet excitation energy $E_{\Delta g}$ of molecular oxygen, however, the quantum yield efficiency needs to be investigated. It is worth mentioning that there are no reports of intersystem crossing for BF_2 aza dipyromethene chromophores, however, there are many reports of the intersystem crossing for the brominated substituted derivatives [15,17,25,26,27]. More investigations including optical dynamics and decay processes are required to fully elucidate these photophysical properties.

The normalized transmittance through the closed aperture for 0.1 g/L solution of sample 4 with theoretical fitting from Eq. (4) is shown in Fig. 5. The peak-valley trends of the closed Z scan for the sample is a signature of negative refractive nonlinearity, which may give rise to self-defocusing behavior. Similar behavior was observed for other

Table 1

Linear absorptions, ground, and excited absorption cross-sections, nonlinear absorptions, nonlinear refractive indices, and optical limiting.

Sample	α/cm	$\sigma_g (\text{cm}^2)$	$\sigma_{\text{ex}} (\text{cm}^2)$	$\beta (\text{m/W})$	$n_2 (\text{m}^2/\text{W})$	O.L. (mW)
1	0.297	2.75×10^{-18}	1.48×10^{-17}	5.52×10^{-6}	1.62×10^{-12}	7.53
2	0.227	2.00×10^{-18}	1.67×10^{-17}	7.65×10^{-6}	1.83×10^{-12}	7.51
3	0.197	2.26×10^{-18}	8.10×10^{-18}	2.19×10^{-5}	1.99×10^{-12}	7.93
4	0.447	3.28×10^{-18}	1.37×10^{-17}	9.83×10^{-6}	1.75×10^{-12}	6.46

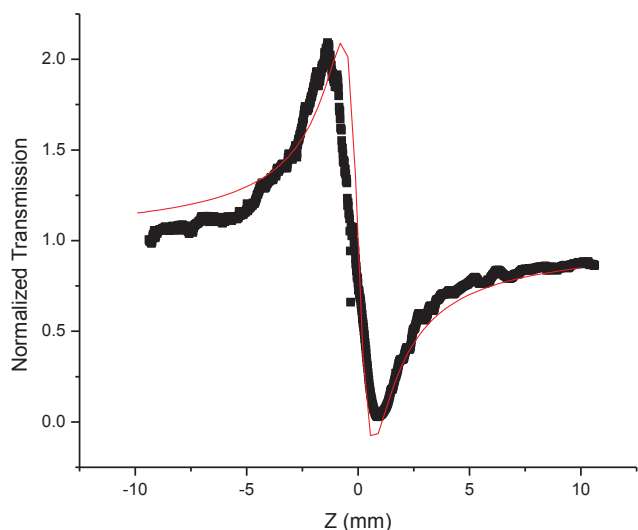


Fig. 5. Normalized transmittance (closed aperture) of sample 4, 0.1 g/L, 10 mW. The solid line is a fit of the data to Eq. (4).

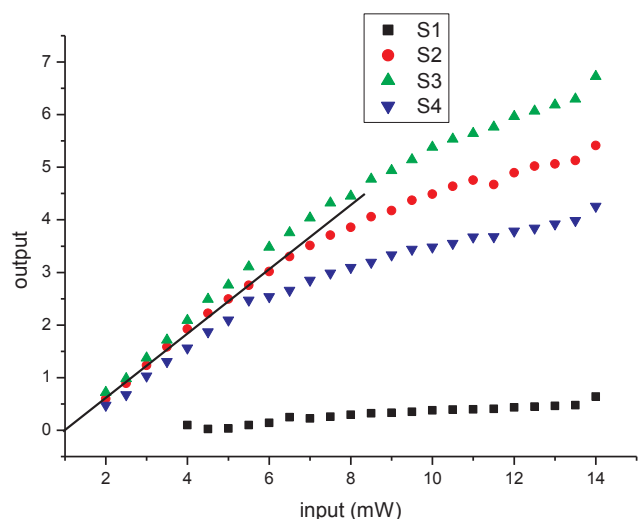


Fig. 6. The optical limiting response of all studied samples at 633 nm.

samples and no nonlinear effect was observed when the Z scan performed with pure THF.

The normalized transmission of the closed aperture Z scan is given by [18]

$$T(z) = 1 + \frac{4x\Delta\phi}{(x^2 + 9)(x^2 + 1)} \quad (4)$$

where $x = z/z_0$, z is the longitudinal distance from the focal point, z_0 is the Rayleigh range of the lens and $\Delta\phi$ is the nonlinear phase change. The normalized closed aperture Z scan data are fitted with Eq. (4) to obtain $\Delta\phi$ values. The nonlinear refractive index n_2 is then related to $\Delta\phi$ by

$$n_2 = \frac{\Delta\phi\alpha\lambda}{2\pi I_0(1 - e^{-\alpha l})} \quad (5)$$

where α is the linear absorption coefficient at 633 nm ($\alpha = 0.021/\text{mm}$) and l is the thickness of the sample. I_0 is the peak intensity at the focus, and λ is the wavelength of the laser beam.

A fit of Eq. (4) to the experimental data is depicted in Fig. 5, Eqs. (4) and (5) were used for the calculation of nonlinear refractive index, the calculated values for the samples are shown in Table 1.

4. Optical limiting

An optical limiter is a device designed to sustain high transmissions at low input intensities and the decreasing transmission of gradually increasing intensities of laser beams. The most important application of this device is the protection of eye, sensitive optical sensors, and components from high-intensity laser beams. The optical limiting process is related at least to one of the nonlinear mechanisms such as nonlinear absorption, which may be associated with reverse saturation absorption, two-photon absorption and nonlinear refractive index change due to the electronic Kerr or thermal effects. The observed nonlinear refractive index of BF₂ aza dipyrromethene chromophore samples were used to demonstrate their limiting performance. Solutions of 0.01 g/L concentration were prepared and placed in a 1 mm cuvette and placed at the position close to valley position, as determined Z scan. The output power was recorded as the power of the incident beam, which varies with neutral density filters. Fig. 6 shows the optical limiting behavior for the samples 1–4. It can be seen clearly from the graph that the transmitted output powers varies linearly at low incident powers and deviate at high incident powers. The values of the limiting threshold were determined when the deviations occur and are given in Table 1. The observed low values of optical limiting threshold suggest the involvement of more than one nonlinear mechanism such as RSA and refractive index change due to the heat.

5. Conclusion

In conclusion, the nonlinear absorption coefficient and the refractive index of BF₂ aza dipyrromethene samples in THF were measured using the Z-scan technique and a CW laser at 633 nm. The Z scan measurements revealed that the compounds exhibit large nonlinear optical properties at low power inputs. We attribute the nonlinear absorption to RSA absorption process and the nonlinear refractive index to the thermal origin. The excited state absorption cross sections for all chromophores were calculated and found to be higher than the ground state absorption cross-section, which is in agreement with the conditions for observing RSA. The pump and probe experiment was used to observe the absorption spectrum of the triplet. Future experiments such as ultrafast transient absorption spectroscopy are needed, to investigate the excited state population of these compounds.

Conflict of interest

DOS declares the following competing financial interest. Patents have been filed on BF₂-azadipyrromethene based NIR fluorophores (EP2493898 and US8907107) in which he has a financial interest.

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