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Nonlinear optical properties of multipyrrole dyes

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Abstract

The nonlinear optical properties of a series of pyrrolic compounds consisting of BODIPY and aza-BODIPY systems are investigated using 532 nm nanosecond laser and the Z-scan technique. Results show that 3,5-distyryl extension of BODIPY to the red shifted MeO_2BODIPY dye has a dramatic impact on its nonlinear absorption properties changing it from a saturable absorber to an efficient reverse saturable absorbing material with a nonlinear absorption coefficient of 4.64×10^{-10} m/W. When plotted on a concentration scale per mole of dye in solution MeO_2BODIPY far outperforms the recognized zinc(II) phthalocyanine dye and is comparable to that of zinc(II) tetraphenylporphyrin.

Introduction

Materials with optimized nonlinear optical (NLO) properties have been the focus of fundamental and applied research in recent years.[1] A wide variety of materials including inorganic and organic semiconductors, natural and synthetic nanomaterials, molecular dyes, and polymer systems,[2–9] display nonlinear optical properties which have found use in variety of applications.[10–16] Organic nonlinear optical materials, in particular, have attracted major attention due to their wide scope and ability to maximize a nonlinear response by tailored modification of their molecular structure.[17–25] Established nonlinear optical organic materials such as the pyrrole-based porphyrins, pthalocyanines and aza/azo-benzenes, possess a large number of delocalized π-electrons, with band-gaps of 2-3 eV and reasonably high nonlinearities.[26,27] The 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene chromophore, more commonly known as BODIPY and often regarded as “porphyrin’s little sister” due to its similarity to the tetrapyrrole macrocycle, is another established class of methine bridged dipyrrole chromophore with unique and attractive photophysical properties.[28] In general, organic NLO materials, and BODIPY in particular, offer the luxury of tunable, sharp, high oscillator strength absorption bands with potentially large two-photon excitation cross

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sections (σ_2).[29–33] For imaging applications in particular, focused near infrared femtosecond pulsed laser excitation is used to induce concerted two-photon $S_0 \rightarrow S_1$ electronic excitation where efficient σ_2 dyes have enabled a high optical contrast with an accurate three-dimensional spatial confinement.[34–36] In the nanosecond excitation regime, recent applications focus primarily on the optical limiting properties of dye molecules achieved by singlet ($S_1 \rightarrow S_2$) or triplet ($T_1 \rightarrow T_2$) based excited state absorption following pulsed excitation of the ground to first excited state ($S_0 \rightarrow S_1$) transition.

The pioneering work of Ziessel, Burgess and Akkaya, among others, has demonstrated how extension of π-conjugated substituents at the BODIPY 3,5-positions can give rise to substantial (> 100 nm) red-shifts in the $S_0 \rightarrow S_1$ electronic transition beyond 600 nm while maintaining a strong absorption coefficient ($\varepsilon \sim 10^5\ M^{-1}\ cm^{-1}$).[37] Following similar structural modification to enhance the nonlinear absorption, here we report a series of π-conjugated pyrrole dyes with favorable tuning of excited state absorption properties. In fact, it is shown below that BODIPY which is a saturable absorber (SA) can be effectively converted to a reverse saturable absorbing (RSA) material upon such modification. Two photon and multiphoton absorption behavior is observed for the series of compounds 1,3,5,7-tetramethyl-6-(4-methylbenzoate)BODIPY (BODIPY); 1,7-dimethyl-3,5-bis(methoxy-4-styrylbenzene)-6-(4-methylbenzoate)BODIPY (MeO_2BODIPY); 1,3,5,7-tetraphenyl-6-aza-BODIPY (aza-BODIPY); 1,7-diphenyl-3,5-bis(4-methoxyphenyl)-6-aza-BODIPY (MeO_2-aza-BODIPY) using the conventional optical Z-scan technique.[38] Structures of bis- and tetra-pyrrole dyes, and their aza analogues, investigated in this study are shown in Fig. 1.

Materials and Methods

Electronic absorption spectra were recorded in spectrophotometric grade tetrahydrofuran (Sigma) on an Agilent 8452 spectrometer in a standard 10.0 mm path length quartz cell. For Z-scan measurements a 2.0 mm path length quartz cell was placed at 45° with respective to the incident laser beam (effective path length = 2.83 mm). Samples with a linear absorption coefficient (α_0) of 345 m^{-1} at the laser excitation wavelength 532 nm were prepared (optical density = 0.3). The output of a frequency doubled Nd:YAG laser (Continuum Minilite II, 532 nm, pulse width ~ 3 ns) was focused on to the sample using a 18 cm focal length lens. The sample was mounted on an automated translation stage (Thorlabs NRT 150) and moved horizontally along the z direction through the focal point of the beam. The beam waist (ω_0) at focal plane was estimated to be 57 ± 5 μm. The energy incident on the sample was controlled by the combination of a half-wave plate and a linear polarizer. The incident laser energy before the focusing lens was ~ 65 μJ. At the focal point, the sample experienced optimum pump intensity, which decreased gradually on either side of the focus. As the intensity of incident light changed, the optical transmittance varied according to the sample's nonlinear electronic absorption properties. Importantly, a linear of the optical detector was verified; laser transmittance was measured as a function of crystal violet concentration in tetrahydrofuran with varying transmittance from 0 to 1 at 532 nm; a correlation better than $R^2 = 0.99$ was obtained when a neutral density filter of OD 1 was placed in front of the detector (data not shown).

Results and discussion

An overlay of the UV/Vis/NIR absorption spectra for ZnTPP, ZnPc, BODIPY, MeO_2BODIPY, aza-BODIPY and MeO_2-aza-BODIPY is presented in Fig. 2. All dyes display a low energy $S_0 \rightarrow S_1$ electronic absorption in the range 515 nm (BODIPY) to 693 nm (MeO_2-aza-BODIPY) with comparable oscillator strengths ranging from $5 - 12 \times 10^4$ M^{-1} cm^{-1}. The electron rich aza derivatives, ZnPc and aza-BODIPYs, each show a significant red shift relative to their methine bridged counterparts, ZnTPP and BODIPY, respectively.

Open aperture Z-scan curves for all samples ($\alpha_0 = 345$ m^{-1}, optical density = 0.3 @ 532 nm) are shown in Fig. 3, where lines represent theoretical fits to the experimental data. The experimental normalized transmission data fit well with nonlinear transmission equations.[39] The unmodified BODIPY system displays a typical SA character. Hence this data fits well to a SA transmittance equation, where the saturation intensity is 1.25×10^{11} W/m^2. In contrast each of the functionalized and core modified BODIPYs show RSA behavior and are best fit to a RSA transmittance equation. To find the origin of this RSA behavior, the nonlinear absorption coefficient behavior was studied at various on-axis intensities (I_0). Obtained Z-scan curves and the corresponding theoretical fits to the experimental data are shown in figure 4. The obtained β values are plotted with respect to I_0 in figure 5. This clearly demonstrates how β is decreases as I_0 is increased, indicating that the observed RSA effect is due to excited state absorption involving the S_1 and S_2 electronic excited states.[40] A summary of nonlinear absorption coefficients are summarized in Table 1. It is also conclusive from the absorption coefficients that nonlinear absorption of the MeO_2BODIPY system is superior to that of ZnPc and on par with ZnTPP.

Due to the difference in molar extinction coefficients (ε) of the compounds under study (Fig. 2), various concentrations had been used to achieve 0.3 absorbance at the laser operating wavelength of 532 nm (Table 1). To make a more meaningful comparison between the various dyes and estimate their contribution to the nonlinear absorption per molar concentration, i.e. to make a true qualitative comparison of nonlinear absorption efficiency at a structural level, the ‘relative nonlinear absorption per mole’ was calculated for each dye with respect to the Z position (Fig. 6). This transformation was achieved by subtracting the linear absorption (0.3 for each dye), dividing by dye concentration (mol L^{-1}) and finally dividing by the maximum absorption response (ZnTPP at Z = 0) to allow a relative comparison of each structure for quantitative purposes. Figure 4 effectively shows which dyes are most efficient at absorbing an additional photon in their excited states with respect to the photon density (Z-position). Noteworthy, MeO_2BODIPY is just as effective as the excellent ZnTPP nonlinear RSA dye. Furthermore, while the aza-BODIPY dyes are about half as efficient as MeO_2BODIPY their nonlinear absorption behavior per mole is at least twice that of their established ZnPc macrocyclic counterpart. Such a plot allows a valuable side-by-side comparison to be made for a series of dyes which can inform on strategic design of future nonlinear absorbing materials for both biological imaging and optical limiting applications.

The power limiting behavior of MeO_2BODIPY is shown in figure 7. Using the Z-scan setup discussed above, the sample was placed at z = 0 (focal plane of the 18 cm focal length lens) and the transmitted energy was recorded as the incident energy was varied. The limiting threshold energy was ~ 200 μJ and the output was clamped at ~ 25 μJ.

Conclusion

The nonlinear optical properties of styryl-BODIPY and aza-BODIPY dye systems show great promise towards the design of future NLO organic materials via an excited state (two-photon) absorption mechanism. In contrast, the unmodified BODIPY dye shows just saturable absorption character at the 532 nm wavelength used. Through designed structural modification in MeO_2BODIPY not only has the BODIPY unit been converted into a reverse saturable absorption material, but its nonlinear absorption coefficient is now competitive with the established ZnTPP and ZnPc dyes.

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- We examined absorption characteristics of BODIPY based π-conjugated pyrrole dyes.
- Pristine BODIPY possess saturable absorption behavior.
- 3,5-distyryl extended MeO_2BODIPY dye depicts reverse saturable absorption.
- Observed nonlinear absorption coefficient is comparable to standard material ZnTPP.

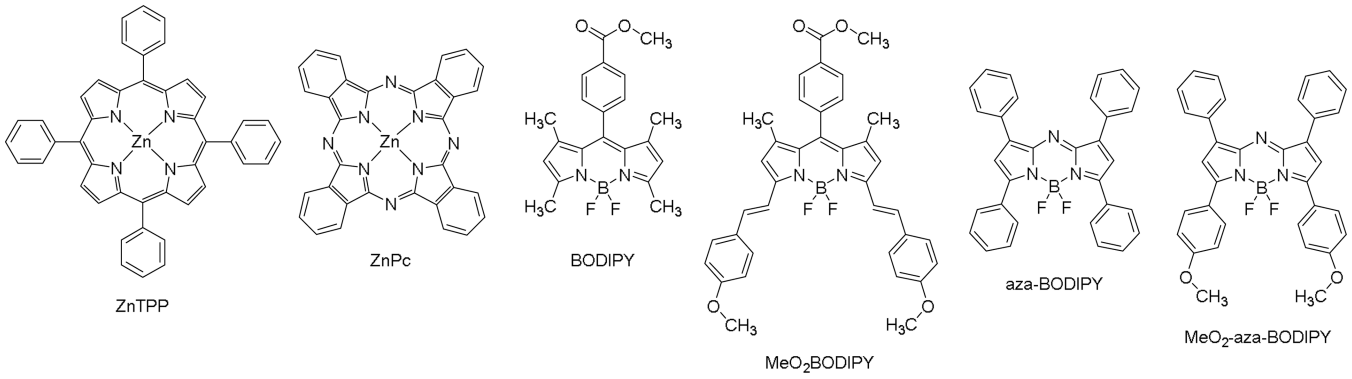

Figure 1.
Structures of bis- and tetra-pyrrole dyes, and their aza analogues, investigated in this study.

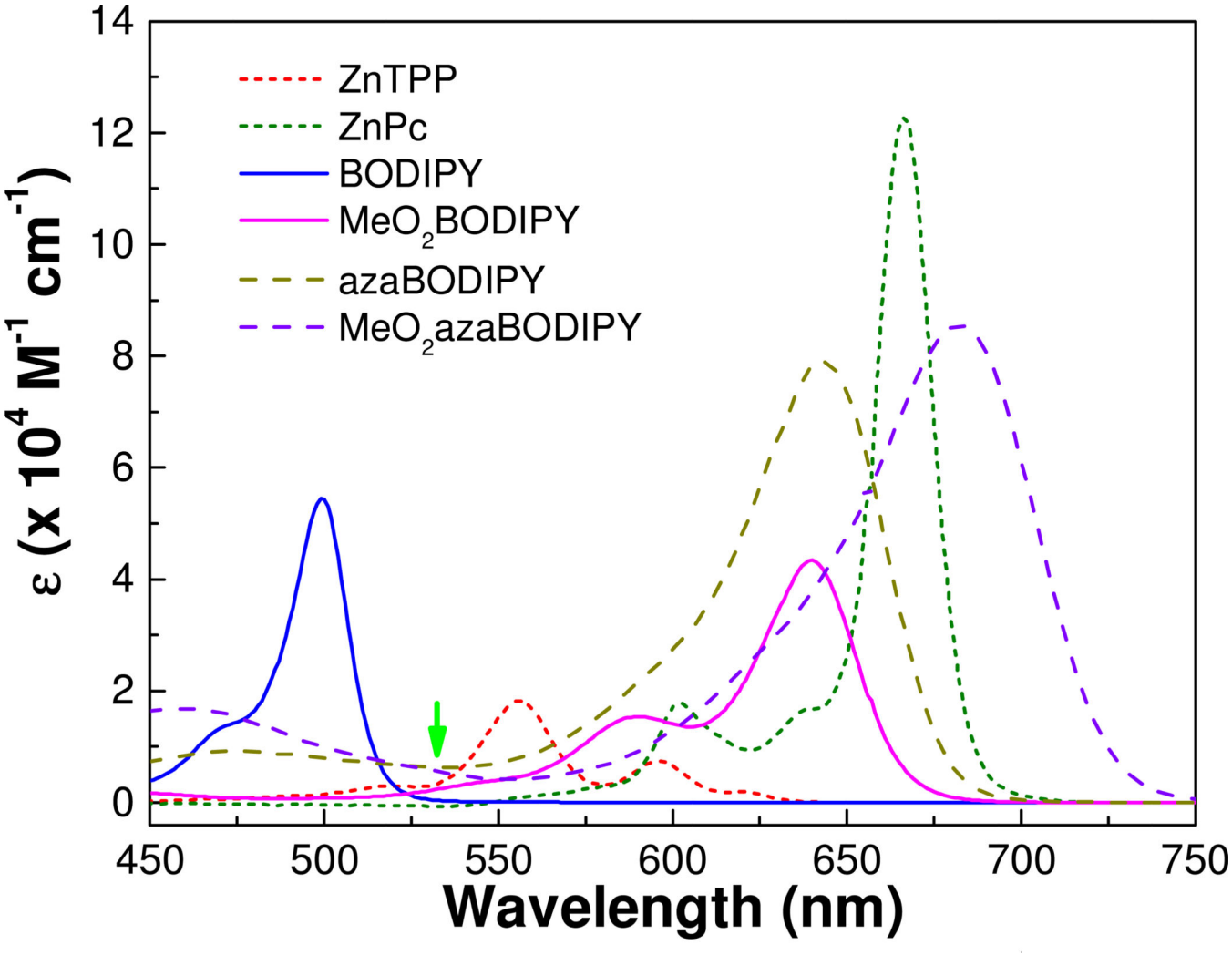

Figure 2.
Electronic absorption spectra of the porphyrin, phtalocyanine, BODIPY and aza-BODIPY series recorded in tetrahydrofuran (arrow indicates laser excitation wavelength).

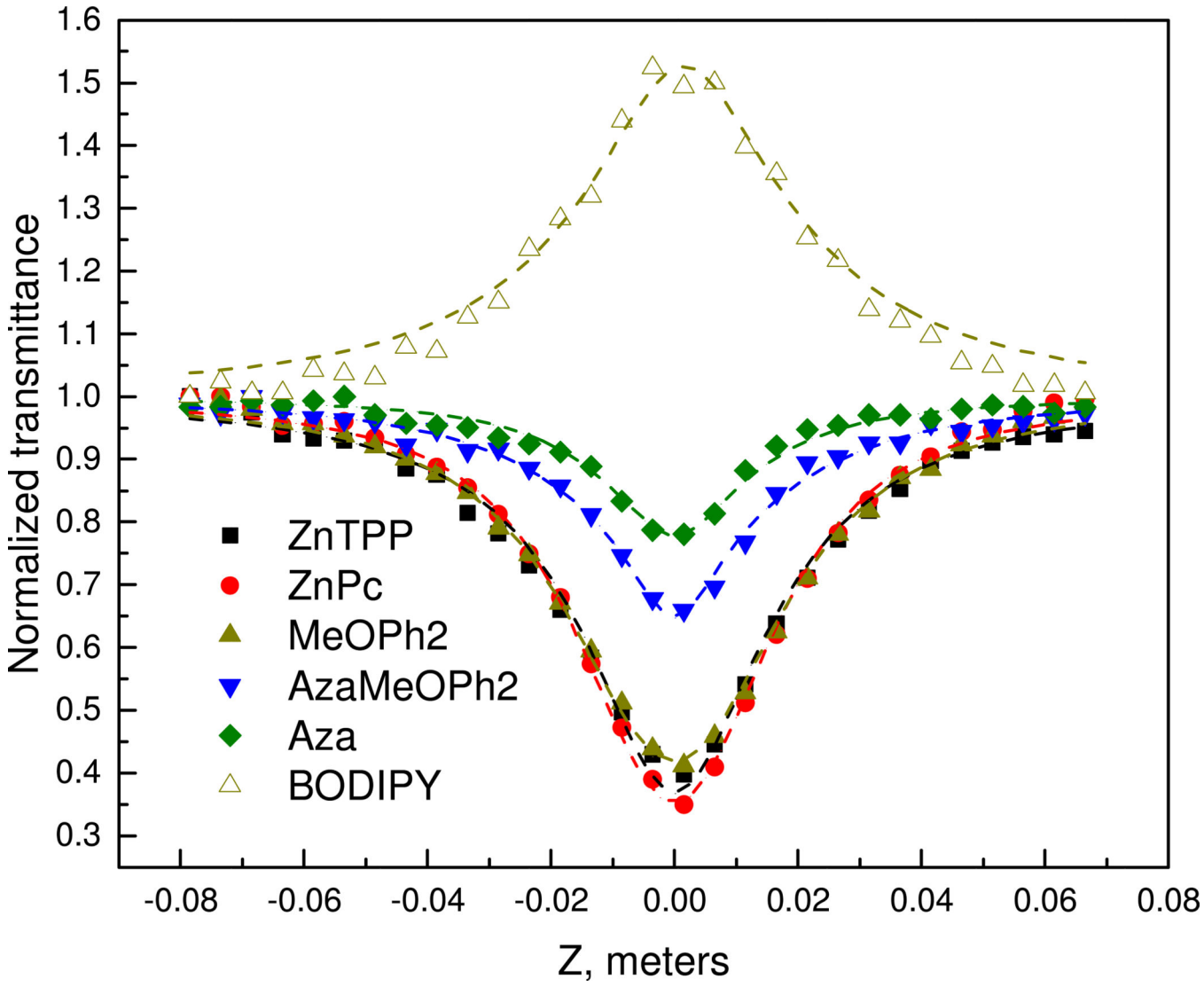

Figure 3.
Open aperture Z-scan curves for the series of pyrrole dyes. The lines are theoretical fit to experimental data.

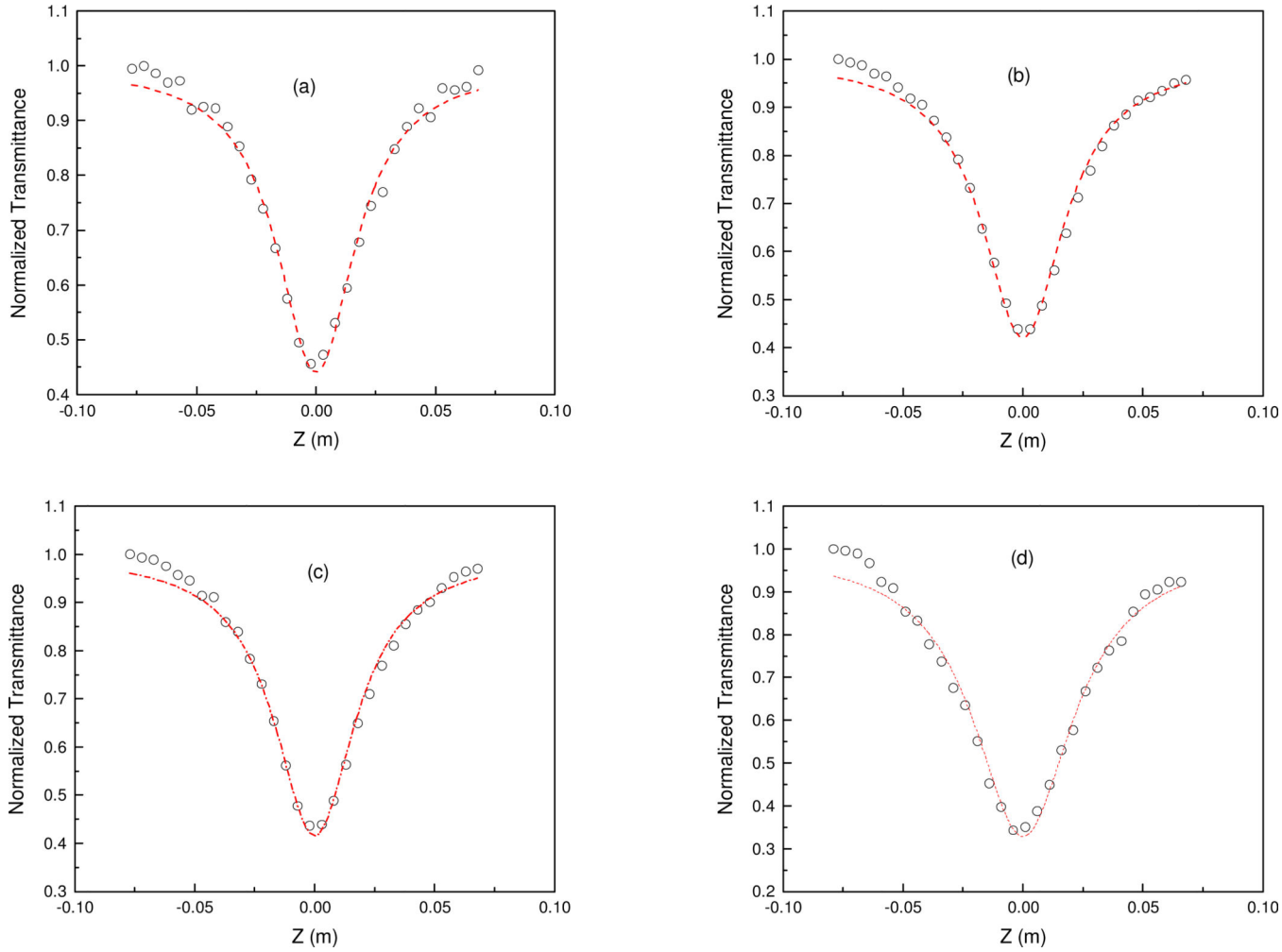

Figure 4.

Open aperture Z-scan curves for $MeO_2BODIPY$ at various on-axis intensities: (a) 1.19 $\times 10^{12}$ W/m^2; (b) 2.1 $\times$ 10^{12} W/m^2; (c) 2.76 $\times$ 10^{12} W/m^2; and (d) 3.31 $\times$ 10^{12} W/m^2. The lines are theoretical fit to experimental data.

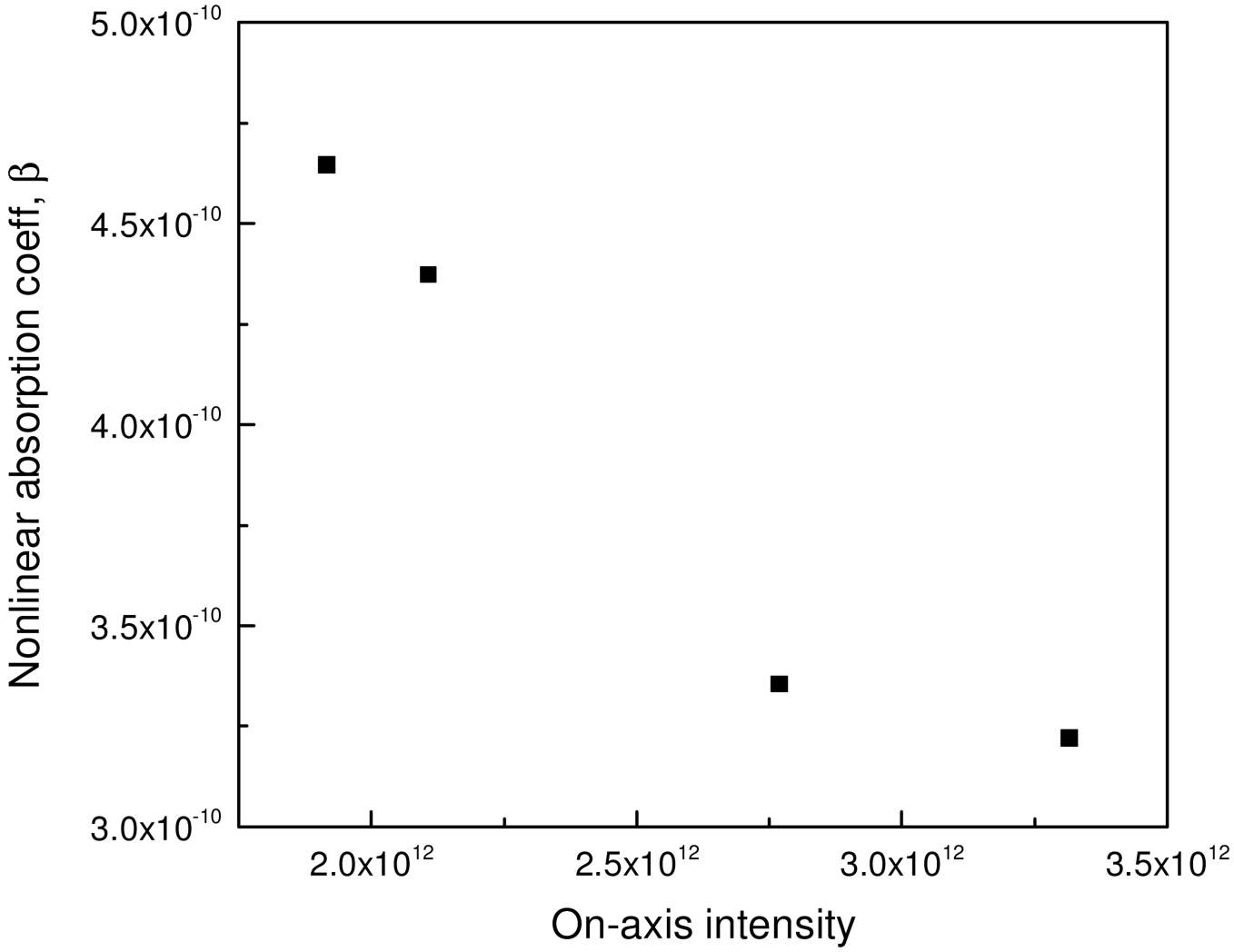

Figure 5.
Variation of the nonlinear absorption coefficient β with on-axis peak intensity (I_0). Decrease of β with I_0 suggests ESA.

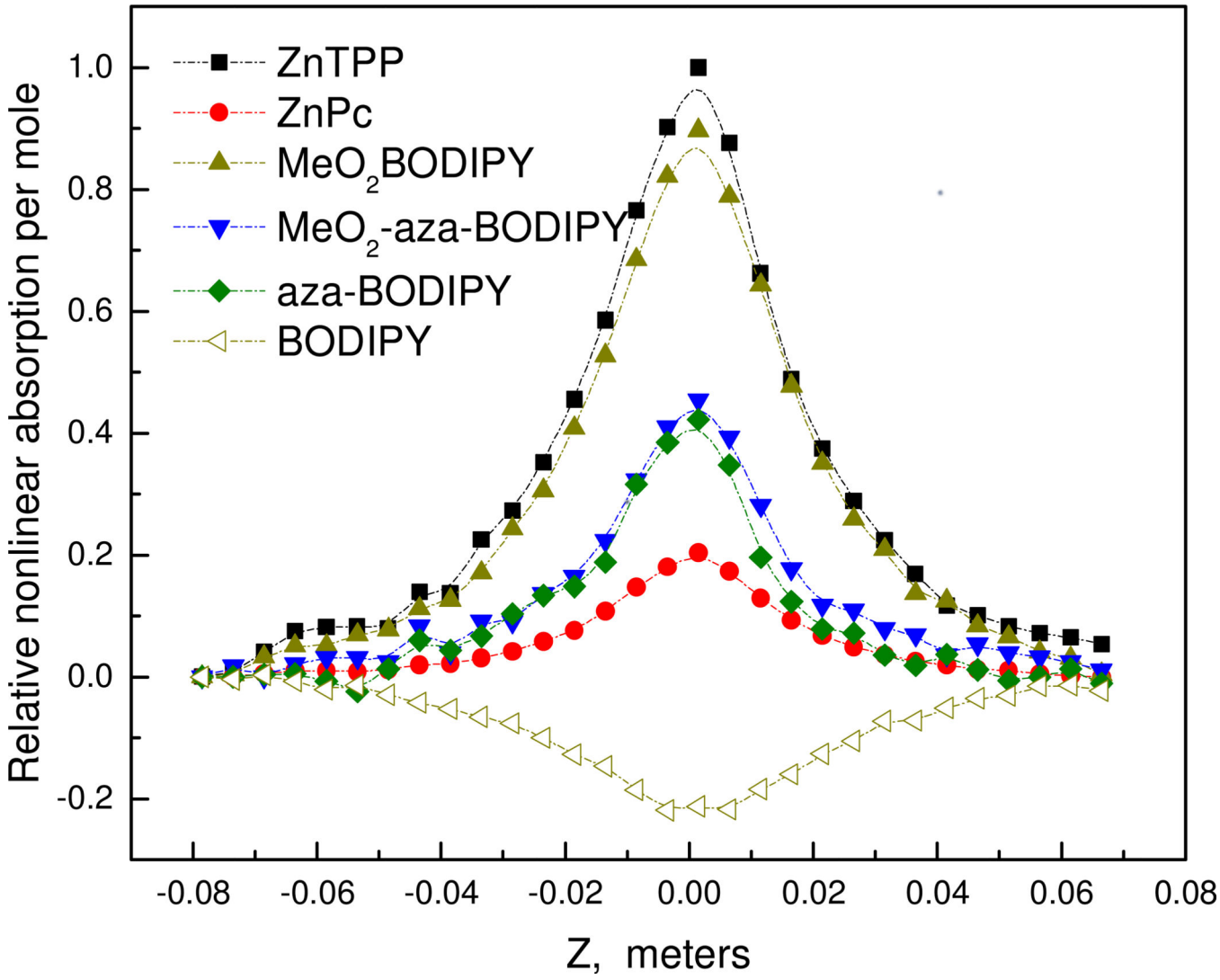

Figure 6.

Z-scan curves for the series of pyrrole dyes plotted as relative nonlinear absorption per mol with concentration of dyes taken into consideration. This plot effectively shows which dyes show the most efficient excited state absorption.

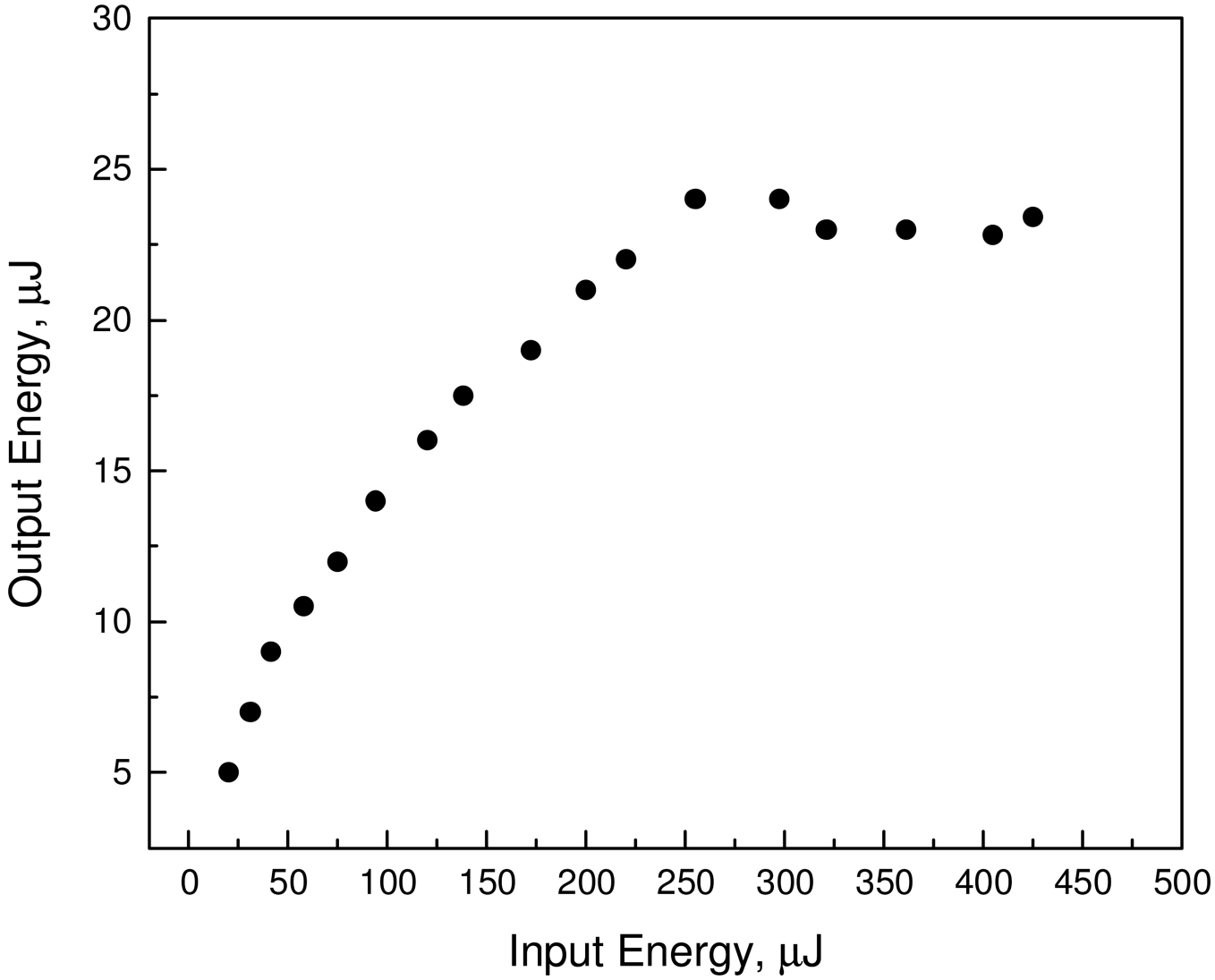

Figure 7.
Optical power limiting behavior for MeO_2BODIPY.

Table 1

Summary of nonlinear absorption coefficients for all dyes recorded using the Z-scan technique.

	Concentration (mol L^{-1})	**On axis intensity, I_0 W/m^2**	**ESA coefficient α_2 m/W**
ZnPc	1.71×10^{-05}	1.54×10^{12}	2.88×10^{-10}
ZnTPP	9.54×10^{-05}	1.93×10^{12}	4.97×10^{-10}
MeO_2BODIPY	1.83×10^{-05}	1.19×10^{12}	4.64×10^{-10}
		2.1×10^{12}	4.37×10^{-10}
		2.76×10^{12}	3.35×10^{-10}
		3.31×10^{12}	3.22×10^{-10}
MeO_2-aza-BODIPY	1.65×10^{-05}	2.14×10^{12}	3.14×10^{-10}
aza-BODIPY	1.03×10^{-05}	2.78×10^{12}	1.71×10^{-10}
BODIPY	3.72×10^{-05}	Saturation Intensity = 1.25×10^{11} W/m^2	