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Media polarity and concentration roles on the third order nonlinear behaviors of thiazine dyes

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ABSTRACT

Nonlinear optical materials play important roles in optics and photonics. In order to improve the performance of these materials, in this paper, we tried to find effective methods for controlling the nonlinear responses of thiazine dyes. Our experimental results indicate that molecular linear properties, media polarity, concentration and excitation beam properties with different contributions play significant roles on the saturable and reverse saturable absorption characteristics of thiazine dyes. In real, competition between these effective parameters leads to appearance of various third order nonlinear responses. Although by excitation wavelengths near the absorption peaks and at high powers, dye molecules tend to indicate reverse saturable absorption characteristics in polar protic solvents by increasing the concentration, saturable absorption characteristics were observed in polar aprotic solvents. Furthermore, the samples displayed the same behaviors in different solvent media at low powers and for excitation wavelengths far from absorption peaks.

Therefore, by controlling the nonlinear responses of thiazine dyes, these materials can indicate both saturable and reverse saturable absorption characteristics that increase their applications in optics and photonics devices.

1. Introduction

Nowadays, materials with nonlinear optical characteristics are important for applications in various field of science such as optical data storage [1,2], optical limiting [3,4], two photon microscopy [5] and upconversion lasers [6,7]. Among various optical materials, organic materials with good photo-thermal stability, dissolvability and easy preparation characteristics are good candidate for studying nonlinearity.

Thiazine dyes with various applications as antioxidant, photosensibilizator, effective staining agent, biological active groups in the treatment of various diseases, and electrochemical and optical sensors [8–10] have gained intense attention during the last years. Moreover, the investigation of third order nonlinear responses of these groups of materials will be useful for finding their other applications. Among various methods [11–18], Z-scan [15–19] technique based on the spatial distortion of a transmitted laser beam is a simple and sensitive single beam technique for measuring the sign and magnitude of both real and imaginary parts of third order nonlinear susceptibility.

Intermolecular interactions as an important factor can have significant effect on the optical properties of organic materials. In this case, molecular surrounding environment and its concentration can play important roles. Although the optical properties of isolated molecules are usually investigated in gas phase, the most of the experimental works are performed in solution state. Under these conditions, various physical, chemical and biological characteristics of solute molecules are affected dramatically by solvent molecules.

In general, solvent dependent phenomena originate from either non-specific (dielectric enrichment) or specific (hydrogen bonding and intermolecular charge transfer) solute-solvent interactions. These solvent effects can be investigated by means of solvent polarity scales and solvatochromic parameters. There are many different chemical and physical processes that individual solvent polarity parameters cannot describe completely the nature and degree of solute-solvent interactions, so multi-parameter solvent polarity scales known as Kamlet-Abboud-Taft [20] polarity parameters were used. Moreover, in a real bulk system, different solvents maybe lead to the solute molecules forming quite different configurations. In this case, solute-solute intermolecular interactions play important roles [21,22].

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In spite of various studies on the linear behaviors of thiazine dyes [8–10,22], unfortunately, it has not been reported a comprehensive study on the possible various methods for controlling their third order nonlinear behaviors. For precise investigation, in this paper, the effect of media polarity, concentration and excitation beam properties on the third order nonlinear absorption coefficients of thiazine dyes were studied. In this case, the third order nonlinear optical responses were studied by Z-scan technique with continuous wave laser irradiations at the wavelength of 632.8, 655 and 532 nm under influence of various excitation powers. The obtained experimental results will help us to control the third order nonlinear properties of thiazine dyes with different methods that can improve their applications in optics and photonics.

2. Experimental

2.1. Materials

Azure A and Methylene blue (Table 1) were purchased from Merck and used without further purification. All the solvents in the study were also of the highest available purity from Merck and the spectroscopic solvent polarity parameters of them were listed in Table 2 [20,23].

Table 1
The chemical structure and molecular weight of the samples under study.

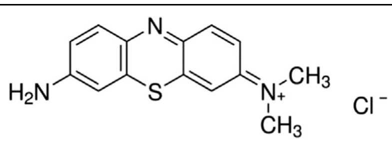
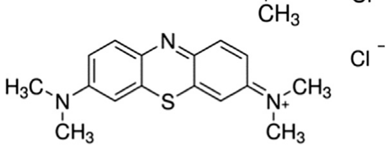
Molecular structure	Molecular weight (g/mol)	Molecular name
	291.80	Azure A
	319.85	Methylene blue

Table 2
Spectroscopic polarity parameters and physical properties of employed solvents.

Solvent	ε_r	n	α	β	π^*
DMSO	46.68	1.479	0.00	0.76	1.00
DMF	38.00	1.43	0.00	0.69	0.88
Methanol	32.7	1.329	0.98	0.66	0.6
Ethanol	24.5	1.361	0.86	0.75	0.54
2-Propanol	19.92	1.377	0.76	0.84	0.48
1-Butanol	17.5	1.399	0.84	0.84	0.47

2.2. Experimental set up

2.2.1. Z-scan technique

In order to measure the third order nonlinear responses of the samples, first Azure A and Methylene blue molecules with the concentration of 10^{-6}, 10^{-5} and 10^{-4} M were dissolved in various solvents (Table 2). Then, the prepared solutions were kept in a quartz cell with the thickness of 1 mm and attached to a translation stage for performing Z-Scan experiment.

As shown in Fig. 1, continuous wave lasers at the wavelengths of 632.8, 655 and 532 nm near and far from the maximum absorption of dye solutions (Fig. 2) were focused on the sample solutions by means of a convex lens (f = 10 cm). In the focal point the beam waist diameter of excitation beams at 632.8, 655 and 532 nm were about 51, 36 and 44 μm, respectively. Sample solutions with different polarity were translated across the focal point along the laser beam propagation and in order to investigate the concentration effect on the nonlinear responses of dye solutions, the measurements were repeated for samples with different concentration. Furthermore, the same experiments were performed for investigation of wavelength dependent and excitation power effects on the third order nonlinear responses of thiazine dyes.

Finally, transmitted light changes were collected by a lens and measured using photo-detector. By using of the transmittance curves and the optical parameters, it is possible to determine the nonlinear absorption coefficients.

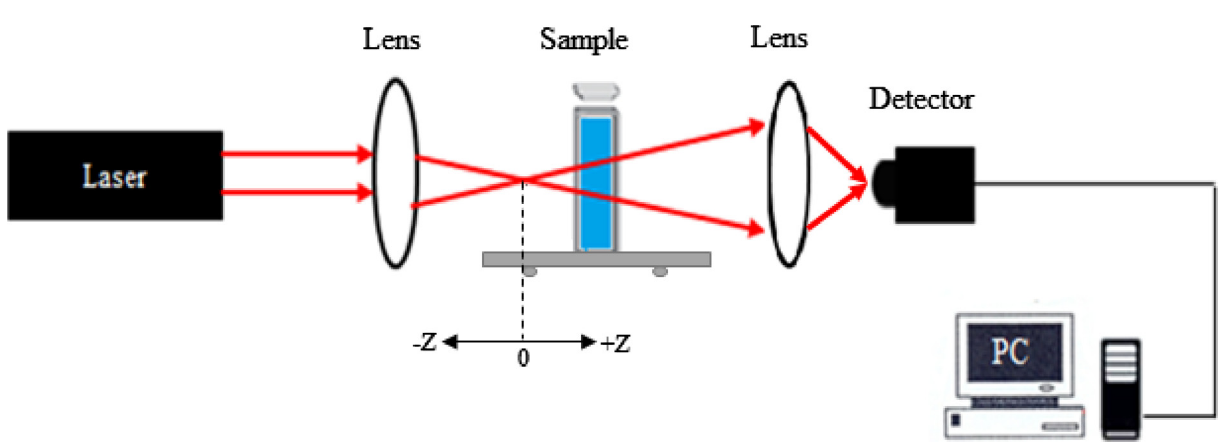


Fig. 1. Open aperture Z-scan setup.

3. Result and discussion

3.1. Calculation of third order nonlinear coefficients

When a strong laser beam passes through a nonlinear material, the light-matter interactions can change the character of incident