



Photophysical and nonlinear optical properties of an azobenzene substituted zinc phthalocyanine



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ARTICLE INFO

Article history:

Received 4 September 2012

Accepted 15 January 2014

Keywords:

Photophysical property

Third-order optical nonlinearity

Zinc phthalocyanine

ABSTRACT

Photophysical property and third-order optical nonlinearity of an azobenzene substituted zinc phthalocyanine (azo-ZnPc) in chloroform solution were studied by UV–Vis spectra method and a picosecond Z-scan technique at 532 nm with pulse duration of 25 ps, respectively. It was found that the azo-ZnPc shows large positive nonlinear refraction and positive nonlinear absorption, exhibiting the defocusing effect and reverse saturable absorption, respectively. The molecular second hyperpolarizability of the azo-ZnPc dyad was measured to be 3.9×10^{-30} esu. All the results suggest that the studied azo-ZnPc dyad may have potential applications in the field of nonlinear optics.

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1. Introduction

Third-order nonlinear optical (NLO) materials have been applied widely in many important technologies including optical recording, optical limiting for sensor protection, photonic switching and optical computing [1–4]. The research of third-order optical nonlinearities of materials has been of great interest during the past decades [5–13]. Among organics, phthalocyanines and related compound have emerged as an important class of materials for third-order nonlinear optics because of their unique highly conjugated two-dimensional π -electron system which gives rise to a large nonlinear optical response. The electronic structure of these molecules can be tailored by either metal substitution at the central binding site or by altering the peripheral and axial functionalities, thus affording great versatility in controlling their photophysical properties. Furthermore, they exhibit exceptional thermal and chemical stability, which makes it feasible to obtain high-quality thin films by successive sublimation. During the last two decades, the third-order nonlinear optical susceptibilities $\chi^{(3)}$

and the nonlinear dynamical properties of phthalocyanines have been intensively investigated both in solutions [14–16] and in thin films [17–19], and these properties were found to be strongly dependent on the stacking arrangement of molecules in the media.

In general, the absorption spectra of monomeric phthalocyanines are dominated by two intense bands, a Soret band in the near ultraviolet region (at around 350 nm) and a Q band in the visible region (at around 670 nm), with a molar extinction coefficient in the range of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ [20]. When electron-donating alkoxy/aryloxy groups are introduced at the periphery closest to the phthalocyanine ring, a large bathochromic shift occurs in the Q band. These large red-shifted phthalocyanines are very soluble in common organic solvents and can be easily be prepared thickness-controlled thin films for practical applications to photonic devices. Herein, in the present study, we report the photophysical and third-order nonlinear optical properties of an azobenzene substituted zinc phthalocyanine measured by picosecond Z-scan technique at 532 nm.

2. Experimental

The azobenzene substituted zinc phthalocyanine (azo-ZnPc) was synthesized as described procedure [21]. The structural formulae of squarylium dyes investigated here are shown in Fig. 1. The azo-ZnPc was dissolved in chloroform at a concentration of $2.8 \times 10^{-5} \text{ M}$ for experiments. The absorption spectrum of each

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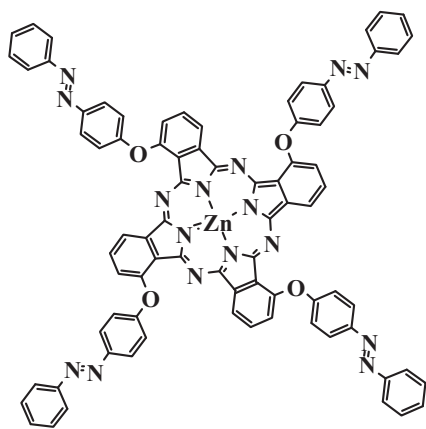


Fig. 1. Chemical structure of azo-ZnPc.

sample solution was recorded at room temperature on a UV–Vis spectrophotometer (UV759).

The third-order optical nonlinearity of the azo-ZnPc was determined by a standard Z-scan technique [22]. This technique, known for its simplicity and sensitivity, relies on the distortions induced in the spatial and temporal profile of the input beam on passing through the sample. It is used widely in material characterization because it provides not only the magnitudes but also the sign of real and imaginary parts of third-order nonlinear susceptibility ($\chi^{(3)}$). The experimental set-up is shown in Fig. 2. The sample is moved along the propagation path (z) of a focused Gaussian beam whilst its transmittance is measured through a finite aperture in the far field, and the sign and magnitude of the nonlinear refractive index n_2 are deduced from the resulting transmittance curve. If the value of n_2 is positive, then the material has a tendency to shrink a laser pulse and is termed “self-focusing”, whilst a negative n_2 characterized “self-defocusing” behaviour. Similar scans using an open aperture yield the nonlinear absorption. From the nonlinear refractive index and nonlinear absorption one can determine the sign and the magnitude of both the real and imaginary parts of $\chi^{(3)}$.

In the present study, a Nd:YAG laser (Model PL2143B, EKSPILA) with a 25 ps pulse width at 532 nm wavelength was used as the light source. The experiment was performed using a Gaussian beam. The laser beam was focused onto the sample by a 150 mm focal length lens, leading to a measured beam waist of 25 μm and the pulse energy of 3.0 μJ at the focus. The on-axis transmitted beam energy, the reference beam energy, and the ratios of them were measured using an energy ratiometer (Rm 6600, Laser Probe Corp.) simultaneously. In order to reduce the possible thermal accumulative effect, the laser repetition rate was set to 1 Hz. For open aperture, all the transmitted power was collected and focused onto detector using another lens (120 mm). The Z-scan measurements were performed with samples placed in a standard 1-mm quartz cuvette. The solution was placed in a high-precision mobile platform moving along the incident light direction (Z). The Z-scan curve, the transmittance as a function of the sample position, could then be obtained.

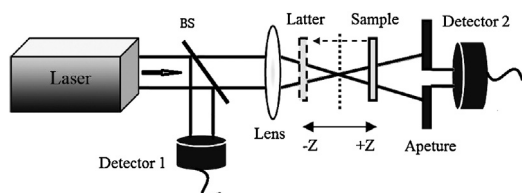


Fig. 2. Setup of Z-scan technique.

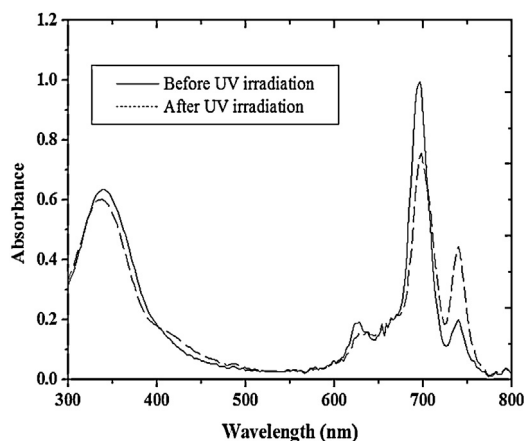


Fig. 3. Absorption spectra of azo-ZnPc before and after UV light irradiation in chloroform.

3. Results and discussion

The UV–Vis absorption spectra of azo-ZnPc before and after UV light irradiation in chloroform are illustrated in Fig. 3. Typical phthalocyanines' UV–Vis spectra were featured by two characterized absorption band, namely B-band and Q-band that could be readily interpreted by using Gouterman's highly simplified four orbital models. For azo-ZnPc, the B-band was overlapped with the $\pi-\pi^*$ transition absorption band of azobenzene units at 300–400 nm. However, in addition to normal Q-band (698 nm), an unusual red-shifted sharp band at 740 nm was observed. Upon the irradiation of 365 UV light, azobenzene units underwent photoisomerization from *trans*-state to *cis*-state. The decrease blue shifted absorption at 340 nm and the increase absorption at 400–500 nm, which is a persuasive evidence of such photoisomerization. Just due to such photoreaction, the absorption band at 698 nm sharply decreased and slight red-shifted to 710 nm.

Fig. 4 shows the normalized transmission of the studied azo-ZnPc without aperture at 532 nm (open aperture, OA) as a function of distance along the lens axis. Each point is corresponding to the average of 5 pulses, and the experimental error was estimated to be within $\pm 5\%$. The filled triangles and open circles are measured data and the solid line is the theoretical fit. The OA curves of azo-ZnPc exhibit the normalized valley, indicating the presence of reverse saturable absorption with a positive coefficient β . The nonlinear absorption coefficient β (m/W) can be obtained from a best fitting

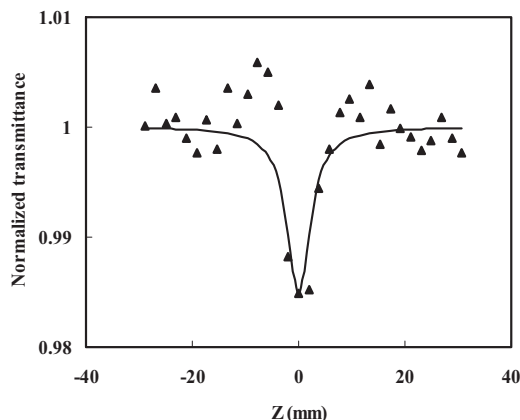


Fig. 4. Normalized transmission of the studied azo-ZnPc without aperture at 532 nm (open aperture, OA) as a function of distance along the lens axis.

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