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Chemical Physics Letters 419 (2006) 417–420
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Nonlinear absorption spectrum of ytterbium bis-phthalocyanine solution measured by white-light continuum Z-scan technique

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Received 27 June 2005; in final form 30 November 2005
Available online 27 December 2005

Abstract

In this work we have measured the nonlinear absorption spectrum of ytterbium bis-phthalocyanine ($YbPc_2$) in chloroform solution employing the Z-scan technique with white-light continuum (WLC) pulses. Two distinct excited state absorption behaviors were observed: a saturable absorption (SA) at the Q-band region and a reverse saturable absorption (RSA) around 530 nm. A three-energy-level diagram was used to explain the experimental results, leading to the excited state absorption cross-section determination from 500 up to 675 nm.

1. Introduction

The nonlinear absorption spectrum determination has crucial importance on materials characterization for both, fundamental and application's point of view. It allows, for instance, the determination of devices optimal operational wavelength, which must combine high nonlinear response and low propagation losses. Moreover, the nonlinear optical properties optimization can only be accomplished if the nonlinear mechanism was understood over a wide spectral range. In this way, efforts aiming the nonlinear absorption spectrum determination combined with the design and synthesis of organic molecules with interesting nonlinear properties have been growing fast in the last years.

Among several new organic molecules, porphyrins and phthalocyanine have deserved special attention, not only because of their potential usefulness in photonic devices, such as passive optical limiters [1,2], but also due to their applications as drugs commonly used in photodynamic therapy [3–5] for cancer treatment and bacterial reduction. Owing to these applications, it is of paramount importance to characterize the population dynamics and spectroscopic parameters of excited states of phthalocyanines [6]. Usually, the degenerate nonlinear spectrum of materials have been determined through the Z-scan technique [7,8], where optical parametric amplifiers (OPA) are used as the excitation source for discrete wavelengths measurements. However, in order to obtain nonlinear spectra with good resolution with this approach, small wavelength increments are required, resulting in a time-consuming procedure. To overcome this disadvantage, new techniques using white-light continuum (WLC) pulses have been proposed [9,10]. In this direction, recently we have introduced a fast WLC Z-scan technique that allows measuring, simultaneously, all the nonlinear absorption in the WLC spectral range in a single scan [11]. Both, resonant and nonresonant nonlinear spectra can be measured by this technique. A similar technique was proposed almost at the same time and independently by Balu et al. [12].

Bis-phthalocyanines are built of two phthalocyanine rings coordinated to a central metal ion. In general, they exhibit attractive optical properties that can be tuned by varying the central metal and/or peripheral side-groups. Macrocyclic compounds, such as phthalocyanines, presents interesting singlet and triplet states which provides strong

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doi:10.1016/j.cplett.2005.12.001

resonant nonlinear effects with fast lifetimes [6,13–15]. In this way, both, saturable absorption (SA) and reverse saturable absorption (RSA) can be observed depending on the excitation wavelength. Owing to these effects, phthalocyanines are promising candidates for the manufacture of optical devices such as, for instance, optical-limiters [16] used to protect eyes and sensor from the incidence of intense laser pulses. In this context, the present work reports the resonant nonlinear absorption spectrum of ytterbium bis-phthalocyanine ($YbPc_2$) from 500 up to 675 nm, determine through the recently proposed WLC Z-scan method [11]. Our results indicate the presence of both a SA at the Q-band region and a RSA around 530 nm. The excited state spectroscopic parameters determination, obtained by modeling a three-energy-level diagram to the experimental results, is of paramount importance in order to understand and propose new applications for this class of organic compounds.

2. Experimental section

The $YbPc_2$ used in this experiment was diluted in chloroform to a concentration of $N_0 = 2{,}2 \times 10^{16}$ molecules/cm^3 in order to perform nonlinear absorption experiments. The linear and nonlinear measurements were carried out in a 2 mm thick quartz cuvette. The absorption spectrum at the UV–Vis region was obtained with a Carry-17 spectrophotometer.

In order to obtain the nonlinear spectrum of $YbPc_2$ we have used the recently introduced WLC Z-scan technique [11]. The WLC used in our experiments was obtained by focusing a 150 fs pulses at 775 nm from a Ti:sapphire chirped pulse amplified system (CPA-2001, from Clark-MXR Inc.) in distilled water. Using about 0.3 mJ laser pulses we were able to generate about 8 μJ of WLC in the visible range in a cuvette with 3 cm path length. A low pass filter was used to remove the strong pump pulse and the infrared fraction of the WLC spectrum. Finally, the WLC beam is re-collimated via an $f = 10$ cm lens and thus employed in the Z-scan technique. The WLC spectrum used in our experiment is showed in Fig. 1. As in the traditional Z-scan method [7,8], the WLC beam is focused and the nonlinear sample is scanned along the z-direction of the beam. After passing through the sample, the WLC beam is totally focused into a spectrometer, as requires the open aperture configuration. By scanning the sample along z-direction each spectral component generates a Z-scan signature accordingly with its nonlinear property at that wavelength, which is normalized to the transmittance far from the focal plane. The spectrometer used in our experiment was an USB 2000 from Ocean Optics. Its resolution of ~5 nm is enough to fulfill the purpose of our experiment. The WLC pulses present approximately 300 nm of band in visible region (450–750 nm) with approximately 4 ps of positive chirp, which is mainly acquired during the generation and propagation in the water cell and optical elements before the sample.

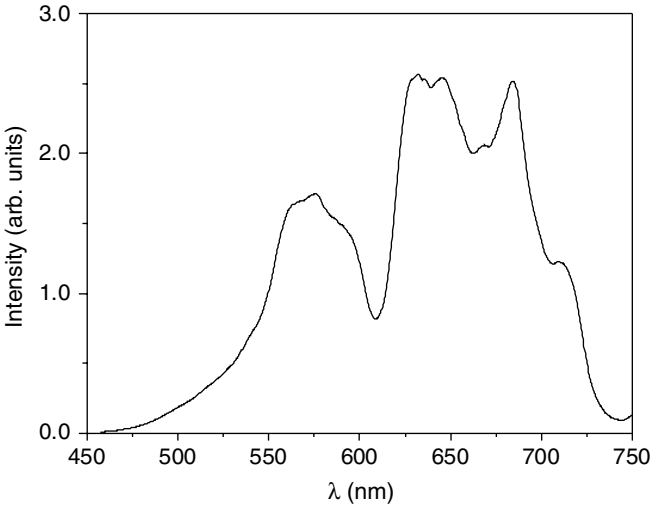

Fig. 1. Typical WLC spectrum generated in the water cell.

3. Results and discussion

In Fig. 2 (solid line) it is shown the linear absorption spectrum of $YbPc_2$ in chloroform, which is similar to those reported in the literature [16–18] and agrees with the energy diagram obtained from the valence-effective Hamiltonian (VEH) calculation [19]. The structure around 670 nm corresponds to the Q-band and is attributed to the transitions from the π (a_{2u}) to the upper π* (e_g^*) orbitals, while the B-band that appears around 360 nm is attributed to the transitions between π (b_{2u}) and π* (e_g^*) orbitals [16,18]. As mentioned in 2, the WLC Z-scan technique is able to simultaneously obtain Z-scan signatures for each wavelength in the WLC (4 ps chirp). From this set of Z-scan curves one are able to determine the normalized transmittance change at the focal plane (ΔT) as a function of the wavelength. An increase in the transmittance at the focus was assigned with positive ΔT values, while negative ΔT indicates a decrease in the transmittance. The line with circles in Fig. 2 shows the nonlinear spectrum (ΔT spectrum)

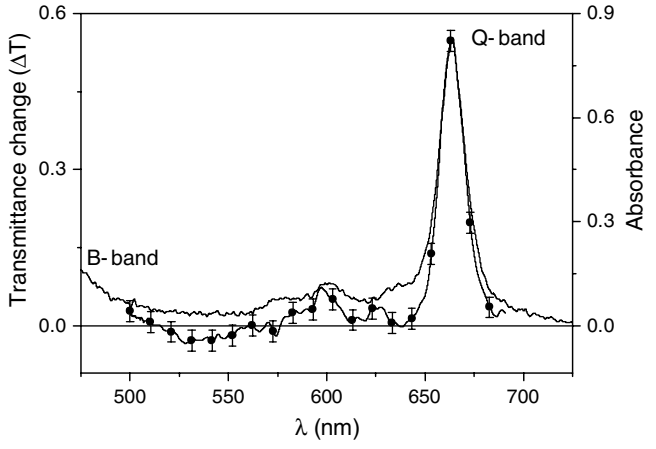

Fig. 2. The linear absorption of $YbPc_2$ solution (solid line) and the normalized transmittance change (ΔT) obtained with WLC Z-scan (line with circles).