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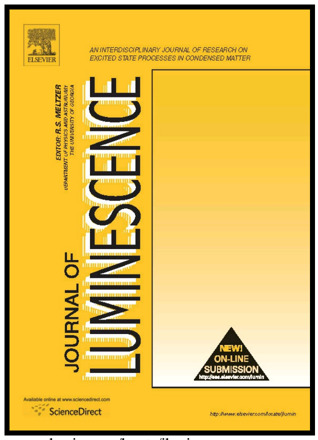

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Third-order optical measurements of porphyrin compounds using Dark-field and D4σ-Z scan imaging techniques

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ABSTRACT

The newly introduced imaging techniques D4σ and Dark-field Z-scan (DFZ-scan) are very much appropriate to measure the third-order nonlinear (NL) refractive index in the presence of high nonlinear absorption (NLA) in condensed matter. To demonstrate the large potential of both techniques we prepared and characterized porphyrins solutions in chlorobenzene and report here on the NL optical properties of 5,10,15,20-Tetraphenyl-21H,23H-porphyrin (TPP)**,** 5,10,15,20-Tetraphenyl-21H,23H-zinc porphyrin (ZnTPP), 5,10,15,20-tetraphenyl-21H,23H-porphyrin cobalt(II) (CoTPP) and 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphyrin cobalt(II) (MCoTPP). The measurements were performed with a laser delivering low repetition rate linearly polarized single picosecond pulses at 1064 nm and 532 nm.

1. Introduction

Because of the large discrepancy found in the literature related to third-order optical nonlinear (NL) coefficients an unbiased comparison of different materials sometimes is very difficult. Hence, development of new NL techniques is still relevant and subject to active research [1, 2, 3] to find simple and sensitive ways to measure the optically induced NL refraction (NLR) despite of the presence of relatively high NL absorption (NLA). Therefore, the newly introduced imaging techniques: DFZ-scan [4] and D4σ-Zscan [5, 6] are applied here to demonstrate their ability to measure the third-order NL refractive index, n_2, in presence of large NLA coefficient, β, as it is often the case with organic materials. The experiments were performed by determining the transmitted laser beam waist relative variation (BWRV) using D4σ intensity profile measurements combined with the Z-scan method [7] in a 4f-system for different porphyrins (Pphs) dissolved in chlorobenzene. Using DFZ-scan we determined the sign and the magnitude of n_2 and β even at relatively high Pphs concentration. The experiments allowed to test all cases of positive and negative NLR and NLA coefficients. Although the synthesis and experimental NL optical characteristics of Pphs have been reported by several groups, the interest in these materials has been renewed due to their useful optical limiting properties (see for example [8, 9, 10, 11, 12] and references therein) here we provide accurate data for some Pphs thanks to the application of D4σ and DFZ-scan.

The unique electronic, optical and biochemical properties [13] as well as the high stability and architectural flexibility of Pph compounds provide a very good basis to finely tune their optical response. Moreover, the ability of Pph molecules to capture light allows their use in sensors based on optical waveguides, frequency converters, and devices for transmission and storage of information [14]. All Pphs have π-conjugated structures and, in general, they exhibit strong NLA and large NLR. In particular, due to the large NL response, the metalloporphyrins have been proposed for optical limiting and all-optical switching [15] in different optical regimes because, in addition to their highly conjugated structure, both metal-to-ligand and ligand-to-metal charge transfer, lead to intramolecular electron delocalization that enhances the molecule hyperpolarizability. The ability to present large NL response in fast and slow timescales (from the ns to the fs regimes) makes the Pphs particularly attractive for photonics. Therefore, characterizing their NL optical properties and identifying the variations in the NL response due to the change of the metal center is of large interest in order to optimize the materials for optical limiting and/or optical switching applications.

2. Experimental section

Commercially available (Sigma Aldrich Co.) Pphs powders were dissolved in chlorobenzene with concentrations varying from 10^{-4} to 10^{-3} M. The NL optical measurements were carried out using linearly polarized 17 ps pulses at 1064 nm and its second harmonic at 532 nm (12 ps), respectively, at 10 Hz repetition rate. The liquid suspensions were contained in 1 mm thick quartz cells.

As mentioned before two techniques were used: DFZ-scan and D4σ-Z-scan. With the D4σ-Z-scan method, the images of a circular aperture at the entry of the system (object plane) are recorded by a single-shot CCD camera located in the image plane of a 4f setup as a function of the sample position that is moved around the focal plane. The open-aperture Z-scan normalized transmittance was numerically processed from the acquired images allowing for simultaneous measurements of NLR and NLA coefficients. However, unlike the traditional closed-aperture Z-scan method, in the D4σ technique the

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