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Reverse saturation absorption spectra and optical limiting properties of chlorinated tetrasubstituted phthalocyanines containing different metals

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ABSTRACT

A highly non-aggregated series of peripherally tetra(2,6-diisopropylphenoxy) substituted phthalocyanines (Pcs) containing different metals (Al, Ga, In and Zn) were prepared and their nonlinear optical properties (NLO), including the optical limiting behavior were investigated. This study explores the effect of the implanted metals along with the peripheral chlorine atoms on the NLO of the prepared complexes, thereby improving their optical limiting performance. The best wavelength at which the Pc complex exhibits the strongest nonlinear effect was determined over the low absorption window region (420–590 nm) comprised between the Q and B bands using a nanosecond pulsed laser with the aid of a *Z*-scan technique. The excited state absorption cross sections (σ_{eff}) have been found to be wavelength dependent with common double peaks at 505 nm and around 485 nm and the highest value was calculated for **Pc1–In** (1.1×10^{-16} cm^2). The figure of merit spectra show different spectral structure when compared to the excited state absorption spectra and the largest figure of merit value was found to be around 107 for **Pc1–In** derivative. In full agreement with reverse saturation results, the optical limiting measurements, carried out at 485 nm and 532 nm for each derivative, show very low optical limiting thresholds at the former wavelength. In the continuous wave excitation regime, the *Z*-scan measurements, which were carried out at 632.8 and 532 nm, showed strong refractive and absorptive nonlinear effects.

1. Introduction

Since its invention in the early 1960s, laser has known a very dramatic improvement in its compactness, efficiency, and operation at a large variety of wavelengths. These improvements have widened its applications to many technological fields. The increased presence of lasers in our everyday lives represents significant hazards to eyesight therefore the protection of human eyes and optical sensors has become a crucial issue. In the military domain for example, aircraft pilots need to be protected against laser devices that operate at a large number of differing wavelengths and cover a wide range of response times. Consequently, optical power limiters (OPLs) have to be designed to block lasers with large optical spectra and response times ranging from picoseconds to microseconds, while continuous wave (CW) sources have to be blocked in civilian applications [1]. An ideal OPL has to be transparent under ambient light conditions; however, it rapidly undergoes large absorption under intense laser light over a broad spectrum, in particular, the 400–800 nm electromagnetic spectral range, which includes many laser sources. In addition, the famous and very widely utilized 1.06 μm wavelength of the YAG:Nd laser has to be separately blocked with an appropriate interferential filter.

Nonlinear optical effects, such as reverse saturation absorption (RSA) and two photon absorption (TPA), are the main mechanisms for optical limiting (OL) [2]. Organic materials, with their large optical parameters and flexibility tailored according to needs are one of the best candidates for OPL applications [3,4]. Phthalocyanine (Pc) and their derivatives have shown very large nonlinear parameters and have been the focus of many research investigations.

Due to their two-dimensional, highly conjugated delocalized π-electron system, phthalocyanines and their analoges display interestingly outstanding optical and electronic properties which render them able to be exploited in many technological applications [5–10]. In addition, the excellent thermal and chemical stability [11], along with the large architectural flexibility in the structure of the phthalocyanines give such material continuous attracting attention toward the modulation of Pc structure (decorating the peripheral position of the Pc ring with different substituent and/or inserting different transition metals) for amplification of the

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