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# Optical limiting properties of zinc phthalocyanines in solution and solid PMMA composite films

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ABSTRACT

The nonlinear absorption and optical limiting (OL) performance of tetra- and octasubstituted zinc phthalocyanine complexes were described in solution and in the solid state using the open-aperture Z-scan technique. The measurements were performed using collimated 4 ns pulses generated from a frequency-doubled Nd:YAG laser at 532 nm wavelength. The polymeric films exhibit a much larger effective nonlinear absorption coefficient in comparison with solution. However, the parameters of the ratio of the excited to ground state absorption cross section and energy-dependent saturation in solution are much better compared to properties in the polymeric film. In terms of the ratio of the excited to ground state absorption cross section, the peripherally substituted complexes show better OL performance than the non-peripherally substituted derivative.





## 1. Introduction

Optical limiting (OL) is an important application of nonlinear optics. It is useful for the protection of optical instruments including the human eye. An efficient optical limiter strongly attenuates intense laser pulses, while exhibiting high transmittance for low-intensity ambient light. Among many functional materials such as fullerenes [1,2], carbon nanotubes [3,4], polymer/nanotube composites [5] and phthalocyanines (Pcs) optically limit nanosecond light pulses in a fairly wide range of the UV/Vis spectrum via strong reverse saturable absorption (RSA) [6]. The nonlinear optical absorption of Pcs can be modified by incorporating different metal atoms into the ring or substitution of peripheral or axial position with different groups [7].

Pcs have low solubility in most organic solvents and they aggregate both in solution and in the solid state [7]. To overcome the solubility problem, a variety of substituents have been attached to the macrocycle in varying numbers and different substitution patterns [7–10]. The peripheral [11] or axial [12] substitution could enhance the solubility of Pcs and thus improve their usability. It was reported that strong donor peripheral alkoxy substituents improve the OL response with low OL threshold. On the other hand, axial ligands lead to a considerable enhancement in optical limiting response due to the presence of a dipole moment perpendicular to the macrocycle in the axially substituted phthalocyanines. Very recently OL properties of octasubstituted gallium and indium phthalocyanines were studied in both solution and host poly (methyl methacrylate) (PMMA) polymer film [13]. It was found that 4-benzyloxyphenoxy group as substituent on the phthalocyanine framework increased the solubility of gallium and indium phthalocyanines. Thus, in this paper, we choose the 4-benzyloxyphenoxy group as substituent on the zinc phthalocyanine framework to increase the solubility of the studied Pcs. Increasing solubility makes the thin film preparation in polymer matrix easy and may improve the optical limiting properties of the studied phthalocyanine complexes. A practical optical limiting device requires the casting of the optically active compounds in the solid state. Most of the OL studies of Pcs have been done in solution [6,7] while there are only fewer reports investigating passive solid state nonlinear optical devices [13–17]. Thus, in an attempt to optimize the OL properties of Pcs we have investigated the OL properties of 4-benzyloxyphenoxy-substituted zinc phthalocyanines (Fig. 1), tetra-substituted at the non-peripheral (**1**) and peripheral (**2**) positions and octasubstituted at the peripheral (**3**) position with the 4-benzyloxyphenoxy group both in solution and incorporated in a host PMMA polymer film.

## 2. Experimental

The synthesis and structural characterization of the investigated compounds have been previously reported [18,19]. For the fabrication of the solid state Pc/polymer films of all investigated

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