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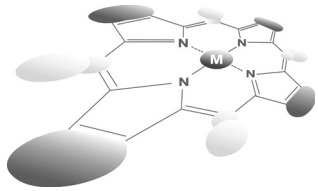

# Photophysical and nonlinear optical study of benzothiazole substituted phthalocyanines in solution and thin films

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*Dedicated to Professor Claudio Ercolani on the occasion of his 80th birthday.*

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**ABSTRACT:** In this study, the photophysical, nonlinear absorption and nonlinear optical limiting properties of zinc and gallium phthalocyanine complexes: tetrakis[(benzo[d]thiazol-2-yl phenoxy) phthalocyaninato]zinc(II) (**3**), tetrakis[(benzo[d]thiazol-2-yl phenoxy)phthalocyaninato] gallium(III) chloride (**4**), tetrakis[(benzo[d]thiazol-2-ylthio)phthalocyaninato] zinc(II) (**5**), tetrakis[(benzo[d]thiazol-2-ylthio)phthalocyaninato] gallium(III) chloride (**6**), were investigated both in solution and when embedded in polystyrene thin films using 532 nm laser excitation at 10 ns pulses. It was also observed that complexes that have higher triplet state absorption also possessed enhanced nonlinear and optical limiting behavior. Superior optical performance was observed when the complexes were embedded in thin films compared to when they are in solution. Complex **6** in thin films gave the highest imaginary third-order susceptibility ($I_m[X^{(3)}]$) and hyperpolarizability ($\gamma$) at $4.61 \times 10^{-7}$ esu and $3.44 \times 10^{-26}$ esu, respectively, with a low $I_{lim}$ value of 0.06 J cm$^{-2}$.

**KEYWORDS:** metallophthalocyanine, benzothiazole, photophysical, nonlinear absorption, optical limiting.



## INTRODUCTION

The past few decades have witnessed a rising interest in metallophthalocyanine (MPcs) due to their wide range of applications in biomedical and material sciences. The versatility of MPcs allows for applications in diverse areas of study including but not limited to photocatalysis [1, 2], photodynamic therapy [3], materials for optical data storage and optoelectronics [4–6], industrial dyes [7] and optical limiters [8]. Optical limiters are materials that decrease the amount of transmitted light with increasing applied intensity. These materials possess both nonlinear absorption and nonlinear refraction.

There has been a growing interest among researchers in the nonlinear optical properties of MPcs due to their delocalized π-electron system [4]. This π-electron system gives them interesting third-order nonlinear optical properties, leading to good optical limiting [9]. Additionally, the moderate ease of structural modification of MPcs without changing their stability and processability offer interesting features. One vital prerequisite for a good optical limiting material is possession of higher absorption cross section in the excited state than in the ground state. This effect yields positive nonlinear absorption coefficients *via* reverse saturable absorption (RSA). It has been found that insertion of heavy metal atom in the cavity of the Pc ring results in increased population of the excited states of the molecule *via* intersystem crossing (ISC) [10]. This leads to large absorption cross-section in the excited state [10]. Hence, the heavy metals, Ga and Zn are employed as central metals in this work.

Heterocyclic compounds containing sulfur and nitrogen, known as benzothiazole and their derivatives, have wide applications due to their biological activities [11]. The photosensitizing and second-order non-linear optical properties of benzothiazole derivatives have been reported [12, 13]. It has been reported that inclusion of a sulfur heteroatom in the π-conjugated system of a chromophore such as a phthalocyanine, favors the enhancement of nonlinearity [14]. Furthermore, thiazole units have been shown to be attractive building blocks

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