



# Photophysical and nonlinear optical properties of the positional isomers of 4-(4-tertbutylphenoxy) substituted cobalt, nickel and copper phthalocyanines

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## ABSTRACT

This paper reports on the third order nonlinear optical properties of cobalt, nickel and tetrakis(4-tertbutylphenoxy)phthalocyaninatocopper(II) isomers, using the Z-scan technique. Metal-free isomers were found to have high nonlinear absorption coefficient ( $\beta$ ) values compared to the metalated isomers. Metal-free C<sub>2v</sub> isomer was found to have the highest  $\beta$  value of  $1.52 \times 10^{-10}$  mMW<sup>-1</sup> in THF. All the metal-free and metal phthalocyanine isomers nonlinear properties were found to be dependent on the singlet state absorption. Imaginary second order nonlinear hyperpolarizability ( $Im[\chi^{(2)}]$ ), ground state cross section ( $\sigma_g$ ), excited states cross sections ( $\sigma_s$  and  $\sigma_i$ ) and two photon absorption (TPA) cross section ( $\sigma_{TPA}$ ) values are reported in this work. The five-energy level model rate equations were used to model the nonlinear response and absorption cross sections.

## 1. Introduction

Over the years, phthalocyanine (Pc) molecules have attracted considerable attention from both fundamental and applied research. Pcs are famously known to form coordination complexes with most elements in the periodic table [1,2]. Therefore, due to their vast properties and tuneable nature they are applied in various fields such as non-linear optics [3], photodynamic therapy [4], fuel cells [5], electro-catalysis [6] and pigments [7]. Pcs are the derivatives of porphyrins with 18 $\pi$ -electron heterocyclic aromatic system [8], which makes their application versatile. Such molecules with delocalised  $\pi$ -electron distribution have been studied extensively for their nonlinear and optical limiting properties [9]. Metal phthalocyanines (MPcs) also exhibit interesting chemical and optical properties. Previous studies have shown that the activity and application of Pcs are also influenced by the nature of the central metal [10]. The ability to change the peripheral substituents [11] and the central metal makes it easy to tailor make these compounds to suit a specific application. Their two-dimensional 18  $\pi$ -electron system make them suitable for application in nonlinear optics (NLO) and they offer a wide range of advantages such as stability and versatility [12,13]. Hence, in the past decade Pcs have been studied extensively for their nonlinear activity. Pcs are known to exhibit strong nonlinear response due to the intensified triplet excited state lifetime resulting

from the  $\pi$ -delocalized system [14,15]. However, in most reported nonlinear optical studies, Pcs are studied as a mixture of isomers (because of the inherent difficulty of separating these isomers). In this work, we show for the first time a systematic analysis of nonlinear optical properties of Pc isomers. The isomers nonlinear optical response and absorption cross sections are determined by Z-scan technique and the five-energy level model rate equations fitting of experimental data. Gounden et al. [16] reported the nonlinear optical properties of metal-free isomers of 2(3),9(10),16(17),23(24)-tetrakis(4-tertbutylphenoxy)phthalocyanine. Their study showed that the symmetry of the Pc influences its NLO properties. Ngubeni et al. [17] demonstrated the NLO properties metal-free isomers of 1(4),8(11),15(18),22(25)-tetrakis(4-tertbutylphenoxy)phthalocyanine and their results were complementary to that of Gounden et al. Hence, in organic materials, there is a significant correlation between structure and nonlinear properties. In this work, we report on the effects of systematically changing the central metal (Ni, Co, and Cu) and symmetry on the optical limiting properties of Pc isomers. The transition metals were chosen because they are known to influence changes in the band structure and can result in varied NLO absorption due to their increasing valence electrons in the d-shell with the decreasing atomic radii [18].

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