



# Nonlinear optical properties of metal free and nickel binuclear phthalocyanines

Kapambwe Peter Kabwe<sup>a</sup>, Marcel Louzada<sup>a</sup>, Jonathan Britton<sup>a</sup>, Temitope Oloruntoba Olomola<sup>a,b</sup>, Tebello Nyokong<sup>a</sup>, Samson Khene<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Rhodes University, PO Box 94, Grahamstown, 6140, South Africa

<sup>b</sup> Department of Chemistry, Obafemi Awolowo University, Ile-Ife, 220005, Nigeria

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## ABSTRACT

This work employs the open and closed Z-scan aperture technique to comparatively study the nonlinear optical (NLO) properties of nickel and metal free 4-*tert*-butylphenoxy phthalocyanine, biphenyl bridged bis-4-*tert*-butylphenoxy phthalocyanine and naphthalene bridged bis-4-*tert*-butylphenoxy phthalocyanine. Density functional theory (DFT) calculations of dipolar and octupolar ( $\Phi_{J=1}$  and  $\Phi_{J=3}$ ) contribution were determined theoretically from hyper-Rayleigh scattering (HRS) response ( $\beta_{HRS}$ ) values.

## 1. Introduction

Considerable effort has been dedicated to the synthesis of novel phthalocyanines (Pcs), with the aim of improving their functional properties. Monomeric and low symmetry Pcs have been largely studied with the aim of optimising their second order nonlinear optical (NLO) properties for applications in practical area such as telecommunication systems, high speed electro-optic switching, data processing and optical limiting [1–5]. Differences in nonlinear absorption coefficient ( $\beta$ ) values are known to be related to third order NLO-effects which are in turn related to geometry relaxation of the molecule. Geometry relaxation is known to be a much slower process with respect to the instantaneous change in  $\pi$ -electron distribution, this results in the observation of large and fast polarizabilities of  $\pi$ -electron networks [6]. Dipolar and octupolar ( $\Phi_{J=1}$  and  $\Phi_{J=3}$ ) contribution are characterised by their differences in charge distribution in response to an applied electric field, resulting in spatial asymmetry of the electron distribution. Differences in  $\beta$  values for different molecules could be explained by differences in instantaneous change in their  $\pi$ -electron distribution, coupled with slower geometry relaxation. Hence, differences in dipolar and octupolar contributions could be used to understand the variation in  $\beta$  values for different complexes, since large  $\beta$  values are expected for molecules possessing large dipole moments. Multinuclear Pcs have shown potential of improving  $\beta$  values [4,5,7,8]. Molecules which are more octupolar are known to show great potential as novel second-order NLO material, due to their diverse and complex charge distribution [9,10]. Binuclear phthalocyanines (Bi-Pcs) have the potential of offering a

more diverse and complex charge distribution compared to normal monomeric Pcs, due to their molecular size and shape. This work studies the nonlinear absorption coefficient ( $\beta$ ) and nonlinear refractive index ( $n_2$ ) of Bi-Pcs in order to further contribute to the study of NLO of Pcs in general.

In this work the Z-scan technique is employed to comparatively study the third order NLO properties of nickel and metal free 4-*tert*-butylphenoxy phthalocyanine ( $H_2Pc$  and  $NiPc$ ), biphenyl bridged bis-4-*tert*-butylphenoxy phthalocyanine ( $BiPh-H_2Pc$  and  $BiPh-NiPc$ ) and naphthalene bridged bis-4-*tert*-butylphenoxy phthalocyanine ( $Naph-H_2BiPc$  and  $Naph-NiBiPc$ ) (Scheme 1). Density functional theory (DFT) calculations were performed, to theoretically determine  $\Phi_{J=1}$  and  $\Phi_{J=3}$  from theoretically calculated second-order nonlinear optical response using the hyper-Rayleigh scattering (HRS) response ( $\beta_{HRS}$ ). Spectroscopic and photophysical properties of the synthesised compounds have been determined using magnetic circular dichroism (MCD), time correlated single photon counting spectroscopy (TCSPC), and UV-visible absorption spectroscopy.

## 2. Experimental

### 2.1. Material

4-Nitrophthalonitrile, 4,4-dihydroxybiphenyl, and 4-*tert*-butylphenol were purchased from Sigma-Aldrich and were used without further purification. The solvents dimethylsulfoxide (DMSO), dichloromethane (DCM), 1-octanol, dimethylformamide (DMF) and

\* Corresponding author.

E-mail address: [s.khene@ru.ac.za](mailto:s.khene@ru.ac.za) (S. Khene).