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Nanosecond optical nonlinearities in low symmetry phthalocyanine nanoconjugates studied using the Z-scan technique

Njemuwa Nwaji, Tebello Nyokong*

Centre for Nanotechnology Innovation, Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

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ABSTRACT

In this study, the photophysical, and nonlinear optical limiting properties of low symmetry tris[(4-benzo[*d*]thiazol-2-ylphenoxy)-2-phenoxyl acetic acid phthalocyaninato zinc (II) (**3**) conjugated to metallic nanoparticles have been investigated using open aperture Z-scan techniques at 532 nm. The nonlinear optical response demonstrated that the studied complex and the nanoconjugates exhibits higher excited state absorption cross-section resulting from S_1 and T_1 compared to ground state absorption. Enhanced optical limiting performance was observed when the complex was conjugated to nanoparticles with **3**SA-AuNPs showing the best optical limiting threshold of 0.39 J/cm^2.

1. Introduction

There has been increasing interest in the design of optical limiters that can afford a measure of protection to optical sensors and the human eye from laser-induced damage. Good optical limiters strongly attenuate high incident light intensity or fluence, while exhibiting high transmittance at low values. The optical limiting properties of variety of materials have been investigated [1–7]. Among the diverse NLO absorbers that have been identified, metallophthalocyanines (MPcs) and their derivatives have emerged as the most promising materials as a result of their large nonlinearities due to thermal stability and highly delocalized aromatic 18 π-electron systems [3–5]. In particular, low symmetry MPcs have been reported to possess enhanced nonlinear optical response compared to their corresponding symmetrical analogues [6], hence asymmetrical Pcs are employed in this work.

Research on blending two or more materials with the aim of developing efficient optical limiters is on the increase. Previous reports have shown significant increase in triplet state parameters of MPcs when conjugated to nanomaterials [7,8]. Enhanced triplet–triplet absorption results in efficient reverse saturable absorption (RSA), which is the predominant mechanism primarily responsible for optical limiting in MPcs.

Metallic nanoparticles such as gold (Au) and silver (Ag) have been shown to possess fascinating optical limiting properties, which are size and shape dependent [9,10]. Nonlinear optical enhancement of metallic nanoparticles has been associated with optical excitation of the surface plasmon resonance (SPR) band of the particles [11]. Despite numerous reports on nonlinear optical properties of MPcs, little attention has been paid to incorporation of low symmetry phthalocyanine to metallic nanoparticles. We compare the effects of self-assembly versus covalent attachment of the MPc complex of interest to Au (AuNPs) and Ag (AgNPs) on the optical limiting performance of the former.

This study describes the comparative photophysical and optical limiting properties of low symmetry tris[(4-benzo[*d*]thiazol-2-ylphenoxy)-2-phenoxylacetic acid phthalocyaninato] zinc(II) (complex **3**) when conjugated to gold (AuNPs) and silver (AgNPs) nanoparticles. Complex **3** possesses one carboxylic acid and three benzothiazole groups which offer dual functionality both for surface assembly onto the nanoparticles as well as covalent linkage to functionalized nanoparticles. Glutathione (GSH) was employed as a capping for the NPs since it possesses both free amino group that can be used to couple with the carboxylic acid of the MPc and thiol group that can stabilize the nanoparticles.

2. Experimental

2.1. Materials

Zinc acetate, dicyclohexylcarbodiimide (DCC), 1-pentanol, dimethylaminopyridine (DMAP), 1, 8-diazabicyclo[5.4.0] undec-7-ene (DBU), 1, 3-diphenylisobenzofuran (DPBF), dimethyl sulphoxide (DMSO), and deuterated dimethylsofoxide (DMSO-d_6) were obtained from Sigma Aldrich®. Tetrahydrofuran (THF), dimethylformamide (DMF), and methanol were purchased from SAARCHEM®. GSH capped AuNPs and AgNPs (represented as GSH-AuNPs and GSH-AgNPs,

* Corresponding author.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

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