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Photophysical and nonlinear optical characteristics of pyridyl substituted phthalocyanine - Detonation nanodiamond conjugated systems in solution

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ABSTRACT

In this study photophysical, nonlinear absorption and optical limiting properties of detonation nanodiamonds (DNDs)-phthalocyanine nanoconjugate systems containing; 2,9(10),16(17),23(24)-tetrakis-(4-pyridyloxy) phthalocyaninato (H_2TPPc), 2,9(10),16(17),23(24)-tetrakis-(4-pyridyloxy) phthalocyanato zinc(II) (ZnTPPc) and 2,9(10),16(17),23(24)-tetrakis-(4-pyridyloxy) phthalocyanato silicon(IV) hydroxide ($Si(OH)_2$TPPc), were investigated in dimethylsulfoxide solution. Pcs were non-covalently linked to nanondiamonds (also covalently linked for $Si(OH)_2$TPPc) and investigated using 532 nm laser excitation at 10 ns pulses for their optical limiting properties. Complexes that have higher triplet state absorption also possessed enhanced nonlinear optical behaviour following reverse saturable absorption mechanism. Superior optical performance is observed when the Pcs had a central metal with axial ligands conjugated to DNDs in solution. Nanoconjugate of DNDs-$Si(OH)_2$TPPc and respective Pc in solution gave the highest imaginary third-order susceptibility ($I_m[X^{(3)}]$) and hyperpolarizability (γ) at 2.91×10^{-8} and 3.17×10^{-8} esu and 3.88×10^{-28} and 4.22×10^{-28} esu, respectively, with I_{lim} value of 0.47 and 0.39 J·cm^{-2}.

1. Introduction

Nanodiamonds (NDs) are interesting carbon-based nanomaterials as a result of their outstanding mechanical performance [1], chemical resistance [2], versatile surface chemistry [3,4], biocompatibility [5], stability [6], low toxicity [7] and unique optical and electrical properties [8,9]. Due to these properties, NDs have found applications in many areas including in wear-resistant polymers, metal coating [2,10], lubricant additives [1], health care products [11], and nonlinear optics (NLO) [12]. On the other hand, metallophthalocyanines (MPcs) have found applications in many areas including in NLO, photocatalysis, electrochemical sensors, photodynamic therapy (PDT), dye-sensitized solar cells (DSSC), and semiconductors amongst others [13–16]. MPcs have received considerable attention as NLO materials due to their large nonlinearities, inherently fast response time, broadband spectral response, ease of processing, thermal stability, and extensive delocalized π electron systems [17–23]. The presence of an extended π electron conjugation system can result in a significant increase in the triplet state population, which leads to improved reverse saturable absorption (RSA) at 532 nm for nanosecond laser pulses [17,24]. NLO materials strongly attenuate optical beams to specific threshold levels under conditions of intense irradiation [25]. Multiphoton absorption, reverse saturable absorption (RSA), nonlinear scattering, and nonlinear refraction areis the dominant mechanisms responsible for NLO behaviour [26]. Both MPcs and NDs are NLO materials and they are combined in this work for the first time for NLO applications. Nanodiamonds synthesised using detonation method (detonation nanodiamond, DNDs) are employed in this work.

It has been previously reported that properties of NDs are dictated by the surface functionalities, diamond core or a combination of both. DNDs have tetrahedral network structures, and comprise a diamond core (sp^3), a middle core ($sp^2 + x$) and a graphitized outer layer (sp^2) that is often partially oxidized [27]. The presence of sp^2 hybridization in DNDs allows for π-π interactions with other π containing molecules such as MPcs, and this is employed in this work. In their pristine state, DNDs contain several functional groups present on the surface including amine, amide, alcohol, carbonyl, and carboxyl [28,29]. These functional groups facilitate the linking of DNDs to other molecules such as Pc, and in this work a $Si(OH)_2$Pc is linked to DNDs via an ester bond in addition to possible π-π interactions.

MPc complexes have been linked to other carbon nanomaterials such as graphene quantum dots (GQDs) with improved NLO behaviour [30–32], but MPc have never been linked covalently or non-covalently to DNDs. DNDs and GQDs (in their pristine state) have different functional groups and are expected to influence NLO behaviour of Pcs differently. The combination of DNDs and Pcs explored in this work, is

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