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Optical limiting response of multi-walled carbon nanotube-phthalocyanine nanocomposite in solution and when in poly (acrylic acid)

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ABSTRACT

Bis{23-(3,4-di-yloxybenzoic acid)-(2(3), 9(10), 16(17), 23(24)-(hexakis-pyridin-3-yloxy phthalocyaninato)} dineodymium (III) acetate (**3**) is linked to amino-functionalized multi-walled carbon nanotubes (MWCNT) to form **3**-MWCNT. Z-scan technique was employed to experimentally determine the nonlinear absorption coefficient from the open-aperture data. The limiting threshold values as low as 0.045 J cm^{-2} were found in solution. The conjugate (**3**-MWCNT) gave better optical limiting behavior than complex **3** alone.

1. Introduction

Carbon nanotubes (CNTs) have appealing properties such as tunable surface functionalities, well-defined hollow interiors, and biocompatibility with living systems [1–3]. CNTs may be either metallic or semiconducting [4]. These properties are the backbone of many applications of CNTs, including in electronics [5–7], optical limiting [8,9], drug delivery systems, electronic devices, sensors and actuators [10,11]. Multi-walled carbon nanotubes (MWCNTs) are a subject of this work. Since the investigation of optical limiting mechanism of carbon based materials including MWCNTs by Sun et al. [12], many researchers have followed up by chemically modifying MWCNTs for optical limiting purposes [13–21].

Phthalocyanines (Pcs), on the other hand, are well known as optical limiting materials [22–25] due to their highly conjugated π–electron system. MWCNTs have been non-covalently functionalized with different metal phthalocyanines by π-π stacking method for NLO studies [26–28]. Covalent attachment of Pcs to MWCNTs for NLO studies is not known even though single walled carbon nanotubes (SWCNT) have been covalently attached to Pcs for this application [29]. Depending on the solvent, an increase or decrease on the NLO parameters of the phthalocyanines was observed in the presence of SWCNT [29]. In this work, we present the optical liming properties of phthalocyanine covalently attached to MWCNTs in solution and when embedded in poly (acrylic acid) thin films. A binuclear phthalocyanines (Bi-Pcs, **3** in Scheme 1) where the Pc molecules are held together by an organic molecule acting as a bridge is employed. Such Pc structures are unsymmetrical. Lack of symmetry is known to improve nonlinear optical behavior [30]. Even though both MWCNTs and Pcs are optical limiting materials, their combination does not always lead to improved NLO behavior [31]. It has been reported that since CNTs solutions are in the form of a dispersion, their optical limiting behaviour is due to scattering combined with possible electronic absorption contributions [31,32]. The aim of this work is to elucidate the mechanism used for NLO for complex **3** in the presence of MWCNTs.

For practical applications, phthalocyanine complexes are embedded in thin films of polymers. Recently [33], poly (acrylic acid) (PAA) was shown to result in improved optical limiting behavior when compared to other polymers such as poly (methyl methacrylate) (PMMA), hence the former is employed in this work. Diaminomaleonitrile is used for surface modification of MWCNTs for linkage to carboxyphenoxy-substituted Pcs.

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