

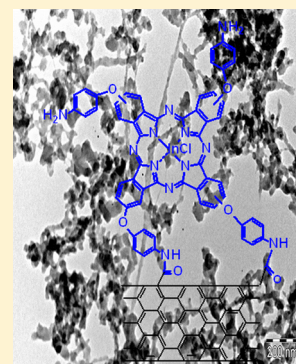
Enhanced Optical Limiting Behavior of an Indium Phthalocyanine–Single-Walled Carbon Nanotube Composite: An Investigation of the Effects of Solvents

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Supporting Information

ABSTRACT: The nonlinear optical behavior of 2(3),9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium(III) chloride (2) and its carbon nanotube composite in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) solutions is described. The nonlinear third-order susceptibility and second-order hyperpolarizability values are also reported. A large nonlinear absorption that increased on covalent linking with single-walled carbon nanotubes (SWCNTs) was observed for the compound in DMSO. The nanosecond nonlinear absorption and the optical limiting behavior of this complex are shown to be dominated by a strong excited state absorption from a two-photon pumped state. The optical limiter using the new nanocomposite material (SWCNT-2) in the appropriate solvent showed a much lower threshold for optical limiting together with a much lower transmission at high fluences than previously reported nanocomposite limiters. The optical properties of the phthalocyanine and its conjugate were found to show high sensitivity toward the change of solvent matrix.



INTRODUCTION

The ability to control the intensity of light in a predictable and predetermined manner is an important manipulation in nonlinear optics (NLO), with applications ranging from optical communications to optical limiting.¹ Materials that exhibit reverse saturable absorption (RSA) are of interest for use in optical limiting (OL) devices, for the protection of sensors and the human eye from intense laser pulses.^{2–6} However, the major drawback in the development of such devices is the lack of appropriate nonlinear materials.

Over the last two decades, there has been a continuing interest in the development of new optical limiters.^{1–13} A good optical limiter must meet demanding specifications as the eye can be damaged by pulses of very low energy. As such, the device must be able to provide sensitive broadband response to long and short pulses and be resistant to laser-induced damage.¹⁴ This paper describes the synthesis and fabrication of a new phthalocyanine-single-walled carbon nanotube composite for use as an optical limiting material.

Different materials such as fullerenes, carbon nanotubes (CNTs), porphyrins, phthalocyanines (Pcs), carbon black suspensions (CBSs), semiconductors, and liquid crystals have been widely studied for optical limiting applications.^{2,6–8,15,16} In spite of the wide variety of materials that have been implemented for use as optical limiters, no single material or combination of materials has yet been identified as an ideal material capable of protecting any given optical equipment from a potential laser threat. Considering this fact, the need for a continued search for materials with satisfactory optical limiting behavior cannot be underestimated. Our aim therefore is to design an improved optical limiting material using a novel

indium(III) phthalocyanine in combination with single-walled carbon nanotubes (SWCNTs).

Among the large number of Pcs that have been examined for OL behavior, lead and indium phthalocyanine derivatives have been identified as good optical limiters, with properties approaching the characteristics necessary for practical applications.^{4,17,18} The extensive exploration of Pcs containing lead(II) or indium(III) as the central metal ions may be attributed to their large atomic size. Large central atoms are known to encourage intersystem crossing to the triplet state by a heavy atom effect.^{19,20} The review by de la Torre et al.²⁰ clearly showed the importance of InPc over ZnPc derivatives in optical limiting. One of the strategies for the development of improved optical limiters is to chemically combine the materials that have already been identified as good optical limiters, such as Pcs and carbon nanotubes.^{2,21,22} To achieve this, we synthesized a new tetraaminophenoxy-substituted indium Pc (Scheme 1) and covalently linked it to SWCNTs for enhanced OL behavior.

CNTs have shown a wide range of interesting properties suitable for applications in many advanced technology fields and are perhaps the most investigated nanomaterial.^{23–26} SWCNTs are functionalized to allow solubility in organic solvents²⁶ and grafting of molecules such as Pcs or porphyrins.²⁷ Previous studies have shown that multiwalled carbon nanotubes (MWCNTs, consisting of multilayers of graphene sheets) and SWCNTs are promising candidates for broadband optical limiting from the visible to the infrared

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