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Enhanced optical limiting behaviour of indium phthalocyanine derivatives when in solution or embedded in poly(acrylic acid) or poly (methyl methacrylate) polymers

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ABSTRACT

The optical limiting performance of indium phthalocyanine-based polymer thin-films with large nonlinear absorption coefficients (β_{eff}) and low limiting threshold intensity (I_{lim}) are described. The absorption cross-sections and the population dynamics of the excited states are also reported. The excited state absorption cross-sections (σ_{exc}) are shown to depend on the transition moment between the T_1 and T_2 states. β_{eff} values have been shown to be related to the population density of the molecules in the T_1 state. The improved optical limiting performance recorded for the investigated phthalocyanine complexes in the presence of polymer matrices has been attributed to the aggregation effects of the complexes in the polymer thin-films. The optical properties of the indium phthalocyanine moieties were found to possess robust sensitivity to a change of the polymer materials.

1. Introduction

There exists a rather extensive literature on optical limiting materials for sensor protection [1–8]. All of these materials rely on optical nonlinearities, and use a variety of nonlinear mechanisms, which include nonlinear absorption (NLA), nonlinear refraction (NLR), induced scattering, and phase transitions [1]. A potential optical limiter is required to exhibit at least one of these nonlinear optical (NLO) processes. The origins of these nonlinear processes vary widely. NLA for example, may be associated with two-photon absorption (2PA), excited state absorption (ESA), or free-carrier absorption [1].

Phthalocyanines (Pcs) among the many possible nonlinear absorbers, are one of the most widely investigated organic compounds for optical limiting application [2]. One of the reasons Pcs have attracted so much attention is the versatility of their methods of synthesis that leads to the combination and modulation of several structural components that can achieve effective optical limiting. The chemistry of Pc macrocycles allows for the variation of the different chemical features, such as the degree of electronic conjugation, the nature of the ring substituents and the central atom, and the ligands attached to the central atom. Broadly speaking, all of these parameters have been largely considered in the effort to develop satisfactory optical limiting devices [2–4,9–20].

In this paper, the NLO behavior of β-tetrakis-(4-(2,3-dihydro-1*H*-inden-1-yloxy))phthalocyaninato indium(III) chloride (compound **2**, Scheme 1b) is presented. The compound showed an incredibly high NLA coefficient (β_{eff}) in dimethyl sulphoxide (DMSO). This behavior is rare, especially when the Pcs are not combined with nanomaterials. The NLA coefficient obtained for this molecule is comparable to those observed for tetraamino-phenoxyphthalocyaninato-indium(III) chloride-CdSe/ZnS composite (InTAPPc-CdSe/ZnS) in DMSO [21], and higher than the previously reported tetraaminophenoxyphthalocyaninato-indium (III) chloride-single walled carbon nanotubes composite [22]. In the current study, the substituent (1-indanol) and the central atom (indium) were carefully chosen for the —C—O—C— bonds rotational flexibility, and the heavy-atom effect, respectively. The rotational flexibility can provide the molecule with variable symmetries, thus providing varieties of geometric isomers, many of which would enhance the molecule's triplet absorption in the same manner as the heavy-atom effect would. The performance of the molecule (**2**) and that of the InTAPPc [22], Fig. 1, were checked in polymer thin-films using poly(acrylic acid) (PAA) and poly (methyl methacrylate) (PMMA) as the polymer sources. The choice of PMMA as a polymer source is based on its long history as a polymeric support material for nonlinear absorbers [23–26].

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