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Improved nonlinear optical behaviour of ball type indium(III) phthalocyanine linked to glutathione capped nanoparticles

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ABSTRACT

The synthesis of ball–type indium phthalocyanine (complex **4**) and its covalent attachment to glutathione (GSH–) capped (Ag, Au, CdTeSe, CdTeSe/ZnO) nanoparticles are reported in this work. Furthermore, their photophysical and nonlinear optical behaviour were investigated. We observed a decrease in the fluorescence quantum yield with corresponding increase in the triplet quantum yield of the nanoconjugates in comparison to complex **4** alone. The reverse saturable absorption was found to be dependent on excited state absorption. The optical limiting threshold ranges from 0.40–0.78 (J/cm^2). The nanoconjugate of the complex **4** with GSH–CdTeSe/ZnO (QD1) accounted for the most improved triplet state parameters and nonlinear optical behaviour in comparison to complex **4** and the other nanoconjugates studied in this work.

1. Introduction

The development of optoelectronic-based technologies, such as optical communications, high-speed electro-optical information processing, short optical-pulse generation, and optical switching requires new nonlinear optical (NLO) materials [1,2]. Intense laser beam can easily cause damage to delicate optical objects, including the human eye. Hence, research in the field of optical limiting (OL) has been on the rise in an attempt to afford some measure of protection against intense laser light [3].

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 highly delocalized aromatic 18 π-electron system [1,3–5]. The mechanism of nonlinear optical behaviour of Pcs arises from possession of higher excited state compared to ground state absorption cross-section, which results in the phenomenon of reverse saturable absorption (RSA) [6,7]. The RSA of Pcs has been associated with intersystem crossing from the lowest excited singlet state (S_1) to the lowest excited triplet state (T_1), resulting in increase in the population of the triplet state [3]. Incorporation of a heavy atom in the central cavity of Pc macrocycle has been known to increase intersystem crossing thereby leading to high population of the triplet state [8]. Phthalocyanines containing more than one ring such as bis-phthalocyanines are known to show improved optical nonlinearities due to their expanded π electron system [9,10]. Hence ball-type Pcs are expected to show improved NLO behaviour. Ball-type Pcs have four bridging substituents on the periphery of each benzene ring of the two Pc units, the latter are arranged cofacially, resulting in a ball like structure. Apart from one literature report [11], optical limiting properties of ball-type phthalocyanines have not received much attention.

On the other hand, the last two decades have witnessed increasing research interest on plausible applications of semiconductor quantum dots (QDs) and other nanoparticles as optical limiting materials [12–14]. In this work, we link a ball-type MPc to glutathione (GSH) capped semiconductor core shell CdTeSe/ZnO (represented as QD1) and core CdTeSe (represented as QD2) and to Ag (AgNPs) and Au (AuNPs) nanoparticles. Semiconductor QDs have been linked to monomeric MPc complexes [15–17] with improved NLO behavior. Conjugates of QDs or any nanoparticles with ball-type Pcs are not known hence are reported here together with their NLO behaviour. QDs are expected to contribute to NLO behaviour of Pcs due to the free-carrier absorption (FCA)

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