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Photophysical and enhanced nonlinear optical response in asymmetric benzothiazole substituted phthalocyanine covalently linked to semiconductor quantum dots

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ABSTRACT

The synthesis of asymmetric benzothiazole substituted phthalocyanines (complexes **3** to **5**) and their covalent attachment to glutathione (GSH) functionalized quantum dots (QDs) are reported in this work. Additionally, their photophysical and nonlinear optical properties were investigated. A decrease in the fluorescence quantum yield with corresponding increase in the triplet quantum yield was observed when the complexes were covalently linked to glutathione (GSH) functionalized cadmium telluride (CdTe) quantum dots. Reverse saturable absorption was found to be predominantly dominated by excited state absorption. The observed limiting threshold values range from 0.29–0.75 J/cm^2.

1. Introduction

Research in the past decades has shown nonlinear optics (NLO) as a key emerging field in photonics and optoelectronics. In particular, the development of efficient optical materials that afford a measure of protection for sensors including the human eye from laser-induced damage has been on the rise within the scientific community [1–3].

Among the many and varied organic chromophores that have been investigated for their optical limiting properties, phthalocyanine (Pcs) and related macrocycles are promising as potential nonlinear optical materials [2–8]. Asymmetric Pcs have been shown to exhibit enhanced second-order nonlinear optical response compared to their symmetric analogue [8], hence are employed in this work.

Apart from phthalocyanines, semiconductor nanocrystals have also received considerable attention in the field of photonics and optoelectronics [9,10]. Strong modification in electronic states of semiconductor quantum dots (QDs) can occur due to quantum confinement which makes them promising third-order nonlinear optical materials working at resonance as well as off-resonance with fast response time [11]. However, the formation of new nanohybrid from the covalent linkage of semiconductor quantum dots and Pcs that could offer enhanced nonlinear optical response has not received much research attentions. Semiconductor QDs have been linked to metallophthalocyanine (MPc) complexes [12–15] with improved nonlinear optical (NLO) behaviour, but studies on asymmetrical Pcs are limited [14], hence are a subject of this work. We have employed mainly CdSe based QDs for linking or mixing with Pc [13–15]. However CdTe QDs showed more improvement in NLO behaviour compared to CdSe (though when embedded in polymer) hence the former are employed in this work [12].

In this study, the photophysical and nonlinear optical response of low symmetry tris[(4-benzo[*d*]thiazol-2-ylphenoxy)-2-phenoxylacetic acid phthalocyaninato] gallium(III) chloride (complex **3**) and tris[(4-benzo[*d*]thiazol-2-ylphenoxy)-2-phenoxylacetic acid phthalocyaninato] indium(III) chloride (complex **4**) when covalently linked to glutathione functionalized semiconductor quantum dots are described. Complexes **3** and **4** possess terminal carboxylic acid ends, which allows for covalent coupling with the amino group of glutathione to form an amide bond. We have previously reported on the optical limiting response of low symmetry tris[(4-benzo[*d*]thiazol-2-ylphenoxy)-2-phenoxylacetic acid phthalocyaninato] zinc(II) (**5**) when surface assembled as well as covalently linked to metallic nanoparticles [16]. This is the first time that this molecule is linked to QDs, and the NLO behaviour of the resulting conjugates is compared with that of conjugates **3** and **4**. Gallium and indium central metals were selected to increase the triplet population through heavy atom effect, which is expected to give an enhanced nonlinear response. Semiconductor quantum dots were selected for use in this study due to their fully quantized system, which makes QDs very stable against thermal perturbation such as intense laser radiation. Additionally, a Förster resonance energy transfer (FRET) based enhancement of NLO response in the presence of semiconductor quantum dots has been demonstrated [17].

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