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The effect of point of substitution and silver based nanoparticles on the photophysical and optical nonlinearity of indium carboxyphenoxy phthalocyanine

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ABSTRACT

Indium(III) chloride 1,8(11),15(18),22(25)-tetra-(3-carboxyphenoxy) phthalocyanine (**1**) and indium(III) chloride 2,9(10),16(17),23(24)-tetra–(3-carboxyphenoxy) phthalocyanine (**2**) were covalently linked to glutathione capped silver nanoparticles (AgNPs-GSH) and silver selenide/zinc sulfide (Ag_2Se/ZnS–GSH) quantum dots via amide bond formation. The photophysical and nonlinear optical behaviour of the metallophthalocyanines and their conjugates with nanoparticles were investigated using the open aperture Z-scan technique. Complex **2** showed enhanced photophysical properties compared to **1**. The conjugates revealed improved triplet state quantum yields (except for **1**-AgNPs-GSH which afforded lower triplet state quantum yields in comparison to **1**) and nonlinear optical activities in comparison to the Pc complexes. The synthesized complexes, nanoparticles and their conjugates could be potential nonlinear optical materials due to their good nonlinear optical activities.

1. Introduction

Nonlinear optical (NLO) devices are being developed in order to protect the eye and other light sensitive objects from intense laser light. NLO materials possess some essential features such as large nonlinear absorption coefficient (β_{eff}), inherent fast response time and efficient optical limiting threshold intensity or fluence (I_{lim}) [1–3]. Among the organic molecules that have been tested for NLO applications, metallophthalocyanines (MPcs) remain one of the most viable materials. The efficient optical nonlinearity of MPcs could be attributed to their extensive 18 π–electron conjugated ring system. In addition, ring substituents on MPcs can be modified, allowing for attachment of other NLO materials such as nanoparticles (NPs) [4,5]. It is also important to note that central atoms and nature of substituents also play an indispensable role in the optical nonlinearity of phthalocyanines [6–10].

On the other hand, silver based nanoparticles (NPs) have been reported to possess NLO properties [11]. AgNPs have found applications in other areas such as in photodynamic therapy [12,13] and as anti-microbial agents [14].

Previous studies in our group have shown that MPcs can form dyad systems with various metal NPs with improved triplet state quantum yields and NLO activities in comparison to the MPcs alone [15–18]. Herein, we report on the covalent linkage of indium(III) chloride 1,8(11),15(18),22(25)-tetra-(3-carboxyphenoxy)phthalocyanine (**1**) and indium(III) chloride 2,9(10),16(17),23(24)-tetra-(3-carboxyphenoxy)phthalocyanine (**2**), Scheme 1, to glutathione (GSH) capped silver NPs (AgNPs–GSH) and silver selenide/zinc sulfide quantum dots (Ag_2Se/ZnS–GSH QDs). The synthesis of complex **2** has been reported [19], while complex **1** is reported in this work for the first time. The effect of the point of attachment of AgNPs–GSH and Ag_2Se/ZnS–GSH QDs on the photophysical and NLO properties of the Pcs will be evaluated. Since both Ag based NPs and Pcs are NLO materials, we expect enhanced NLO behaviour of the conjugates through synergistic effect. In addition, the dyad system of the MPc complexes with silver based NPs is expected to afford enhanced triplet state absorption and NLO behaviour due to heavy atom effect. Even though MPcs have been linked to AgNPs [19], this is the first time that Ag based QDs are linked to Pcs. Also core/shell quantum dots show enhanced optical properties compared to the core [20,21], hence core/shell Ag_2Se/ZnS–GSH QDs are employed in this work and compared to AgNPs following linking to MPc complexes.

The nonlinear optical behaviour of the NPs, Pc complexes and their conjugates were tested in solution (dimethylsulfoxide) using open aperture Z-scan technique at excitation wavelength of 532 nm with 10 ns pulse length and laser energy of ~70 μJ.

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