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Nonlinear optical responses of carbazole-substituted phthalocyanines conjugated to graphene quantum dots and in thin films

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ABSTRACT

Three different phthalocyanine complexes substituted with carbazoles were conjugated to graphene quantum dots (GQDs) through π–π stacking. The morphologies, sizes, and crystallinities of the nanoconjugates were determined using Raman spectroscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, and X-ray diffraction. The nonlinear optical (NLO) properties of the metallophthalocyanines alone and when conjugated to the GQD nanomaterial in different solvents, as well as after having been embedded in thin films, were studied. The effects of the different substituents and solvents on the NLO properties of the metallophthalocyanines were evaluated. Enhancements in the photophysical properties of the complexes upon conjugation with the nanomaterial were observed. Fluorescence quantum yields, fluorescence lifetimes, triplet quantum yields, and triplet lifetimes were measured for the complexes, and for their conjugates in DMSO.

1. Introduction

The past decades have seen the application of lasers in many and diverse fields and the intense radiation from lasers poses great dangers to optical sensors and the human eye [1]. The development of materials that can transmit light of low intensities and absorb harmful high-intensity light are garnering huge research interest. These materials are known as optical limiters (OLs) and they may be used to generate high-harmonic frequencies and to modify optical devices [2–5].

Organic materials have begun to be considered as good OLs owing to low-cost synthesis methods and their nonlinear susceptibilities [6,7]. Nonlinear optical materials with high solubilities, linear transmittances, and high laser-damage thresholds are preferred [8].

Among potential OL materials such as fullerenes [9], porphyrins [8], and phthalocyanines [10], the phthalocyanines (Pcs) have been found to satisfy the majority of these criteria. Pcs with extensive 18-π-electron systems and large optical nonlinearities have been investigated as promising potential materials for NLO applications [11,12].

The optoelectronic properties of Pcs can be controlled by chemical modification, specifically, by axial and peripheral substitutions and by exchange of the central metal atom [13]. It has been found that insertion of a heavy metal atom into the cavity of the Pc ring enhances intersystem crossing (ISC) rates; accordingly, the population of the excited states will be increased and a large absorption cross section for the excited states is obtained [14].

The formulation of an optically active compound in a solid support is one of the practical techniques that has been used to enhance OL properties via an increase in photo-stability [15]. Hence, the complexes in the present study were also formulated in solid polystyrene thin films.

Graphene-based quantum dots (GQDs) have been extensively investigated because they are non-toxic, soluble in aqueous and non-aqueous solvents, easily synthesized, and can be further functionalized [16]. Although enhanced nonlinear optical responses of porphyrins and Pcs upon covalent linking to GQDs have been reported [17–19], the optical limiting properties of Pcs linked to GQDs via π–π interactions has not received much attention. The delocalized π-electrons in the planar structure of GQDs promote π–π interactions with the π-conjugation systems of other aromatic molecules [20], such as porphyrins and phthalocyanines [21].

In this report, we present an investigation of the NLO behavior of a series of three carbazole-containing phthalocyanines, both in the presence of GQDs and when the Pcs are formulated in polystyrene thin films. The tricyclic structure of carbazole, with two six-membered benzene rings fused onto ether, enhances π-conjugation which is known to improve optical limiting properties [22].

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