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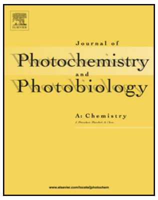

Fluorescence behavior of nanoconjugates of graphene quantum dots and zinc phthalocyanines

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ABSTRACT

Graphene quantum dots (GQDs) and zinc phthalocyanines interactions in different modes (covalent and non-covalent) are reported in this study. GQDs were covalently attached to the following complexes: zinc tetraamino phthalocyanine (ZnTAPc) via amide coupling, zinc tetracarboxyphenoxy Pc (ZnTCPPc) (π–π interaction) and cationic zinc tetrapyridiloxy Pc (ZnTmPyPc) (ionic interaction). GQDs fluorescence was quenched in the presence of the ZnPc derivatives. The nanoensembles of GQDs–ZnPcs showed stimulated emissions of the ZnPcs. The suggested quenching mechanism is through Förster resonance energy transfer (FRET). These novel nanoensembles hold promise for various optical and luminescence based applications.

1. Introduction

Graphene quantum dots (GQDs) are luminescent carbon-based nanomaterials [1]. GQDs are part of the family of carbon nanomaterials such as carbon nanotubes, fullerenes, graphene, graphene oxide and carbon dots. The uniqueness of GQDs amongst this class of carbon nanoparticles stems from the presence of quantum confinement and edge effects in their graphene-like cores. Similar to conventional semi-conductor QDs [2], GQDs have a tunable band gap and high photoluminescence activity. Interestingly, GQDs have been found to exhibit superior characteristics compared to conventional semiconductor quantum dots and other carbon-based nanoparticles in terms of their excellent biocompatibility, low toxicity, good water dispersibility [3], large optical absorptivity, high fluorescence activity and excellent photostability [4]. These properties have thus generated interest in their applications in fields such as nanosensor fabrication, drug delivery, photocatalysis, photovoltaics and photodynamic therapy (PDT) [5,6].

On the other hand, metallophthalocyanines (MPcs) have attracted significant interest because of their unique physicochemical properties and potential applications. MPcs can easily be conjugated to a wide array of nanomaterials due to the presence of reactive ring substituents [7,8]. The conjugation of MPcs to nanomaterials has led to enhanced photophysical and photochemical properties [9,10]. Molecular and supramolecular ensembles incorporating both MPcs and carbon-based materials (fullerenes, carbon nanotubes, graphene oxide, graphene and carbon dots) have been fabricated and their photophysical properties widely reported [11–14], but no studies have been reported involving MPcs and GQDs. GQDs can act as energy donors upon interaction with organic compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP) leading to the quenching of their fluorescence via Förster resonance energy transfer (FRET) [15,16]. GQDs can also act as electron donors upon interaction with for example, metal ions by photo-induced electron transfer (PET) process [17]. The luminescence properties of GQDs are defined by physical or chemical interactions taking place at their surface and edges. Such interactions have led to either fluorescence quenching or enhancement and are the basis for molecular recognition of ions and small molecules [18]. Owing to the electron donating characteristics of GQDs and the characteristic behaviour of MPcs as both electron donors and acceptors, the photophysical properties of GQDs in the presence of MPcs is highly desired. This study investigates the fluorescence behaviour of GQDs upon interaction with zinc phthalocyanine derivatives in order to explore novel strategies for the modification of GQDs surface and edge states for tailored nanosensor development. The ZnPc derivatives studied are Zn tetraamino phthalocyanine (ZnTAPc, Scheme 1), Zn tetracarboxyphenoxy phthalocyanine (ZnTCPPc, Scheme 2) and Zn [2,9,16,23-tetrakis [4-(*N*-methylpyridyloxy)]-phthalocyanine (ZnTmPyPc, Scheme 2).

This work reports for the first time on the fluorescence properties of GQDs–Pcs nanoconjugates. The effects of various modes of interactions; covalent and non-covalent on the fluorescence behavior of the host-guest hybrid ensembles are also

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