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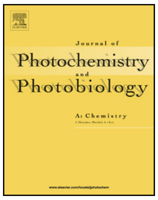

Fluorescence behavior of nanoconjugates of graphene quantum dots and zinc phthalocyanines

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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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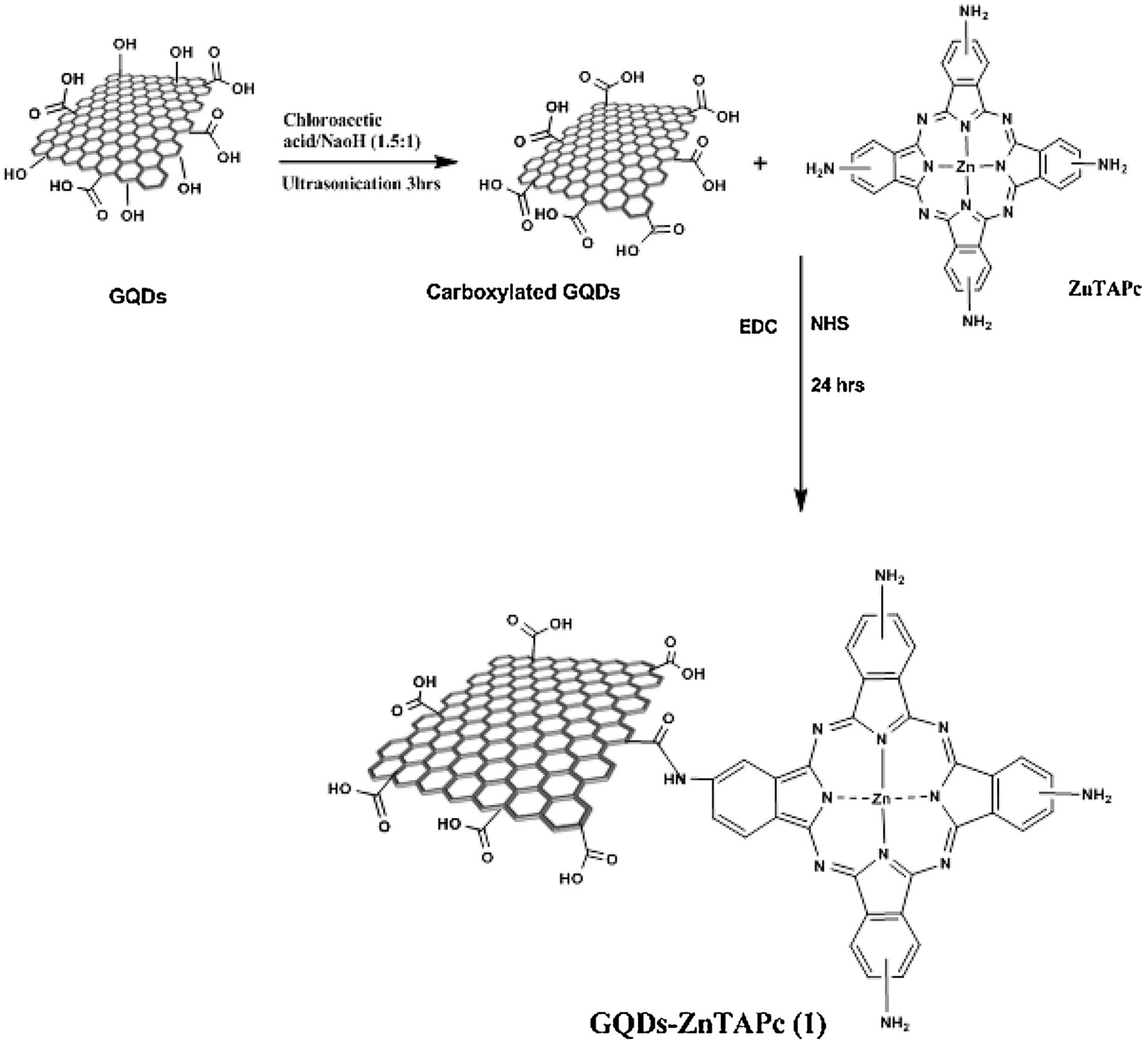

Scheme 1. Covalent linkage of GQDs and ZnTAPc via amide coupling.

reported. It is expected that the fluorescence of GQDs will be quenched in the presence Pcs as is the case with semiconductors QDs. Fluorescence quenching of semiconductors QDs by Pcs is well documented [19] as well as FRET as the interaction mechanism between QDs and Pcs [8,19,20].

2. Experimental

2.1. Materials

Natural graphite powder (<20 μm), chloroacetic acid, Rhodamine 6G, zinc phthalocyanine (ZnPc), dialysis membrane tubing (MWCO 1.5 kDa, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS)) were obtained from Sigma–Aldrich. All aqueous solutions were prepared using ultra-pure water obtained from a Mili-Q Water system (Millipore Corp. Bedford, MA, USA). All other reagents and solvents were obtained from commercial suppliers and used as received. MPcs: 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) were synthesized according to previously reported procedures [21–23].

2.2. Instrumentation

Excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Ground state electronic absorption spectra were performed on a Shimadzu UV-2550 spectrophotometer in the range 300–800 nm. Infra-red spectra were collected on a Bruker Alpha model FT-IR Spectrometer with platinum-ATR. A Metrohm Swiss 827 pH meter was used for pH measurements.

X-ray photoelectron spectroscopy (XPS) analysis was done using an AXIS Ultra DLD (supplied by Kratos Analytical) using Al (monochromatic) anode equipped with a charge neutralizer, the following parameters were used: the emission was 10 mA, the anode (HT) was 15 kV and the operating pressure below 5×10^{-9} Torr. A hybrid lens was used and resolution to acquire scans was at 160 eV pass energy in slot mode. The centre used for the scans was at 520 eV (width of 1205 eV) with steps at 1 eV and dwell time at 100 ms. as reported before [24]. The high resolution scans were acquired using 80 eV pass energy in slot mode. A nonlinear least squares curve fitting procedure was used. The core level binding energies (BEs) were aligned with respect to the C 1s binding energy (BE) of 284.5 eV.

X-ray powder diffraction patterns were recorded on a Bruker D8 Discover equipped with a Lynx Eye detector, using Cu-Kα