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Sn(IV) porphyrin-biotin decorated nitrogen doped graphene quantum dots nanohybrids for photodynamic therapy

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ABSTRACT

Photodynamic therapy (PDT) is a minimally invasive therapeutic procedure for cancer treatment. This study focuses on the synthesis, photophysicochemical properties, and PDT activity of Sn (IV) porphyrin (**2**), when linked to biotin decorated nitrogen doped graphene quantum dots (B-NGQDs). The porphyrin complex **2** was conjugated through an ester bond to B-NGQDs to form **2**-B-NGQDs. Singlet oxygen quantum yield increased for **2** when linked to B-NGQDs to form **2**-B-NQGDs. The dark toxicity and photodynamic therapy studies were conducted for **2**, NGQDs and their conjugates using MCF-7 breast cancer cells. The cell viability for dark toxicity of all the compounds was above 90%, and **2**-B-NGQDs showed high PDT activity at a concentration of 40 μg/mL with cell viability of 22%.

1. Introduction

Photodynamic therapy (PDT) is currently used as an alternative treatment for cancer, and there is evidence that suggests that PDT has the potential to be widely applicable to a wide range of human cancer [1]. PDT is a minimally invasive treatment modality for diseased cancer cells, which uses laser light of appropriate wavelength, a viable photosensitizer to generate cytotoxic reactive oxygen species (ROS, including singlet oxygen) to eradicate diseased cells [2].

Graphene quantum dots (GQDs) are carbon-based nanomaterials that are photostable, biocompatible, soluble in aqueous and non-aqueous solvents, minimally toxic, photoluminescent, and are excellent electron donors [3]. The presence of carboxyl and hydroxyl groups on GQDs surface and edges enable covalent attachment, electrostatic interactions and hydrogen bonding with other suitable moieties [4]. GQDs have been extensively used for targeting and delivery of therapeutic agents to the tumor sites [5]. Doping GQDs with nitrogen to form NGQDs not only increases the charge mobility of the graphitic lattice, but also lowers the energy band gap [6]. In this work NGQDs are linked to biotin (to give B-NGQDs), through an amide bond and the conjugate is linked a Sn(IV) porphyrin (complex **2**) axially through an ester bond (to give **2**-B-NGQDs). The resulting conjugate is employed for PDT.

Biotin is a micronutrient that is required for cellular functions and specifically for cell growth, it is present in larger amounts in cancer cells than in normal cells [7]. Therefore, attaching biotin to a drug that is for cancer treatment helps the drug to locate in the cancer cells. Biotin has been linked to pristine (not N doped) GQDs followed by adsorption of a phthalocyanine (related to porphyrins) [8]. The current work reports for the first time on linking of a porphyrin to B-NGQDs, via an ester bond.

Porphyrins are aromatic macrocyclic structures that are well known as photosensitizers in photodynamic therapy (PDT) [9]. GQDs are also known PDT agents [10]. A combination of two PDT agents (porphyrins and GQDs) has been previously shown to improve PDT through synergistic effect [11]. In this work, a porphyrin containing morpholine complex **2** is employed, morpholine is a known anticancer agent [12]. Porphyrins asymmetrically substituted with morpholine ligands are known and their use for PDT has been reported [13]. However, Cu was employed as a central metal in the literature report. In this work we use a heavy Sn(IV) central metal. The heavy Sn(IV) encourages intersystem crossing to the triplet state, resulting in improved PDT activity [14]. The Sn(IV) porphyrin will then be conjugated to B-NGQDs through an ester bond.

2. Experimental

2.1. Materials

N,*N*-Dicyclohexylcarbodiimide (DCC), 4-dimethylamino pyridine

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