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Theoretical and photodynamic therapy characteristics of heteroatom doped detonation nanodiamonds linked to asymmetrical phthalocyanine for eradication of breast cancer cells

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ABSTRACT

An amide mono substituted benzothiozole phthalocyanine: zinc(II) 3-(4-((3,17,23-tris(4-(benzo [d]thiazol-2-yl) phenoxy)-9-yl)oxy) phenyl)amide phthalocyanine (NH_2BzPc) was covalently linked to undoped and heteroatom doped detonation nanodiamonds (DNDs): B@DNDs, P@DNDs, S@DNDs, N@DNDs, and S&N@DNDs There is a drastic decrease in highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) energy gaps for nanoconjugates compared to DNDs alone. B@DNDs-NH_2BzPc, S&N@DNDs-NH_2BzPc, and P@DNDs-NH_2BzPc showed superior photodynamic therapy (PDT) effects. DNDs-NH_2BzPc also had a small HOMO-LUMO gap, but did not show improved PDT activity compared to the Pc alone, suggesting doping of DNDs is important. This study shows improved PDT effect on Michigan Cancer Foundation-7 breast cancer lines at 7.63%, 7.62% and 6.5% cell viability for P@DNDs-NH_2BzPc, S&N@DNDs-NH_2BzPc and B@DNDs-NH_2BzPc, respectively.

1. Introduction

Detonation nanodiamonds (DNDs) are carbon-based nanomaterials which have found a wide range of medical applications including in drug delivery [1–3], and bioimaging [4,5]. The surface of DNDs contains a complex array of groups, including carboxylic acids, esters, ethers, lactones, amines, etc [6]. In this work, the carboxylic surface groups of DNDs are employed to link to the NH_2 group of a metallophthalocyanine (MPc). The presence of π groups in DNDs also allows for π-π interactions with MPcs. DNDs have different functional groups compared to other carbon nanoparticles (such as graphene carbon nanotubes (g-CNTs), fullerene (C_{60}), graphene quantum dots (GQDs) and carbon nanodots (CDs)) hence will influence the photophysical and photodynamic therapy (PDT) of cancer activities of MPcs differently. DNDs doped with boron, phosphorus and nitrogen heteroatoms have been employed in drug delivery, but not in photodynamic therapy (PDT) [7].

Diseased cancerous tumor cells can be selectively eradicated using PDT. This cancer modality has attracted interest due to its minimal invasion. The therapy utilizes laser light of appropriate wavelength, a viable photosensitizer to generate cytotoxic singlet oxygen species in order to eradicate diseased cells [8]. The three components (the photosensitizer, visible light and molecular oxygen) are nontoxic when separate, however when the photosensitizer is activated by visible light, it is first excited to the singlet state and under appropriate conditions, undergoes intersystem crossing to the excited triplet state where it reacts with molecular oxygen leading to the production of reactive oxygen species (ROS), including singlet oxygen, capable of inducing stress on tumorigenic cells [8]. There are several reports on the use of organic complexes and nanomaterials in cancer treatment and imaging [9–12], however MPcs are known as excellent photosensitizers for PDT [13,14].

Metallophthalocyanines (MPcs) have been vastly utilised across a broad spectrum of applications such as: imaging, nonlinear optics, photodynamic antimicrobial chemotherapy (PACT) and PDT because of their excellent physical and chemical properties [8,15,16]. The ability of MPcs to absorb in the near infrared region of the electromagnetic spectrum (allowing for deep tissue penetration) and to efficiently generate singlet oxygen and other reactive oxygen species (ROS) are amongst some of the properties that have attracted interest in Pcs as potential PDT agents [17–20]. In this work, an unsymmetrical NH_2 substituted ZnPc (Zn(II) 3-(4-((3,17,23-tris(4-(benzo[d]thiazol-2-yl)

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