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Characterization of conjugates of $NaYF_4$:Yb,Er,Gd upconversion nanoparticle with aluminium phthalocyanines

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ABSTRACT

$NaYF_4$:Er/Yb/Gd upconversion nanoparticles (UCNP) capped with amino groups were covalently attached to chloro aluminium tetrasulphonated phthalocyanine (ClAlTSPc) and chloro aluminium tetracarboxy phthalocyanine (ClAlTCPc). The conjugates were characterized using different techniques such as infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). There was a decrease in the intensity of fluorescence emission spectra of the UCNPs at 658 nm in the presence of the phthalocyanines. This decrease indicates an energy transfer between the donor UCNP and conjugated accepting phthalocyanine (Pc), due to Förster resonance energy transfer (FRET). FRET efficiencies of 18% and 21% for ClAlTSPc and ClAlTCPc, respectively, were obtained. Oxygen generation by ClAlTSPc following FRET was proved.

1. Introduction

Upconversion nanoparticles (UCNPs) convert low energy to high energy light [1–5]. The upconversion mechanism relies on a sequential absorption of multiple photons. Typically UCNPs consist of a host matrix and dopant lanthanide ions [4]. The most common UCNPs are Er^{3+}/Yb^{3+} co-doped hexagonal $NaYF_4$ crystals which display ultraviolet, blue, green, red, and near infrared (NIR) emissions [4]. These type of UCNPs have found uses in bioimaging, analytical assays, drug delivery systems and in reactive oxygen species generation [1,3,6,7].

On the other hand, phthalocyanines (Pcs) have found applications as non-linear optical (NLO) materials, in dyes and pigments, light-emitting diodes, photoconductors in laser printers, photosensitizers for photodynamic therapy (PDT) of cancer, electrochromic materials to mention a few [8–13]. Photodynamic therapy (PDT) involves the combination of a photosensitizing drug (e.g. Pcs) and light in the presence of molecular oxygen to obtain a therapeutic effect. The electronically excited photosensitizer (e.g. Pc) transfers energy to ground state molecular oxygen to produce cytotoxic singlet oxygen resulting in irreversible photo-damage of the tumor cells [14]. In this study we look at two different Pcs, namely chloro aluminium tetrasulphonated Pc (ClAlTSPc) and chloro aluminium tetracarboxy Pc (ClAlTCPc). ClAlTSPc was chosen since Photosens® (a mixture of sulfonated aluminum phthalocyanines) is already in clinical trials for PDT [10]. In this work we link ClAlTSPc to UCNPs via a sulphonamide bond and compare the photophysical behaviour of the conjugate to that of ClAlTCPc-UCNPs formed though amide bond. ClAlTCPc has been incorporated inside the silica shells of silica-coated $NaGdF_4$:Yb,Er/$NaGdF_4$ nanoparticles and the conjugate was found to be efficient in generating cytotoxic singlet oxygen under near-infrared (NIR) light irradiation [15]. In other studies, when silicon phthalocyanine dihydroxide ($(OH)_2SiPc$) was covalently grafted (through axial ligation) to mesoporous silica coated UCNPs, generation of singlet oxygen was observed [16]. In the current work, ClAlTCPc is covalently linked to $NaYF_4$:Yb/Er/Gd@Si@NH_2 UCNPs using the ring substituents for the first time. Linking via ring substituents, instead of through axial ligation, is preferred since the latter is limited to some central metals. In addition, the Pcs employed in this work are easily synthesized. Thus, this work allows for a future development of a wide range of Pc-UNCPs conjugates for various applications. Gd^{3+} doping in $NaYF_4$:Yb/Er/Gd@Si@NH_2 UCNPs assists in the control of the nanoparticle size and shape.

We have recently reported on the linking of Al octacarboxy phthalocyanine to $NaYF_4$:Yb/Er/Gd@Si@NH_2 UCNPs, but with no observable Förster Resonance Energy Transfer (FRET) between the two [17]. FRET is a non-radiative energy transfer between a donor (UCNPs) and a suitable energy acceptor (Pc). FRET was also not observed when an unmetalated tetrathiophenoxy phthalocyanine

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