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Nanoconjugates of CdTe@ZnS quantum dots with cobalt tetraamino-phthalocyanine: Characterization and implications for the fluorescence recognition of superoxide anion

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ABSTRACT

The covalent linking of thiol-capped CdTe@ZnS QDs with cobalt tetraamino-phthalocyanine (CoTAPc) has been successfully carried out. Several techniques such as time-resolved fluorescence measurements, thermal gravimetric analysis, transmission electron microscopy and spectrophotometric techniques were employed to characterize the nanoconjugates. Covalent binding of the QDs with CoTAPc resulted in the fluorescence quenching of the former. In the presence of varying concentrations of superoxide anion ($O_2^{\bullet-}$), the fluorescence of the QDs in the conjugate was gradually enhanced and the detection limits obtained were 2.1 and 2.4 nM for the smaller and larger QDs, respectively. Based on the excellent selectivity displayed by the nanoconjugates towards $O_2^{\bullet-}$ over other biologically active species, a potential nanosensor was developed.

1. Introduction

Colloidal semiconductor nanoparticles known as quantum dots (QDs) are monodisperse crystalline clusters whose physical dimensions are smaller than the bulk-exciton Bohr radius and have attracted a great deal of interest over the past decade [1–3]. Their unique optical properties stem from their quantum size effect, size-tunable photoluminescence, and excellent photostability. Due to their exceptional qualities, they have been used as an alternative to conventional molecular probes for applications in bio-imaging, bio-labelling, bio-targeting and sensing [4–8]. A number of QD-based probes based on analyte-induced changes in photoluminescence have been reported [9,10]. Also, QDs conjugated to macrocylic compounds have been used as a means of modifying the surface properties of QDs and thus improving their ability to act as novel fluorescent probes with excellent selectivity towards target species.

Carrillo-Carrión et al. have reported an optical nanosensor for fullerene (C_{60}) using CdSe@ZnS QDs coated with calix[8]arene [11]. Also, a β-cyclodextrin modified CdTe QDs have been reported as fluorescence nanosensor for acetysalicyclic acid [12]. 15-Crown-5 functionalized CdSe@ZnS QDs have been employed for K^+ ion recognition [13] and the use of a porphyrin conjugated CdSe QDs for the direct sensing of Zn^{2+} ion [14] has been reported.

Metallophthalocyanines (MPc) are 18π-electron macrocyclic complexes which have a similar structure to the porphyrins [15–17] and are widely employed as chemical sensors [18–20]. Unlike the QDs-porphyrins conjugates [14,21,22] which have been reported to form inclusion complexes with guest molecules, the fluorescence property of MPc-coated QDs for molecular recognition has never been researched.

In this work, we have synthesized and characterized conjugates of cobalt tetraamino-phthalocyanine (CoTAPc) with 3-mercaptopropionic acid (MPA) capped CdTe@ZnS QDs. The amino groups of the MPc were used to form an amide bond with the carboxylate groups of the QDs, resulting in the formation of a QDs-Pc nanocomplex. Co was chosen as a central metal for the Pc because Co tetrasulphonated-phthalocyanine (CoTSPc) have been reported to mimic the activity of Cytochrome c [23,24]. Cytochrome c is known to be selective towards superoxide anion ($O_2^{\bullet-}$) when coupled with QDs [25,26]. Hence, we chose Co as a central metal for the TAPc ring and investigated its ability to selectively recognize $O_2^{\bullet-}$ when coupled to the QDs. CoTAPc can be covalently linked to QDs forming a stable amide bond. Hence, CoTAPc was employed in this work instead of CoTSPc.

$O_2^{\bullet-}$ is a reactive oxygen specie (ROS), formed as a reduced intermediate of molecular oxygen through enzymatic reactions associated with normal metabolism [27], and has been reported to be associated with various pathological conditions [28,29].

ZnS was used to coat the core CdTe because it is known to be non-toxic [30] and we recently reported that core–shell QDs have better luminescence sensitivity and selectivity towards ROS than their

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