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Quinoline derivative-functionalized carbon dots as a fluorescent nanosensor for sensing and intracellular imaging of Zn^{2+}

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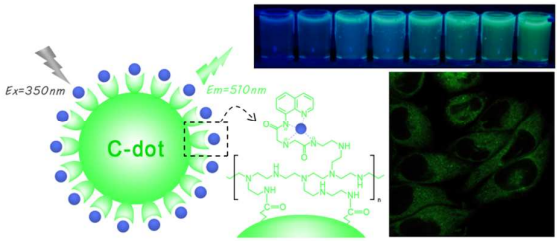
Surface functionalization of nanomaterials with highly specific recognition elements, such as biomolecules and organic molecules, has made possible many novel nanosensors for bio/chemical analysis and target bioimaging. In this report, a fluorescent nanosensor which exhibits highly specific recognition capability towards Zn^{2+} over competing metal ions, has been developed through covalently functionalizing carbon dots (C-dots) with the quinoline derivatives which show response to Zn^{2+}. The nanosensor exhibits excellent water solubility, biocompatibility, and cell-membrane permeability, and demonstrates highly selectivity towards Zn^{2+} with a detection limit as low as 6.4 nM. Additionally, the rapid response of the nanosensor towards Zn^{2+} can be achieved within 1 min. The large amount of recognition units on the outer surface of an individual nanoparticle enables the signal amplification, hence making the immediate and highly sensitive detection of Zn^{2+} possible. Therefore, a reliable and highly specific nanosensor has been demonstrated for both rapid quantitative detection of Zn^{2+} in aqueous solution and real-time imaging of intracellular Zn^{2+}, suggesting its potential and significance in bioanalysis and biomedical detection in the future.

1. Introduction

Surface functionalization of nanomaterials with highly specific recognition elements, such as biomolecules and organic molecules, has made possible many novel nanosensors for bio/chemical analysis and target bioimaging.[1-5] Carbon nanodots (C-dots) which comprise quasispherical nanoparticles with sizes below 10 nm, are becoming both an important class of imaging probes and a versatile platform for developing high-performance nanosensors, due to their fascinating properties such as aqueous solubility, tunable surface functionalities, non-blinking, excellent biocompatibility and cell membrane permeability.[4-7] Surface functionalization of C-dots is paving the avenue towards quantitative detection, high efficient fluorescent imaging, and real-time tracking of targets.[8-20] For example, water-soluble C-dots have been covalently conjugated with AE-TPEA[8] and AE-TPY[9] for the detection of Cu^{2+} and pH in biological systems, respectively. AE-TPEA-functionalized C-dots were also integrated with CdSe/ZnS QDs to develop a ratiometric strategy for intracellular sensing of Cu^{2+}.[10] Taking advantages of two distance-dependent phenomenon, namely color change of AuNPs and FRET, a dual-mode nanosensor with both colorimetric and fluorometric readout for the discriminative detection of GSH under physiological conditions was developed in our group.[12] Cao and co-workers demonstrated that C-dots which can give two-photon luminescence under excitation of 800 nm were able to label both the cell membrane and the cytoplasm of MCF-7 cells without reaching the nucleus.[19]

Zinc ion is the second most abundant transition-metal ion in the human body and plays pivotal roles in biological systems such as facilitating enzyme regulation, gene expression and neural related signal transmission.[21,22] Due to its important biological roles, research interests to develop new probes for Zn^{2+} detection and monitoring with high sensitivity and selectivity is substantially growing in recent years. Of all methods for detecting Zn^{2+}, fluorescence is believed to be the most effective way to determine the concentration, together with visualization of subcellular distribution of Zn^{2+} in living cells. Several fluorescent sensors for Zn^{2+} have been described, including quinoline derivatives,[23-25] rhodamine derivatives,[26-29] pyrene derivatives,[30,31] fluoresceins derivatives,[32] cyanines derivatives,[33] and *etc*. Quinoline based molecules have been studied extensively for Zn^{2+} detection, because of their pH insensitivity and metal-coordination. However, most of quinoline-based probes targeting Zn^{2+} still suffer from poor solubility and bad cell permeability, or lack of efficient selectivity to detect intrinsic levels of Zn^{2+} in biomedical systems.[23]

Since nanoparticles can shelter the probes from interferences and can transport the probes with neglecting their intrinsic solubility, the functionalization of nanoparticles with fluorescent probes is becoming an attractive strategy to develop new sensors for detecting Zn^{2+} *in vitro* and *in vivo*.[34-38] In present report,



Functionalization of carbon nanodots (C-dots) with quinoline derivatives enables a highly sensitive and specific nanosensor for Zn^{2+} sensing in aqueous solution and Zn^{2+} imaging *in vivo*.