View Article Online
DOI: 10.1039/C8NR03879A

Nanoscale

COMMUNICATION

Mercury Ion-DNA Specificity Triggers a Distinctive Photoluminescence Depression in Organic Semiconductor Probes Guided with Thymine-Rich Oligonucleotide Sequence.

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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DNA strands recently found to play a role in crystallizing organic semiconductors as a substitute to conventional surfactants. Such DNA-guided organic semiconductor particles possessed recognition ability to complimentary target DNAs, resulting in "enhanced luminescence" due to the lesser degree of non-radiative dissipation. Apart from this, in this present study we developed selective recognition of mercury ions by utilizing DNA probes having ion-specific thymine-rich motif. Strikingly, the specific ion-DNA interaction triggered rather a distinctive "depressed luminescence" emitting from the particles. Mercury ions found to be present both at the surface and the inner regions, which was discovered to relate drastic morphological distortion of the particles as evidenced by elemental, electron microscopic, and confocal fluorescence microscopic analyses. This novel phenomenon discovered would expand technological values of organic semiconductors conjugated with oligonucleotides toward a wider range of target-specific applications.

Introduction

Since the double helix structure of DNA was revealed[1], DNA has been considered not only a natural biological information carrier, but also a useful construction material with various functions. Inspired by the unique physical and chemical properties of DNA, scientists have taken advantage of DNA to construct nano-objects of well-designed architectures[2]. For example, the unique base-pairing rules and structural features of DNA can assemble plasmonic nanoparticles into structures with useful properties[3]. Additionally, DNAs have been used to precisely position proteins[4], carbon nanotubes[5], and other functional components into deliberate patterns using DNA tile-based approaches or a DNA-origami strategy[6].

π-Conjugated molecules are effective materials with excellent optical and electrical properties such as organic photonics[7], biosensors[8], etc[9]. Especially, as one of the famous display materials, tris (8-hydroxyquinoline) aluminum (Alq_3) has been intensively studied for its application to electroluminescent cells since it was first reported[10]. Because of potential applications to nanoscale optoelectronic devices, one-dimensional (1D) Alq_3 nanowires or rods that are fabricated by various methods have attracted much attention[11]. Recently, synthesis of a DNA-guided organic semiconductor through a facile solution route for the first time was reported by our group[12]. Single-strand DNA (ssDNA) guiding an organic semiconductor plays a unique role in crystallization[12(a)]. As continuation of this research, we have imparted a biological recognition function to the ssDNA-guided Alq_3 rods for the first time that only specific DNA-DNA recognition triggers photoluminescence (PL) enhancement by specific surface binding to complimentary DNA[12(b)]. Therefore, the development of ssDNA-guided organic semiconductors with various functions should be important. In the present study, we gave the ssDNA-guided organic semiconductor another function: specific interaction of toxic heavy metal, mercury in this research. According to the literature, when mercury ions are present, a G-quadruplex or hairpin-shaped DNA conformation is formed due to coordination bonds: thymine-mercury-thymine[13]. Therefore, DNA-guided organic semiconductors act as a responsive fluorophore, and DNA molecules serve as the recognition probe that can selectively bind to mercury ions. To the best of our knowledge, this is the first demonstration of interaction of mercury ions via alteration of the PL emission of Alq_3 materials.

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DOI: 10.1039/x0xx00000x
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