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Simultaneous enhancement in phosphorescence and its lifetime of PtOEP-peptide assembly triggered by protein interaction

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ABSTRACT

We fabricated hybrid nanoparticles consisting of organic semiconducting material with peptide sequence to reflect the target protein interaction. A phosphorescent OLED material, platinum octaethylporphyrin (PtOEP) was self-assembled by reprecipitation with the A17 peptide (YCAYYSPRHKTTF) selected as a probe ligand in order to recognize heat shock protein 70 (HSP70). The phosphorescence intensity of the PtOEP-A17 assembly was enhanced by 125 % after treatment with HSP70. The specificity of the protein interaction was confirmed in both solution and solid states of the PtOEP-A17 assembly against to BSA and nucleolin. We figured out that the phosphorescence lifetime of PtOEP-A17 assembly after exposed to HSP70 increased significantly to 153 ns from initial 115 ns. These simultaneous enhancements in phosphorescence and lifetime triggered by the specific protein interaction would open new applications of PtOEP, a representative material of light-emitting device fields.

1. Introduction

Organic semiconductors have become important in recent applications of technology, owing to their successful utilizations in optoelectronic applications such as organic light-emitting diodes (OLEDs) [1]. Organic semiconductors based on polymers and small molecules have advantages in simple molecular tailoring for optimal properties, highly flexible structure, and low-cost fabrication [2,3]. Recently, advanced optoelectronic devices have been studied using phosphorescent materials, so both the singlet and the triplet states participate in the emission process [4–6]. A well-known phosphor is platinum octaethylporphyrin (PtOEP). PtOEP has powerful intersystem crossing, because spin-orbit coupling is enhanced by the heavy atom effect of Pt. [7–9] Interesting characteristics of PtOEP were also studied for applications including oxygen sensing [10,11] and triplet-triplet annihilation upconversion [12,13]. In the field of bio-applications, PtOEP can have the advantages of avoiding autofluorescence via long-lived emission and relatively longer excitation wavelength (~ 510 nm). Nevertheless, there has been few approaches utilizing PtOEP toward bio-related fields.

One distinctive approach integrates a biological application with OLED material, tris(8-hydroxyquinoline) aluminum (Alq_3). Alq_3 was hybridized with DNA oligomers and aptamers to enable DNA recognition and protein interaction [14–19]. The fluorescence enhancement from the Alq_3-single strand DNA hybrid assembly was obtained after the forming of DNA double helix [14]. Alq_3 crystals hybridized with the DNA aptamer were also studied to detect the target protein by fluorescence increase [15]. However, for more comprehensive biofield applications of OLED materials, investigations on the assembly utilizing peptide ligands have been much desired.

In this study, we describe the enhancement of photoluminescence (PL) of PtOEP-peptide assembly induced by specific protein interaction (Scheme 1). Enhancement in phosphorescence intensity and lifetime is a hot topic for the advanced application such as persistent afterglow imaging, biotherapy, anti-counterfeiting and others [20–22]. As a phosphor emitter, PtOEP was chosen because of its longer lifetime (~0.1 μs) than fluorescent material such as Alq_3 (~1 ns). PtOEP was self-assembled with peptide ligand forming hybrid crystals by reprecipitation method, which was first discovered as peptide hybridized OLED material. Peptide aptamer, whose folding structure is an important factor to bind target, maintained their structure after hybridizing with OLED material. A17 peptide aptamer was used to recognize a heat shock protein 70 (HSP70), which increase the cells' sensitivity to apoptosis

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