Macromolecular Research

Communication

DOI 10.1007/s13233-018-6141-x

www.springer.com/13233 pISSN 1598-5032 eISSN 2092-7673

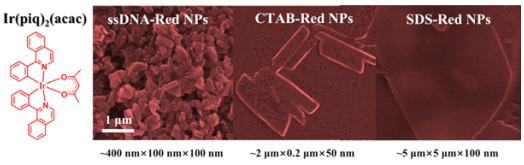
Fabrication of Red-Light Emitting Organic Semiconductor Nanoparticles *via* Guidance of DNAs and Surfactants

Jin Hyuk Park[†,1]
Seung Hyuk Back[†,2]
Hyeon Mun Jeong[1]
Dong June Ahn[*,1,2]

[1] Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea
[2] KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Korea

Received April 30, 2018 / Revised May 24, 2018 / Accepted May 25, 2018

Abstract: Organic semiconductor materials for fabricating organic light emitting diodes (OLEDs) have attracted significant attention in the field of novel optical and optoelectronic devices. Particulation of OLEDs' emitting materials in small-scale has been limited only to tris(8-hydroxyquinoline) aluminum (Alq_3) that emits green-light. In this study, we attempted to fabricate, for the first time, red-light emitting nanoparticles of phosphorescent organic semiconductor of bis(1-phenylisoquinoline) (acetylacetonate) iridium ($Ir(piq)_2(acac)$). Rectangular particles with length and thickness of ~2 μm and ~50 nm were fabricated with guidance of cetyltrimethylammonium bromide (CTAB) and micro-plates with length and thickness of ~5 μm and ~100 nm were fabricated by sodium dodecyl sulfate (SDS). By contrast, single-stranded DNA (ssDNA) induced nano-rods with dimension of ~400 nm in length and 100 nm in thickness. Hence, the choice of guiding agents resulted in distinctive crystal characteristic so that the nanorods by ssDNAs showed UV absorption with a red-shift in metal-ligand charge transfer (MLCT) by 54 nm whereas the particles by surfactants did 35 nm compared to the dissolved precursor. Higher was the ssDNA-guided nanorods in relative phosphorescence of the intensity at 610 nm over that at 695 nm than the surfactant-guided particles.



Keywords: red-light emitting nanoparticles, organic semiconductors, DNAs, surfactants, bis(1-phenylisoquinoline) (acetylacetonate) iridium ($Ir(piq)_2(acac)$).

1. Introduction

π-Conjugated molecules are effective materials having better optical and electrical properties for organic photonics, biosensors, *etc.*[1-5] Especially, Since Tang and VanSlyke first discovered an efficient low-voltage driven organic light emitting diode (OLED) based on tris(8-hydroxyquinoline) aluminum (Alq_3) among π-conjugated molecules in 1987,[6] the great potential of OLEDs as electroluminescent devices in various display applications has been recognized and there has been enormous progress in the design of efficient OLEDs.[7-9] The emitting layer of OLED consists of a film structure with nanometer-scale thickness and small molecules like Alq_3, tris(2-phenylpyridine) iridium(III),[10] bis[2-(4,6-(difluorophenyl)pyridinato-C^2,N)] iridium(III),[11] *etc.* In particular, iridium organometallic complexes are considered good phosphorescent materials[12] because of the spin-orbit effect caused by the heavy metal ion. Many studies have been dedicated to the fabrication of particles based on organic phosphors.[13-21] Particle syntheses with small molecules for OLED emitting materials have been reported.[22-26] Our group previously reported the fabrication of Alq_3 microparticles assisted by fluorescence dye-labeled DNA and confirmed a change in the optical properties of the Alq_3 rod, where the Förster resonance energy transfer (FRET) effect[25] and specific DNA-DNA recognition by bio-recognitive microparticles triggered photoluminescence (PL) enhancement.[26] Particulation of emitting semiconductor in small-scale has been currently limited only to Alq_3. In this study, we fabricated particles by a facile synthetic method using bis(1-phenylisoquinoline) (acetylacetonate)iridium(III) ($Ir(piq)_2(acac)$), a phosphorescent material showing highly efficient electroluminescence in OLED,[27] for the first time. Our objective of this study is the fabrication of red-emitting organic semiconductor nanoparticles under synthetic conditions; by positive and negative surfactants, and single-strand DNA (ssDNA) used to guide the particle formation.

2. Experimental

$Ir(piq)_2(acac)$, cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), tetrahydrofuran (THF), and chloroform (≥99%) were purchased from Aldrich. Oligonucleotides were synthesized by Bioneer. The ssDNA sequence was used: NH_2-5′-ATCCTTATCAATATTTAACAATAATCC -3′.

The particles were fabricated by modification of a previously reported method.[27] Commercially available $Ir(piq)_2(acac)$ powder (3.05 mg) was dissolved in THF (2 mL) to obtain a 1.53 $mg{\cdot}mL^{-1}$ stock solution. The surfactant solutions were prepared by dissolving ssDNA or CTAB or SDS in deionized water. The concentrations of the ssDNA, CTAB, and SDS solutions were 0.8 μM, 1 mM, 8.2 mM, respectively. The stock solution (2 mL) of the precursor was injected into the surfactant solution with vigor-

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF, 2017R1A2B3006770 and 2017M3D1A1039421) and a Korea University Grant.

***Corresponding Author:** Dong June Ahn (ahn@korea.ac.kr)
[†]These authors contributed equally to this work.