



Showcasing research from Prof. Dong June Ahn and Prof. Jinsoo Joo at Korea University, Korea

Oligonucleotide assisted light-emitting Alq3 microrods: energy transfer effect with fluorescent dyes

Oligonucleotide assisted Alq3 microrods show a significant photoluminescence variation owing to the Förster resonance energy transfer to Cy3-oligonucleotides. Versatile nucleotide manipulation would open up wider applications of Alq3-based materials.

As featured in:



See Jinsoo Joo, Dong June Ahn *et al.*, *Chem. Commun.*, 2013, **49**, 5360.

Oligonucleotide assisted light-emitting Alq3 microrods: energy transfer effect with fluorescent dyes†

Cite this: *Chem. Commun.*, 2013, **49**, 5360

Received 17th February 2013,
Accepted 15th March 2013

DOI: 10.1039/c3cc41255e

www.rsc.org/chemcomm

Chunzhi Cui,^a Dong Hyuk Park,^{abc} Jeongyong Kim,^d Jinsoo Joo^{*b} and Dong June Ahn^{*a}

Oligonucleotide assisted tri(8-hydroxyquinoline) aluminium (Alq3) microrods were prepared for the first time. When hybridized with oligonucleotide labeled by Cy3 fluorescent dye, a significant photoluminescence variation of the Alq3 microrods was observed due to Förster resonance energy transfer, unlike when Cy5-oligonucleotide was used. Versatile nucleotide manipulation would open up wider applications of Alq3-based materials, based on this fundamental observation.

As one of the most successful electroluminescent organic materials, Alq3 was first used for efficient low voltage driven organic light emitting diodes by Tang and Van Slyke.¹ Thereafter, metalloquinolates have been intensively studied for their application in electroluminescent materials.^{2,3} Many studies on Alq3 have focused on device optimization for high luminescence and long-term stability.^{4,5} In particular, one-dimensional (1-D) Alq3 nanowires or microrods have attracted much attention because of their potential applications in nanometer-scale optoelectronic devices.^{6–9} For example, the field emission properties were reported with amorphous Alq3 nanowires prepared by vapor condensation.⁷ Recently, synthesis of surfactant-assisted Alq3 microrods or sub-microwires through a facile solution-phase route has been reported.^{9–11} Organic π -conjugated materials such as polydiacetylene and polythiophene derivatives in conjunction with oligonucleotides possess optical functions useful for target- or environment-responsive behavior.^{12–16} Therefore, development of novel Alq3-based materials showing well-controlled optical properties by oligonucleotide functionalization would be of much significance.

Herein, we report the facile self-assembly growth of Alq3 in oligonucleotide-containing solutions to fabricate hexagonal shaped crystalline microrods. When the oligonucleotide labeled with Cy3 fluorescent dye was used, a significant FRET resulted from the interaction between the Alq3 molecules and the dye. However, in the case of the Cy5 fluorescent dye, a low FRET phenomenon is observed. To the best of our knowledge, there are no reports on the preparation of Alq3 microstructures with the aid of biomolecules such as oligonucleotide as well as their optical functions. Oligonucleotide-assisted 1-D Alq3 microrods studied here can be extended to applications in effective biosensors owing to their excellent crystalline structure and optical properties generating the FRET effect, with the organic crystal rod waveguide as a chemical sensor.¹⁷ Novel Alq3 microrods were prepared by a facile re-precipitation method.^{18,19} First, commercially available Alq3 powder was dissolved in tetrahydrofuran (THF) at a concentration of 1 mg ml⁻¹. A 400 μ l aliquot of the stock solution was injected into 10 ml of aqueous oligonucleotide solution (100 nM) under vigorous stirring (*ca.* 900 rpm) for 10 min. Subsequently, the mixture was kept at room temperature for 10 h. The oligonucleotide sequence used was the 27-mer anthrax lethal factor (NH₂-5'-ATC CTT ATC AAT ATT TAA CAA TAA TCC-3'). The image obtained using scanning electron microscopy (SEM) (Fig. 1(a)) shows that the Alq3 particles prepared in deionized water exhibit irregular macroscopic shapes.

In contrast, it can be clearly observed that the Alq3 prepared in oligonucleotide solution has successfully self-assembled in the form of a hexagonal prismatic microrod, as shown in Fig. 1(b). A similar structure has been observed when synthesis was performed using a microemulsion method involving surfactants.¹⁰ Fig. 1(c) and (d) show that insertion of Cy3 and Cy5 fluorescent dyes at the 3' end of the oligonucleotide had no effect on the particulate morphology and resulted in similar hexagonal prismatic shape and size, as compared to the case of preparation with the aid of non-labeled oligonucleotide. In addition, the presence of oligonucleotide in the Alq3 microrods was confirmed using energy dispersive X-ray spectroscopy (EDS) combined with high-resolution transmission electron microscopy (HR-TEM) and Fourier transform infrared spectroscopy (see Fig. S1 and S2, ESI†). Fig. 1(e), (f), and (h) show the images obtained by using a charge coupled device (CCD).

^a Department of Chemical and Biological Engineering, and KU-KIST School of Converging Science and Technology, Korea University, Seoul 136-713, Korea.
E-mail: ahn@korea.ac.kr; Tel: +82-2-3290-3301

^b Department of Physics, Korea University, Seoul 136-713, Korea.
E-mail: jjoo@korea.ac.kr; Tel: +82-2-3290-3103

^c Division of Nano-Systems Engineering, Inha University, Incheon 402-751, Korea.
E-mail: donghyuk@inha.ac.kr

^d Department of Physics, University of Incheon, Incheon 406-772, Korea.
E-mail: jeongyong@incheon.ac.kr; Tel: +82-32-835-8222

† Electronic supplementary information (ESI) available: Description of detailed analysis of HR-TEM images, EDS, FTIR spectra, SEM images, XRD patterns, and PL spectra. See DOI: 10.1039/c3cc41255e