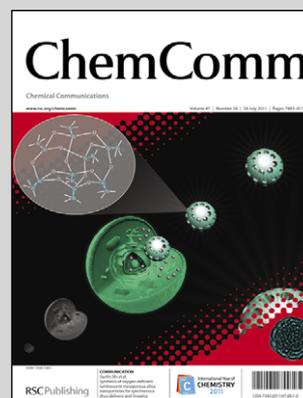


Showcasing research from Professors Jinsoo Joo and Dong June Ahn (Korea University) and Professor Jeongyong Kim groups, Korea

DNA detection using a light-emitting polymer single nanowire

Optical DNA detection is presented using a light-emitting polymer single nanowire (NW). The luminescence color of the polymer single NW was changed from green to red after attaching the probe-DNAs and then luminescence intensity of the NW was dramatically enhanced by hybridizing target-DNAs.

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DNA detection using a light-emitting polymer single nanowire†

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Functionalization of light-emitting poly(3-methylthiophene) (P3MT) nanowires (NWs) with probe-DNA (p-DNA) and their label-free recognition of target-DNA (t-DNA) were correlated quantitatively with both the photoluminescence (PL) color and intensity of P3MT NWs.

The efficient hybridization of biological materials with functional condensed matter is important for biological sensing in terms of accuracy, sensitivity, and signal response time.^{1–3} The use of low-dimensional nanomaterials has advantages for DNA and protein detection owing to their sensitivity, accuracy, and physical size matching.^{4–7} π -Conjugated materials have been assessed as active systems for biological sensing^{8–11} because of their better compatibility with biological materials and their optical and electrical signal generation properties.^{9–11} Most of the studies of π -conjugated polymer-based biosensing have shown their usefulness in the solution states.^{9–12}

An efficient method for DNA detection without a fluorescent dye on the nanoscale can be proposed through the use of a single strand of light-emitting polymer NWs with lightly-doped states. The doped conducting polymers have been used for various solid-state sensors.¹³ Biological materials can be detected readily through variations in the light-emitting characteristics of polymer NWs with high signal amplification when the appropriate receptors are linked to the surfaces of the NWs. The light-emitting P3MT material is a promising system to study dopant-mediated DNA detection in fluorescence chain reaction (FCR) enhanced PL because of the formation of doping-induced bipolaron (*i.e.*, cationic) states.¹⁴

Herein, light-emitting P3MT NWs were electrochemically prepared using dodecylbenzene sulfonic acid (DBSA) or tetrabutylammonium trifluoromethane sulfonic acid (TBACF₃SO₃) as a dopant based on an anodic alumina oxide nanoporous template. The p-DNA was attached easily to the P3MT NWs

through electrostatic interactions between the sulfuric trioxide (SO₃⁻) group from the dopant and the terminal amine (NH₃⁺) group attached to the end of the p-DNA. A green to red color change of a single P3MT NW was observed after attaching the p-DNA. The PL intensity was enhanced dramatically by hybridizing the target-DNA (t-DNA) onto the P3MT/p-DNA single NW, which was confirmed through the quantum yield (Φ_{QY}) measurements. The PL enhancement of the P3MT/p-DNA + t-DNA single NW was detectable for t-DNA concentrations from 100 aM to 100 nM. Using 1-mer mismatched t-DNA, the PL intensity of the single NW was weaker than that of the NW using perfectly matched t-DNA.

Fig. 1 shows the nanoscale luminescence characteristics, such as luminescence color charge-coupled device (CCD) images and laser confocal microscope (LCM)^{15,16} PL images and spectra of an isolated single strand of as-prepared, p-DNA attached, and t-DNA hybridized P3MT NWs with DBSA dopants. The luminescence color of the P3MT(DBSA) single NW was green with relatively low brightness. When coupled with p-DNA, the luminescence color of the P3MT(DBSA) single NW changed from green to red (Fig. 1a and inset of Fig. 1a). The red-shift of the luminescence color of the NW through coupling with p-DNA was attributed to conformational modification of the P3MT main chains by electrostatic interactions between the SO₃⁻ group of the NW and the NH₃⁺ group and the negatively charged phosphate backbone of the wrapping p-DNAs. After hybridization with t-DNA, the luminescence intensity of the P3MT(DBSA) single NW was enhanced considerably compared to that of the as-prepared and p-DNA-immobilized P3MT(DBSA) NWs (Fig. 1b). The LCM PL spectra of the single NWs were compared (Fig. 1c). For quantitative analysis of the LCM PL spectra, the maximum intensity of the LCM PL spectrum of the as-prepared P3MT(DBSA) NW was used as the reference unit value. The main PL peak of the as-prepared single NW was observed at approximately 554 nm. When coupled with p-DNA, the main PL peak of the NW was red-shifted to approximately 640 nm and its intensity decreased slightly. Upon hybridization of the P3MT(DBSA)/p-DNA NW with t-DNA, the maximum intensity of the LCM PL peak was enhanced dramatically up to approximately six times compared to that of the as-prepared NW. This is consistent with the results of the color CCD and 3-D LCM PL images (Fig. S4, ESI†). The change in the luminescence characteristics of P3MT(DBSA) NWs was also studied using 1-mer mismatched t-DNAs. When the p-DNAs were coupled with the 1-mer mismatched t-DNAs (100 nM concentration),

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† Electronic supplementary information (ESI) available: Description of detailed analysis of FT-IR spectra, LCM PL images, and quantum yield, real-time DNA detection movie, and comparative DNA detection study using dedoped-P3MT NWs and solvent effects. See DOI: 10.1039/c1cc11362c

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