



# Enhanced single molecule fluorescence of conjugated polymer poly(3-hexylthiophene) on silver-nanocubes



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## ABSTRACT

We investigate the enhancement of poly(3-hexylthiophene) (P3HT) single molecule fluorescence using silver-nanocube as substrates. Results show that the silver nanocube substrate enhances the single molecule fluorescence of P3HT by about 7 folds and effectively improves the photophysical stabilities of individual P3HT molecules by delaying the photobleaching process. We find that the increase of the radiative decay rates, resulted from the coupling between photogenerated excitons and surface plasmon, is directly related to the observed fluorescence enhancement of P3HT. The enhanced local field provided by the silver-nanocube substrate also contributes to fluorescence enhancement via coupling. This coupling depends on the overlap between the emission frequency of the fluorophore and the surface plasmon field provided by the substrate. As the emission wavelength of the fluorophore gets closer to the surface plasmon resonance of silver nanocubes, the coupling becomes stronger, leading to greater fluorescence enhancement.

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## 1. Introduction

To date, measurements and devices based on molecular fluorescence have been widely used in fields such as chemistry, molecular biology, materials science, photonics, and medicine. Detection sensitivities of the applications such as single molecular detection [1–3], DNA sequencing [4,5], and monitoring circulation in the heart and retina [6] all depend directly on the inherent brightness of the molecular fluorophore [7]. Enhancing the molecular fluorescence is important, because it will presumably improve both sensitivity and efficacy of the fluorophore-based techniques.

Metal-enhanced fluorescence (MEF), also called surface-plasmon enhanced fluorescence, has emerged as a new method for fluorescence enhancement. Metallic nanostructures using noble metals (Ag, Au, Pt) can greatly enhance the fluorescence of adjacent fluorophores, increase their photo-stabilities, decrease lifetimes due to increased radiative decay rates, and increase the distances for fluorescence resonance energy transfer (RET). A wide range of metal nanostructures such as continuous thin films [8,9], island-like nanostructures [10], nanorods [11], and nanowires [12], have been used to enhance fluorescence of various fluorophores,

including quantum dots [13,14], small dye molecules [12,15–17], and conjugated polymers [10,18]. Despite extensive researches on fluorescence modification by noble metal nanostructures, the role of the plasmon resonance energy with respect to a fluorophore's excitation and emission energies has not been well understood [7]. Previous studies have focused primarily on the high quantum yield quantum dots and small dye molecules, while much less on the low quantum yield conjugated polymers [12–14,16–18]. Enhancing fluorescence from fluorophores with intrinsic low quantum yield is important, because it will expand the applications and improve the performance of fluorophores such as conjugated polymers in organic devices.

In organic devices, film morphology and interactions between polymer chains have been reported to impact the overall performances of these devices. In bulk materials, the complex intermolecular interactions of the polymer are closely associated with morphological changes at nanometer scale. For example, variations in nanometer-scale morphology will lead to large changes in molecular properties of the polymer [19]. Therefore, it is very difficult to distinguish whether the morphology or the inter polymer interaction or both contribute to the overall optical and electrical properties of these devices. Poly(3-hexylthiophene) (P3HT), as a great conjugated polymer with high charge carrier mobility, excellent film forming properties and high environmental stabilities, has been employed as a model polymer to investigate the optical

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and electrical properties of conjugated polymers in organic devices [20]. Hu and his colleagues have used single particle spectroscopy to study the correlation between spectroscopic and morphological properties of single nanoparticle of P3HT/PCBM composite [21]. Their results reflect the overall contributions from multiple molecules because each composite nanoparticle is comprised of several or dozens of molecules. Intra-molecular energy relaxation and migration of P3HT's isolated chains in dilute chloroform solution have been investigated using time- and energy-resolved fluorescence [22]. The sub-100 fs spectral migration and depolarization observed in isolated P3HT chains have been assigned to the strong coupling between electronic excitation and the intramolecular nuclear degrees of freedom, which is also responsible for rapid dynamic exciton localization. However, P3HT in organic devices are usually in solid film morphology, and heat-induced crystallization appears to improve the efficiencies of the devices. The morphologies of P3HT chains in thin films are therefore different from those in solutions, and the properties of single P3HT molecule in the actual applied environment are not identical to those in solutions. In addition, the regioregularity of P3HT molecules can both influence the bulk film morphologies and properties, and play an important role in isolated chain conformations, thus affecting the absorption and emission properties [23]. Moreover, the external electromagnetic field can alter the absorption and emission properties of the fluorophores. Taken together, it is important to study the single molecule fluorescence of the conjugated polymers in solid matrix and to examine the influence of plasmonic resonance energy on absorption and emission of the fluorescent molecule.

Various hybrid nanostructures of  $\pi$ -conjugated polymers with nanoscale metals have been fabricated and applied to photoluminescence (PL) enhancement through surface plasmon resonance (SPR) coupling by Joo's group [24], such as coaxial bi-layered polymer-metal hybrid nanotubes (NT), serial-type hybrid nanowires (NW), hybrid polymer NW with attached metal nanoparticles (NPs), and hybrid polymer NP with metal NPs. Those hybrid nanostructures, using light-emitting polythiophene (PTh) [25], poly(3-methylthiophene) (P3MT) [26], poly(3-butylthiophene) (P3BT) [27], poly(2-methoxy-5(2'-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) [28] and nanoscale metals, have shown several tens even hundreds times enhancement in PL intensity. Though these results are quite inspiring, the template-based synthetic method or re-precipitation method seems to be a little complex and those methods limit the morphologies of metal nanostructures to be nanotubes, nanowires or nanoparticles. Moreover, those studies are still on the bulk film level. In this communication, we developed a very simple method to fabricate an effective nanostructure for investigating the optical properties of regiorandom P3HT (rra-P3HT) isolated chains in poly(methylmethacrylate) (PMMA) matrix. In our strategy, metal nanostructures with different morphologies can be easily replaced and applied to PL enhancement, which makes it very valuable to organic-based displays and nanometer-scale optoelectronics. Here, we focused on the SP-enhanced single molecule fluorescence on silver nanocube substrate, and ulteriorly revealed the interactions between rra-P3HT molecules and silver nanocube substrate.

## 2. Experimental section

### 2.1. Materials

Regiorandom P3HT (rra-P3HT) was purchased from Echo Chemical Co. Ltd., Taiwan,  $M_w = 68$  kDa; PMMA with average molecular weight  $M_w = 600$  kDa was synthesized by radical polymerization with AIBN as initiator. Toluene for HPLC ( $\geq 99.9\%$ ) was purchased from Sigma-Aldrich.

### 2.2. Preparations of samples

Glass cover slides and quartz substrates were first cleaned in a solution with a volume ratio of 30%  $H_2O_2$  in water to  $H_2SO_4$  of 3:7 for 24 h. After that, all substrates were sonicated in distilled water for 15 min for 5–6 times. Before using, all substrates were dried with a stream of nitrogen and treated with UV ozone in plasma cleaner for 10 min. Both P3HT and PMMA were first dissolved in toluene and afterward appropriate concentrations were prepared by adding the P3HT solution into the PMMA solution. At last, the concentrations of P3HT were adjusted to  $1 \times 10^{-2}$  mg/mL and  $1 \times 10^{-6}$  mg/mL, respectively, for the ensemble and single molecule experiments. From these solutions, thin films (thickness  $\sim 100$  nm) were spin-coated onto thoroughly cleaned substrates. After the spin coating process, all samples were vacuum-dried at  $50^\circ C$  for 8 h to remove the residual solvents. The concentration of the density and the amount of P3HT were strictly controlled. Firstly, the concentrations of P3HT and PMMA matrix were strictly controlled and then the complex solution was mixed adequately for more than 24 h before using. Secondly, the thickness of polymer films was also controlled through controlling the speed and time during the spin-coating process.

### 2.3. Single molecule measurements

A total internal reflection fluorescence microscopy (Leica AM TIRF) equipped with an Ar ion laser was utilized to study P3HT at single molecule level. For total internal reflection fluorescence (TIRF) microscopy, the focus was adjusted to the interface between the sample and coverslip, and the laser was aligned to achieve the optimum angle of reflection. All TIRF images were acquired at a depth of 150 nm. All images were acquired using a Leica AM TIRF microscope DMI6000 (Leica Microsystems) with an attached Hamamatsu EM-CCD camera, using HCX PL APO 100 $\times$  oil objective with numerical aperture of 1.47 and appropriate filter cubes. The excitation power of the laser was 20 mW at the samples.

### 2.4. Ensemble measurements

UV-vis absorption spectra were recorded with a PerkinElmer Lambda750 UV-vis-NIR spectrophotometer. Both steady state and time-resolved fluorescence measurements were taken on a FLS-920 spectrometer (Edinburgh Instruments, Ltd.). For steady state measurements, the samples were excited by Xe lamp at 488 or 520 nm. Time-resolved measurements were carried out by using a pulse laser with an excitation wavelength of 405 nm. The Raman spectroscopic analysis was performed on a Renishaw in Via Laser micro-Raman spectrometer equipped with an Ar ion laser as the excitation resource (633 nm). The laser beam was focused with an objective lens (Lycar 50 $\times$ , N.A. = 0.75). Spectra were obtained within 20 s of exposure.

## 3. Results and discussion

All samples were prepared by spin-coating the P3HT and PMMA containing solution on the blank glass/quartz substrates or the silver nanocube substrates, as shown in Fig. 1(a). The silver layer was spin-coated from the silver nanocubes colloid solution in ethanol at an appropriate concentration. We assume that the emission from the fluorophore close to the silver nanocubes (green) is enhanced, while that far from silver nanocubes (red) remains the same as the fluorophore on bare glass. Silver nanocubes, prepared by chemical reduction of silver nitrate through a polyol process [29], have a mean edge length of  $\sim 150$  nm, with slightly truncated corners and edges [Fig. 1(b)]. The thicknesses of the complex polymer layers on both substrates measured by Veeco Dektak 6M stylus profiler

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