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## Enhanced Two-Photon Emission in Coupled Metal Nanoparticles Induced by Conjugated Polymers

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Received September 13, 2010. Revised Manuscript Received October 7, 2010

Interactions between noble metal (Ag and Au) nanoparticles and conjugated polymers as well as their one- and two-photon emission have been investigated. Ag and Au nanoparticles exhibited extraordinary quenching effects on the fluorescence of cationic poly(fluorinephenylene). The quenching efficiency by 37-nm Ag nanoparticles is  $\sim 19$  times more efficient than that by 13-nm Au nanoparticles, and 9–10 orders of magnitude more efficient than typical small molecule dye–quencher pairs. On the other hand, the cationic conjugated polymers induce the aggregate formation and plasmonic coupling of the metal nanoparticles, as evidenced by transmission electron microscopy images and appearance of a new longitudinal plasmon band in the near-infrared region. The two-photon emissions of Ag and Au nanoparticles were found to be significantly enhanced upon addition of conjugated polymers, by a factor of 51-times and 9-times compared to the isolated nanoparticles for Ag and Au, respectively. These studies could be further extended to the applications of two-photon imaging and sensing of the analytes that can induce formation of metal nanoparticle aggregates, which have many advantages over the conventional one-photon counterparts.

### Introduction

In the past decades, intensive research has been carried out in preparation of noble metal nanoparticles (NPs) of various sizes and shapes due to their unique optical properties and wide range of potential applications in catalytic, nonlinear optics, chemical and biological sensing and bioimaging.<sup>1–6</sup> In particular, metal NPs display unique optical property known as surface plasmon resonance (SPR), which arises from the collective oscillation of the conduction band electrons.<sup>7</sup> These SPR bands are sensitive to the morphology of the metal NPs as well as the surrounding dielectric media, and can be tuned from blue to near-infrared.<sup>8</sup>

Nobel metals are generally known as nonfluorescent. Photoluminescence in gold was first observed by Mooradia in 1969 with quantum yield as low as  $10^{-10}$ .<sup>9</sup> Boyd et al. later observed much higher photoluminescence from metal films with rough surfaces.<sup>10</sup> The luminescence quantum efficiencies of Au nanospheres and Au nanorods have been determined to be  $10^{-6}$  and  $10^{-4}$ , respectively.<sup>11,12</sup> The significantly enhanced photoluminescence in rough metal surface or metal NPs is generally attributed to strong local electric fields, which result in enhancement of the radiative recombination rates. Although metal NPs are poor light emitters under one-photon excitation, silver and gold NPs were

found to exhibit enhanced two-photon excitation emission,<sup>13–16</sup> which was ascribed to enhanced excitation efficiency due to the increased local electric field induced by localized SPR.

NPs having longitudinal plasmon modes at the near-infrared region, coincident with a biological transparency window, are particularly attractive candidates for two-photon photoluminescence agents. The plasma resonance can be tailored to near-IR by preparing anisotropic nanostructure such as nanorods or nanowires.<sup>17,18</sup> Alternatively, it can be tuned by assembling NPs into one-dimensional (1-D) or two-dimensional (2-D) nanostructures.<sup>19,20</sup> Strong two-photon photoluminescence was previously observed from gold nanorods or aggregated NPs on glass substrate.<sup>21</sup> It is usually difficult to control the aggregation of NPs on the substrate, as NPs randomly aggregate themselves as the solvent evaporates. In addition, it is difficult to use nanoaggregates on substrate in the applications in homogeneous environment. It is thus preferred to assemble NPs in solution to control their aggregation for their potential applications.

Previously we observed the formation of a gold nanochain induced by conjugated polymers, which could be utilized as a surface enhanced Raman spectroscopy (SERS) substrate with an enhancement factor of 400 times compared to the one made of isolated NPs.<sup>22</sup> Here in this work, we further demonstrated that

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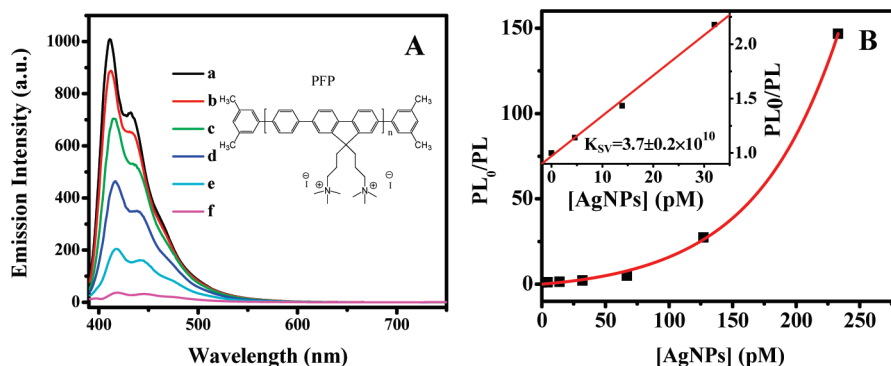
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**Figure 1.** (A) One photon excitation fluorescence spectra of PFP (2.5  $\mu\text{M}$  in repeat units) in the presence of different concentrations (0, 4.6, 13.9, 32, 67, and 127 pM) of 37 nm Ag NPs (a–f). (B) Plot of PFP quenching versus concentration of Ag NPs. The inset is the linear dependence in the low quencher concentration regime.

conjugated polymer-induced aggregation of Ag and Au NPs in homogeneous solution could result in significant enhancement in two-photon excitation emission. The two-photon emission of Ag and Au NP aggregates were found to be enhanced by 51 times and 9 times, respectively compared to the isolated ones. The formation of metal NP aggregates could be induced by many biologically important species.<sup>23–25</sup> Plasmonic coupling-induced two-photon emission enhancement could be utilized to develop many potential applications such as two-photon bioimaging and sensing, which possess many advantages compared to their one-photon counterparts.

## Experimental Section

**1. Materials.** Silver nitrate ( $\text{AgNO}_3$ , 99%) and gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.9%) were purchased from Aldrich. Trisodium citrate dihydrate (99%) was obtained from Fluka. Poly[(9,9-di(3,3'-*N,N'*-trimethylammonium)-propyl-fluorenyl-2,7-diyl)-*alt-co*-(1,4-phenylene)] diiodide salt (PFP) (MW 10 000–15 000) was purchased from American Dye Source. All chemicals were used as received without further purification. Water used in the preparation of all samples was purified with cartridges from Millipore (NANOPure, Barnstead, NH, USA) to a resistivity of 18.0  $\text{M}\Omega \cdot \text{cm}$ .

**2. Methods.** **2.1. Preparation of Ag NPs.** Ag NPs were prepared by using a citrate reduction method.<sup>26</sup> 4.5 mg  $\text{AgNO}_3$  was dissolved in 100 mL of  $\text{H}_2\text{O}$  and brought to boiling. Six milliliters of 1% sodium citrate solution was then added. The solution was kept boiling for 1 h. The prepared Ag colloids have a plasmon band with band maximum at 414 nm and a mean diameter of 37 nm. Ag NPs were purified by centrifugation at 9000 rpm for 10 min to remove the excess citrate ions.

**2.2. Instrumentations and Characterizations.** Transmission electron microscopy (TEM) images of NPs were taken from a Philips CM10 TEM microscope (at an accelerating voltage of 100 kV). Pictures of the samples were taken by using a Canon 500D DSLR camera. Ultraviolet–visible (UV–vis) extinction and one-photon excitation fluorescence spectra were measured by using a SHIMADZU UV-2550 spectrophotometer and a SHIMADZU RF-5301PC fluorometer, respectively.

The two-photon excitation fluorescence was measured by using a Spectra Physics femtosecond Ti:sapphire oscillator (Tsunami) as the excitation source. The output laser pulses have a central

wavelength at 800 nm with pulse duration of  $\sim 80$  fs and repetition rate of 80 MHz. The samples were excited by directing a tightly focused laser beam onto the sample. The emission from the sample was collected at a  $90^\circ$  angle to the direction of the excitation beam to minimize the scattering. The fluorescence signal was directed into a CCD (Princeton Instruments, Pixis 100B) coupled monochromator (Acton, Spectra Pro 2300i) with an optical fiber. A 750 nm short pass filter was placed before the spectrometer to minimize the light scattering from the excitation light.

## Results and Discussions

Positively charged conjugated polymers and negatively charged metal NPs can interact through electrostatic attractions and display interesting properties. Conjugated polymers are fluorescent molecules and have been utilized in many biological applications.<sup>27–31</sup> It has been previously reported that fluorescence of conjugated polyelectrolytes near gold NPs could be dramatically quenched, which was called superquenching.<sup>32</sup> On the other hand, conjugated polymers can induce aggregation of metal NPs.<sup>22,23</sup>

Here we observed that the negatively charged Ag NPs can quench the emission of cationic conjugated polymer, PFP, with very high efficiency (Figure 1). The samples were excited at the absorption maximum of PFP, 380 nm. Upon gradual addition of 37-nm Ag NPs, the PFP emission was significantly quenched, almost all the emission was quenched after addition of 127 pM Ag NPs. The results indicate that one Ag NP can quench lots of PFP fluorophores ( $> 1000$  repeat units).

Fluorescence quenching is usually described by the Stern–Volmer equation,  $\phi_0/\phi = 1 + K_{\text{SV}} [\text{Quencher}]$ , where  $\phi_0$  and  $\phi$  are fluorescence quantum yields of the fluorophore in the absence and presence of the quencher.  $\phi_0/\phi$  is equal to the ratio of the fluorescence being quenched. The Stern–Volmer constant  $K_{\text{SV}}$  generally describes the quenching efficiency. At low concentrations of Ag NPs,  $\phi_0/\phi$  versus quencher concentration is linear, and the quenching process follows the Stern–Volmer relationship, which gives a Stern–Volmer quenching constant of  $K_{\text{SV}} = 3.7 \times 10^{10} \text{ M}^{-1}$ . At high concentrations of Ag NPs,  $\phi_0/\phi$  versus quencher concentration is nonlinear. The quenching process deviates from the Stern–Volmer relationship and

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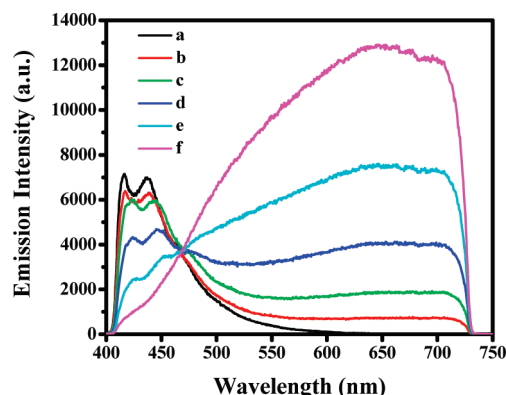
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**Figure 2.** Two-photon emission spectra of PFP (2.5  $\mu\text{M}$  in repeat units) in the presence of Ag NPs with concentrations of 0, 4.6, 13.9, 32, 67, and 127 pM (a–f). The excitation power was 200 mW.

displays a superquenching behavior.<sup>32</sup> Similar quenching experiments were also performed by using 13-nm gold NPs. The quenching efficiency by Ag NPs is  $\sim 19$  times more efficient than 13 nm Au NPs ( $K_{\text{SV}} = 1.98 \times 10^9 \text{ M}^{-1}$ , see the Supporting Information), and 9–10 orders of magnitude more efficient than typical small molecule dye–quencher pairs. Energy transfer is believed to be the primary reason for the observed superquenching.<sup>32</sup> The perfect spectral overlap between Ag NPs absorption and PFP emission (Figure S2) and very strong SPR absorption band of Ag NPs ensure efficient energy transfer from conjugated polymers to the metal NPs. In addition, quenching efficiency is amplified by exciton delocalization within the conjugated polymer.<sup>33</sup> Electrostatic interactions between conjugated polymers and Ag NPs result in the formation of a 1-D or three-dimensional (3-D) assembly of PFP/Ag NPs, which will further amplify the quenching effect. It was also believed that electron transfer between the conjugated polymers and metal NPs might also be responsible for the observed quenching effects.<sup>34</sup>

However, the results are strikingly different when we performed the similar experiments under two-photon excitation (Figure 2). Femtosecond laser pulses with central wavelength at 800 nm were used as the excitation source. Upon addition of Ag NPs, the PFP emission was gradually quenched, similar to the one-photon excitation case. However, another new broad emission band appeared at the longer wavelength side (500–700 nm), concomitant with the gradual decreases of PFP emission. This new emission became even much brighter than that of original PFP in the absence of any Ag NPs under excitation at 800 nm femtosecond laser pulses.

The effects are more evident when we did the similar experiments by gradual addition of PFP into a fixed concentration (127 pM) of Ag NPs instead (Figure 3). In the original Ag NPs solution without any PFP, the emission is very weak. Only a rising tail extending to near-IR was observed, which might be mainly due to the scattering. However, a broad band emission between 500 and 700 nm appeared upon addition of conjugated polymers and increased dramatically when more PFP was added. We could even directly observe a very bright orange-yellow color with the naked eye. The emission at 600 nm was enhanced by a factor of 51 upon addition of 5.0  $\mu\text{M}$  PFP. Gold NPs displayed similar enhancement of two-photon emission, by a factor of 9 upon addition of conjugated polymers (see Supporting Information).

This new broadband emission is believed to arise from two-photon excitation emission of aggregated Ag NPs induced by conjugated polymers. To confirm the two-photon excitation nature of the emission, the power dependence of the emission under excitation of 800 nm femtosecond laser pulses was measured for the sample with 127 pM of Ag NPs and 2.5  $\mu\text{M}$  of PFP (sample e). The loglog plot of the emission intensity versus laser power gives a slope of 1.9, confirming that the emission arises from two-photon excitation. The multiphoton excitation nature of the emission was further confirmed by exciting the samples using a continuous wave (CW) laser of the same total power at 800 nm, no emission could be detected at all (line h in Figure 3A).

It is well-known that the metal nanorods typically have much stronger two-photon excitation emission than spherical metal NPs.<sup>35</sup> It has also been known that conjugated polymers can induce aggregate formation of Au NPs and display extinction spectra similar to that of Au nanorods.<sup>22</sup> The enhanced two-photon excitation emission of the complex is likely due to the formation of Ag NP aggregates.

Formation of Ag aggregates can be confirmed by TEM images and UV–vis extinction spectra. Figure 4A,B shows the TEM images of isolated and aggregated Ag NPs. In the presence of PFP, the negatively charged Ag NPs form a nanochain structure consisting of several NPs. The UV–vis extinction spectra of Ag NPs also undergo significant change upon addition of cationic PFP. Upon addition of PFP, the transverse SPR absorption of Ag NPs at 414 nm decreased, and another new band appeared in the longer wavelength region (500–900 nm). An obvious color change from yellow to dark green was observed (Figure 4C inset). The new band further shifted to longer wavelength when more PFP was added. The extinction spectra of Ag NPs/PFP are similar to those of metal nanorods, which further confirm the formation of chainlike structure. The longitudinal resonance band of Ag NP aggregates shifted to longer wavelength with more PFP added, suggesting an increased chain length at higher concentration of polymers. When 2.5  $\mu\text{M}$  PFP was added, the longitudinal SPR mode was centered at 800 nm. The resulting complex was very stable, and no obvious precipitation was observed after several days.

The formation of Ag NPs aggregate is believed to be induced by electrostatic interactions between cationic PFP and negatively charged Ag NPs, which bring individual Ag NPs into proximity to cause plasmonic coupling. The plasmon coupling causes the SPR band to develop into two modes,<sup>36</sup> as demonstrated in Figure 4B. The formation of the new longitudinal plasma band in the near-IR range, on one hand, provides an enhanced local electric field. On the other hand, the near-IR Plasmon band might provide an intermediate state for the two-photon absorption processes. Both factors will greatly enhance the two-photon excitation efficiency and result in significantly enhanced two-photon emission.

It was previously demonstrated that white light continuum radiation, in addition to two-photon photoluminescence, can be generated by illuminating picosecond laser pulses at gold dipole antenna due to strong field enhancement at the antenna feed gap.<sup>16</sup> The white light continuum was found to follow a fourth order power law on the excitation intensity. Here in our experiments, the emission is believed due to two-photon excitation since it follows a second order power law on excitation intensity. Two-photon photoluminescence has also been observed in clusters of closely spaced gold NPs or aggregates and have found applications in bioimaging,<sup>15</sup> which was believed due to enhancement by

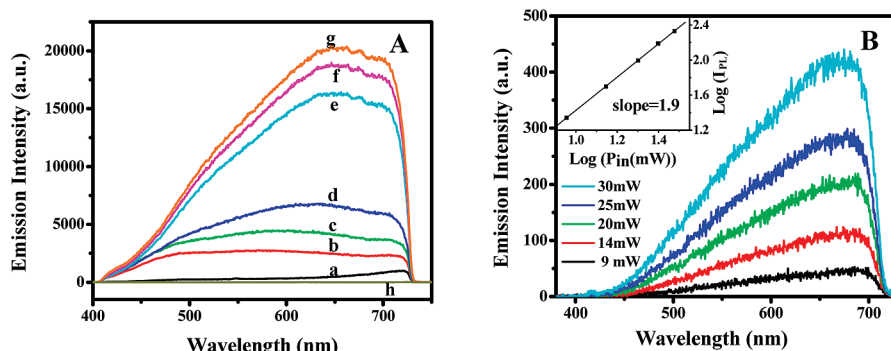
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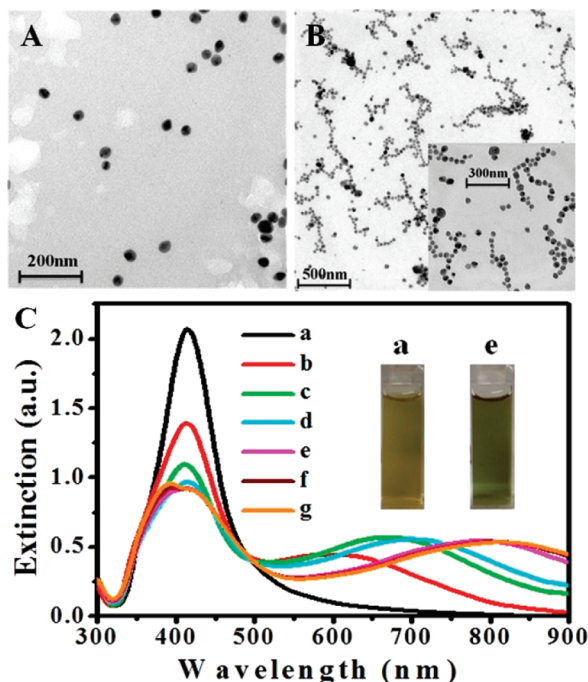
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**Figure 3.** (A) Two-photon luminescence of Ag NPs (127 pM) in the presence of different concentrations of PFP (0, 0.25, 0.5, 1.25, 2.5, 3.75, 5.0  $\mu\text{M}$  from a to g). The excitation power is 200 mW. h is for Ag NPs in the presence of 5.0  $\mu\text{M}$  of PFP (sample g) but under excitation of a CW laser of the same average power. (B) Power dependence of the emission of Ag NPs/PFP complex under excitation of 800 nm femtosecond laser pulses for the sample with 127 pM of Ag NPs and 2.5  $\mu\text{M}$  of PFP (sample e).



**Figure 4.** TEM images of (A) isolated Ag NPs and (B) aggregated NPs (127 pM Ag NPs in the presence of 0.5  $\mu\text{M}$  PFP). (C) UV-vis extinction spectra of 127 pM Ag NPs in the presence of PFP with concentrations of 0, 0.25, 0.5, 1.25, 2.5, 3.75 and 5.0  $\mu\text{M}$  (in monomer repeat units) from a to g.

the strong localized SPR. Here we used conjugated polymers to induce the formation of longitudinal plasmon resonance, which will result in enhanced two-photon excitation emission. Most recently, Heeger et al. reported a colorimetric detection method to identify different forms of DNA, proteins and some small molecules, which were based on the different aggregation degree of gold NPs induced by many biomolecules with different conformations.<sup>23</sup> We have also found that other ions or polyelectrolytes having opposite charges to that of metal NPs, such as  $\text{Na}^+$  and poly(allylamine hydrochloride), can also induce the aggregation of metal NPs, can thus enhance the two-photon emission of metal NPs. Our studies could be further extended

to the applications of two-photon imaging and sensing. For example, pH induced aggregation of metal NPs inside the cells could be potentially useful for cancer cell imaging.<sup>37</sup> Charged membrane could induce the aggregation of oppositely charged metal NPs, which could be potentially utilized in two-photon bioimaging. Analytes that can induce the aggregation of metal NPs could be quantitatively detected by two-photon sensing. Two-photon imaging and sensing have many potential advantages over their conventional one-photon counterparts such as deep penetration and noninvasive in situ detection.

## Summary

Metal nanoparticles have been known as efficient fluorescence quenchers to suppress the emission of strongly fluorescent conjugated polymers. In this work, we demonstrated conjugated polymer-induced formation of metal NP aggregates, which display significantly enhanced two-photon excitation emission efficiency. Two-photon emission of Ag NP and Au NP aggregates were found to be enhanced by factors of 51 and 9, respectively, compared to the isolated ones. The origin of the enhancement was ascribed to the formation of longitudinal plasmon absorption band in the near-IR region. The longitudinal plasmon band, on one hand, provides enhanced local electric field; on the other hand, it provides an intermediate state for the two-photon absorption processes. Both effects will greatly enhance the two-photon excitation efficiency and result in significantly enhanced two-photon emission. The aggregation of metal nanoparticles could be induced by other oppositely charged polyelectrolytes, which could be further extended to promising applications in the quantitative and qualitative novel two-photon detections of biomolecules.

**Acknowledgment.** This work is supported by DSTA Singapore (R-143-000-432-422) and the Faculty of Science, National University of Singapore (R-143-000-403-112).

**Supporting Information Available:** Details of interactions between PFP and Au NPs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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