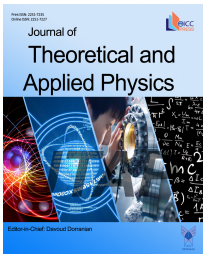

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# Strong plasmon–exciton coupling in Au nanoparticle conjugated MEH−PPV polymer

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**Original Research**

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**Abstract:**

This study investigates the effects of incorporating gold nanoparticles (Au NPs) into a MEH−PPV polymer on its fluorescent properties. Analysis of the fluorescence spectrum of the polymer reveals a significant increase in fluorescence intensity upon the addition of Au NPs. Further investigation using Laser Induced Fluorescence (LIF) spectra demonstrates that the purified polymer emits light at 480 nm and 532 nm, with additional peaks attributed to energy transfer mechanisms. This study shows cases the potential of gold nanoparticles to enhance the fluorescence of light-emitting polymers such as MEH−PPV, thereby having implications for applications like LED fabrication, sensor development, and bio imaging. The results highlight the capability of gold nanoparticles to augment fluorescence intensity and energy transfer, opening avenues for future research and improvement.

**Keywords:** Plasmon Coupling; Light-Emitting Polymer; MEH-PPV; LAL; Au NPs

## 1. Introduction

In recent years, the light−emitting polymers (LEPs) have received great attention due to its unique characteristics, it is that not only provide flexibility and light weight, but also provide a large surface area for interaction and low−cost devices [1, 2]. A semiconductor conjugated polymers are among the most successful and important of these materials for use as active materials in optoelectronic devices due to their high photoluminescence (PL) quantum yield [3], large gain cross section [4], wide emission spectrum [5], and ability to be electrically pumped [6].

One of the most the semiconductor conjugated polymersispoly(1−methoxy−4−ethylhexyloxyparaphenyl enevinylene) (MEH−PPV) [7].The MEH−PPV is considered a promising future for electroluminescent organic semiconductor materials for optoelectronic devices, it is cheaper, easier to manufacture, and exhibits intense photoluminescence in the visible spectrum, it making perfect for use in optoelectronic applications [8], such as the polymer light−emitting diodes (PLEDs) [9], the photodiodes photovoltaic [10], and the field−effect transistors [11]. Despite the many advantages of the LEPs, there are many obstacles facing researchers interested in this field, including those related to the thermal stability of the LEPs and others related to optoelectronic devices based on the LEPs, because they are considered to have weak properties to separate and transfer of the electron−hole [12].To overcome these problems, several techniques have been proposed, including a well−established strategy of combining between LEPs and a metal nanoparticles, this will greatly improve the performance of the optical devices based on light−emitting polymers [13]. By revising the literature, there are several studies showing improvements in the optoelectronic properties of the MEH−PPV mixed with nanomaterials, such as $TiO_2$ and $SiO_2$ [14]. Laser−Induced Fluorescence (LIF) is a powerful spectroscopic technique that utilizes laser light to analyze molecules and atoms, providing insights into their composition and behavior. [15]. Nanoparticles can be produced using the pulsed laser ablation method at different concentrations. The method involves using a laser to ablate a target material in a liquid medium [16]. The coupling between plasmons generated by nanoparticles and excitons created in light−emitting polymers enables energy transfer and boosts both absorption and emission processes. This coupling holds significant implications for optoelectronic applications like improving light emission

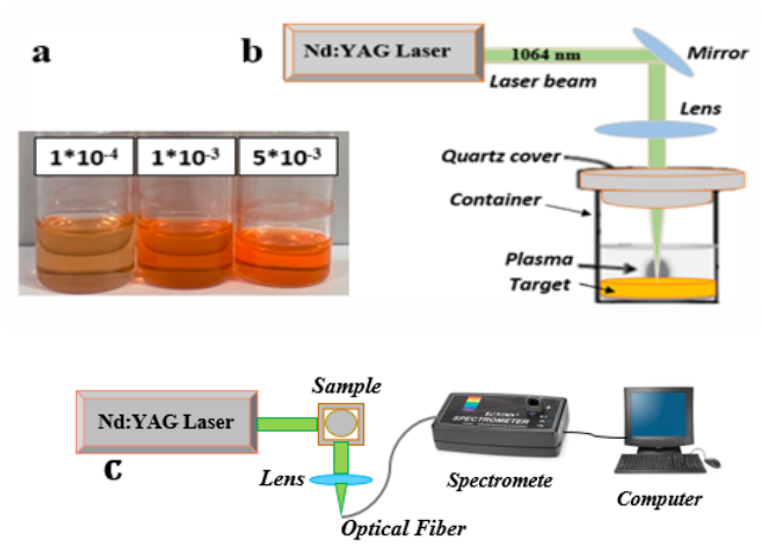


**Figure 1.** a) the image of the MEH−PPV polymer samples with different concentrations, b) the setup of the Pulsed laser ablation in liquids. c) the setup of the LIF technique.

in organic LEDs, creating highly sensitive sensors, and enhancing light absorption and charge generation in solar cells. Damasiano et al. studied the optical properties of the effect of plasma on light-emitting polymers and copolymers containing oxadiazole units and found that they exhibited photoluminescence in the blue spectral range upon UV irradiation. Wohlgenannt and Vardeny studied blue−emitting polymers, identifying PA bands related to triplet excitons and charged polarons. The study explores the effect of surface plasmon resonance (SPR) on the optoelectronic properties of MEH−PPV polymer by combining gold nanoparticles (Au NPs) with MEH−PPV polymer. The researchers used laser ablation in liquids (LAL) to produce gold nanoparticles mixed with dissolved toluene in different concentrations. This research provides valuable insights for researchers, potentially enhancing photonic device development based on light−emitting polymers.

## 2. Materials and Experimental Procedure

In this study, the light−emitting polymer (MEH−PPV) with a molecular weight of 276.4 was purchased from Sigma−Aldrich, Germany, which it was dissolved in a Toluene (C7H8) using three different concentrations ($1 \times 10^{-3}$, $5 \times 10^{-3}$, and $1 \times 10^{-4}$ M), as shown in Fig. 1 a. The Toluene solvent (molecular weight 92.14) is products' the Sisco Research Laboratories (SRL) Company.

In addition, the gold NPs were experimentally prepared from a pure gold target (purity >99.9%with a thickness of 2 mm,) by the Pulsed Laser Ablation in Liquids method (PLAL). The PLAL setup works with a Q−switched Nd: YAG lasers operated with wavelength 1064 nm, pulse width 5 ns, repetition rate 10 Hz, and with 80 mJ energy per pulse focused directly on the gold target, the setup is shown in Fig. 1 b.

Thereafter, the Au NPs were created with three different concentrations (a number of different pulses; 250 pulse, 500 pulse, and 750 pulse). Three concentrations of the MEH−PPV polymer are mixed with each of concentration of Au nanoparticles colloids at a ratio of (50:50) and use for LIF measurement under the Nd: YAG laser as shown schematically in Fig. 1 c.

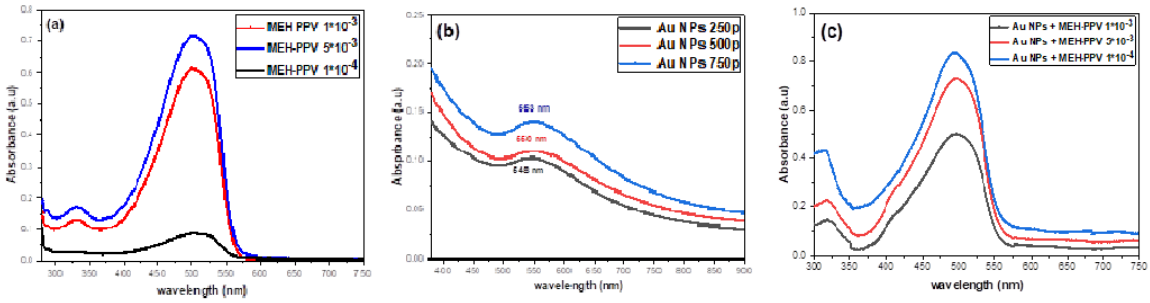


**Figure 2.** Absorption spectrum of a) the MEH−PPV in different concentrations, b) the Au NPs in different laser pulses, and c) the matrix between Au NPs and MEH−PPV in different concentrations.

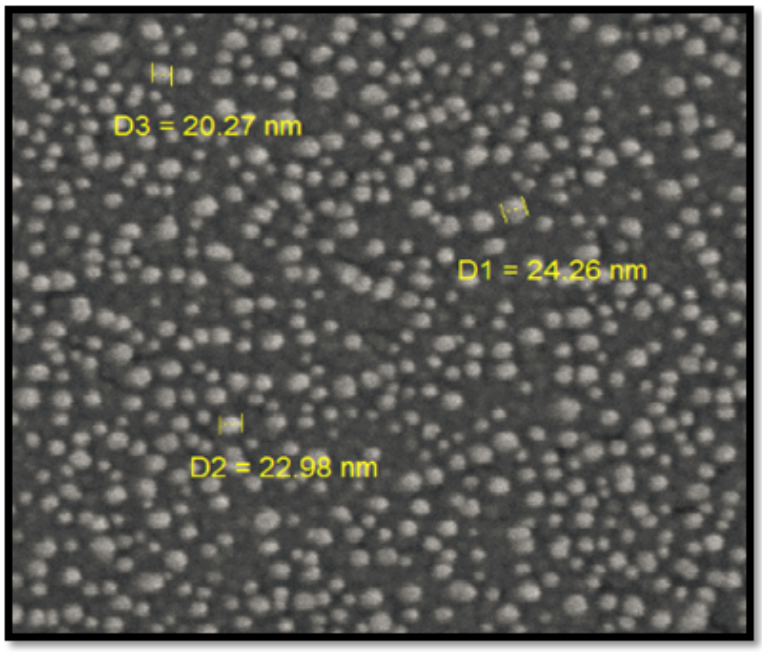


**Figure 3.** SEM image of Au nanoparticles which was attended by laser ablation.

## 3. Results and discussions

The optical spectroscopy of the different concentrations of the Au NPs with the MEH−PPV polymers, which was measured using a 190− 900 nm UV–Vis spectrophotometer (model CECIL7200 Korea) as shown in Fig. 2.

The absorption spectrum of the MEH−PPV dissolved in toluene increases with increasing concentration, as shown in 2 a. The absorption spectra of the Au NPs increase with a slight red shift in wavelength when the number of laser pulses is increased that create by the PLAL method, this is due to the Au NPs increased dispersed in the toluene. This leads to an increase in the size of some nanoparticles due to their agglomeration, which leads to an increase in the refractive index of the medium and the appearance of the red shift, the behavior is shown in 2 b. The Au NPs selected with the highest number of laser pulses and mixed with the MEH−PPV polymer. Where we noted the improvement of the absorption spectra of the polymer and the Au NPs matrix compared to the pure polymer for all concentrations, as shown in 2 c. This improvement in properties is caused by coupling between the plasmon and the exciton in polymer host medium.

Fig. 3 shows the top view SEM images of Au nanoparticles which was attended by laser ablation. As shown in the figure, the gold nanoparticles form a regular spherical body with a Nano−size ranging from 20 to 24 nanometers.

From the point of view of fluorescence spectrum, it confirms that addition of nanoparticles has a significant effect on the fluorescence intensity of MEH−PPV polymer (Fig. 4). The black line in the graph represents the fluorescence spectrum of the MEH−PPV polymer without the addition of any nanoparticles. As we introduce progressively higher concentrations of nanoparticles, there is a significant improvement in fluorescence intensity.

Initially, when Au Np 250p is added, there is a significant increase in the fluorescence intensity. This increase becomes more evident when Au Np 500p is added. However, when the concentration reaches Au Np 750p, a decrease in the fluorescence spectrum is observed. This decrease can be attributed to the cooling phenomenon caused by the higher concentration of nanoparticles. Based

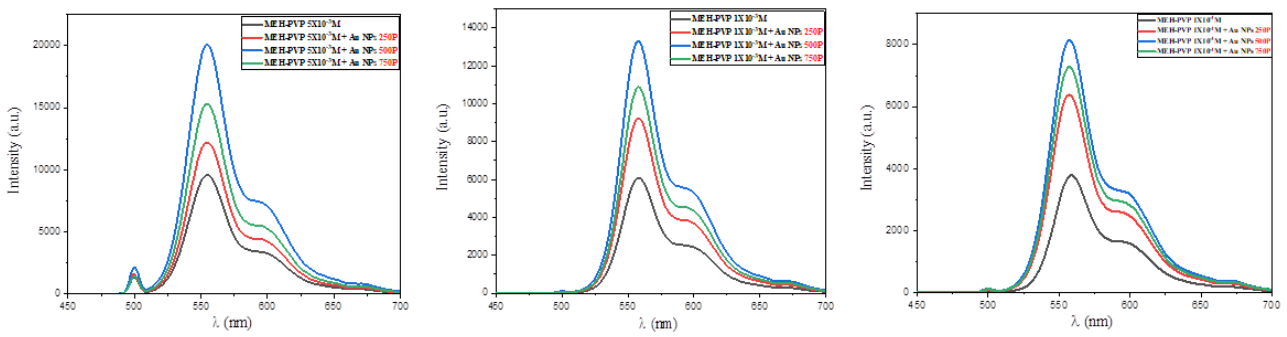


**Figure 4.** Fluorescence spectrum of MHE-PPV polymer with Au nanoparticles at different concentrations.

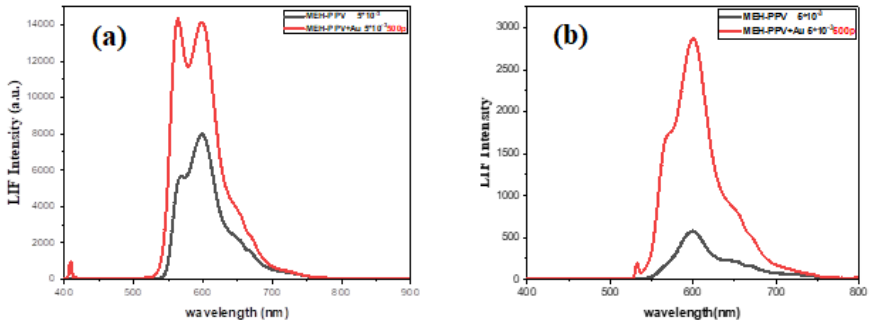


**Figure 5.** LIF intensity for MHE-PPV polymer with the maximum excitation concentration of Au nanoparticles (a) at 480 nm wavelength and (b) at 532 nm wavelength.

on these observations, it can be concluded that the optimal emission spectrum of the MEH−PPV polymer occurs when the nanoparticle concentration is 500p.

Furthermore, the LIF spectra of two samples were analyzed for their LIF spectra: the first sample was made entirely of MEH−PPV polymer, whereas the second sample included both the polymer and gold nanoparticles. Both samples were excited at a wavelength of 480 nm to get these spectra as shown in Fig. 5 a. This shows that the pure polymer emits light, especially at this wavelength when triggered at 480 nm in the LIF spectra of the pure polymer sample. However, the second peaks in the LIF spectra in the sample containing gold nanoparticle referee that the polymer content gold nanoparticles alter the polymer's capacity to emit light and These peaks are most likely the result of the interaction between the polymer and the gold nanoparticles. This behavior may be explained by the fact that gold nanoparticles function as localized surface Plasmon resonators, which may improve the polymer's emission characteristics. The observed peaks in the LIF spectra may be attributed to energy transfer mechanisms that are induced by the interaction between the polymer and the gold nanoparticles. The first peak, which is weaker in intensity, indicates a change in the emission wavelength from the pure polymer's wavelength. This alteration might be explained by modifications to the polymer's electrical structure or energy levels brought on by the presence of gold nanoparticles. On the other hand, the presence of gold nanoparticles is indicated by the second peak's increased intensity, which shows a large increase in emission. The greater emission intensity at this particular wavelength suggests that the interaction between the polymer and the gold nanoparticles promotes more effective energy transfer mechanisms. In conclusion, the MEH−PPV polymer's ability to produce light is affected by the inclusion of gold nanoparticles. Due to the interaction between the polymer and the gold nanoparticles, two peaks that arise in the LIF spectra of the sample containing gold nanoparticles reflect changes in the emission wavelength and intensity. For this system to be optimized for particular applications and to gain a better understanding of the underlying mechanics, more investigation and characterization will be required. As a result, laser induce fluorescence has been shown to have a significant impact on light−emitting polymers. The process involves using ultraviolet lasers to activate the polymer surface.

The LIF spectra presented in this figure show significant changes in the light−emitting properties of the MEH−PPV polymer upon introduction of gold nanoparticles. The most obvious effect is an increase in the intensity of the shine. Gold nanoparticles, which are well known for their unique optical properties, including surface Plasmon resonance (LSPR), likely contribute to this enhancement. The LSPR effect increases the interaction between the nanoparticles and the incident light. Thus, when the polymer is excited at a wavelength of 532 nm, it absorbs more energy due to the presence of gold nanoparticles as shown in Fig. 5 b. This amplified absorption and more efficient energy transfer led to an increased intensity of the emitted light, accounting for the observed increase in luminescence intensity. One can see here the coupling between plasmon of AuNPs and exciton of LEP happens.

Furthermore, the results indicate a subtle shift in the peak wavelength of fluorescence, from approximately 599.4 nm for the pure polymer to roughly 600.3 nm for the polymer−gold nanoparticle mixture. This slight shift suggests an alteration in the energy levels of the polymer, likely influenced by changes in its local environment brought about by the addition of the gold nanoparticles. It's also noteworthy to mention that while gold nanoparticles generally enhance luminescence intensity, they can potentially quench fluorescence if they reside too close to the polymer's fluorophores. However, in this particular experiment, the enhancement effect clearly outweighs any potential quenching impact. In conclusion, this experiment underscores the potential of gold nanoparticles to amplify the luminescence of light−emitting polymers, such as MEH−PPV. Such an enhancement could have significant implications for industries reliant on luminescence, including the manufacturing of light−emitting diodes (LEDs), the development of sensors, and bio imaging. The potential of light−emitting polymers is further highlighted by laser−induced fluorescence spectroscopy.

## 4. Conclusion

In sum, we produce gold NPs by laser ablation in liquid method and mix it by MEH−PPV polymers in different

concentrations to study the exciton plasmon coupling between metallic NPs and polymer as a host medium. The best emission spectrum of MEH−PPV polymer concentration upon addition of nanoparticle concentration to 500p were achieved. The LIF spectra presented in this study show significant changes in the light−emitting properties of the MEH−PPV polymer upon introduction of gold nanoparticles when we used 532 nm wavelength to excitation.

**Ethical approval**:
This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval does not applicable.

**Authors Contributions**:
All authors contributed equally to performing experiments, analyzing data, and writing the paper.

**Availability of data and materials**:
The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflict of Interests**:
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



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