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The Optical Properties Enhanced of Light-Emitting Polymer PFO: A Plasmon-Exciton Interaction Perspective

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تحسين الخواص البصرية لبوليمر PFO الباعث للضوء: منظور تفاعل البلازمون والإكسيتون

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ABSTRACT

Background:
The current experimental study presents the effect of silver nanoparticles (Ag NPs) on improving the optical properties of a light-emitting polymer (LEP) based on Plasmon-Exciton Coupling.

Materials and Methods:
A Poly(9,9-di-n-octylfluorenyl-2,7-diyl)(C29H41) polymer (PFO) is one of the light-emitting polymers that has distinctive optical properties when it is dissolved by toluene different concentrations.
Further, the Ag NPs are experimentally synthesized by pulsed laser ablation in liquids technique to be subsequently mixed with the PFO polymer at different concentrations.

Results:
Based on the results, the Plasmon properties possessed by the Ag NPs improved the absorbance and fluorescence spectra of the PFO polymer for all concentrations. In addition, the light-induced fluorescence spectra are improved under the influence of laser beams by adding the Ag NPs to the PFO polymer.

Conclusion:
The current study showed that with increasing the concentration of the Ag NPs in the PFO polymer solution, a red shift appeared in the wavelength of the absorption and fluorescence spectra. This wavelength shift is most likely the result of the strong interaction between the plasmon of the Ag NPs and the exciton of the PFO polymer under the influence of laser light. In turn, this interaction can lead to changes in the energy states of the PFO polymer thus improving its optical properties.

Key words: Plasmon-Exciton Coupling, Light-Emitting Polymer, the PFO Polymer, LAL, the Ag NPs.

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INTRODUCTION

In the last years, scientists have been widely interested in improving the properties of materials to be optimally employed in industry. Among the materials that have received wide attention are light-emitting polymers (LEPs), due to their distinctive properties known for their flexibility, lightweight, and expansive surface area for interaction, present cost-effective opportunities for devices fabrication [1].

Among the LEPs, semiconductor conjugated polymers are the most interesting because they have properties that make them promising for use, including high photoluminescence (HPL), effective quantum yield [2], broad gain cross-section [3], wide emission spectrum [4], and ability to be electrically pumped [5].

Furthermore, a Poly(9,9-di-n-octylfluorenyl-2,7-diyl)(C29H41) polymer (PFO) is considered one of the most important the semiconductor conjugated LEPs. The PFO is touted as a promising material for the future of optoelectronic devices due to its affordability, ease of manufacture, and intense photoluminescence in the visible spectrum [7]. These attributes make PFO an ideal candidate for numerous optoelectronic applications such as polymer light-emitting diodes (PLEDs), photovoltaic photodiodes, and field-effect transistors (FETs) [8,9].

Despite these advantages, the widespread adoption of LEPs is hampered by significant challenges, include issues related to their thermal stability and limitations in electron-hole separation and transfer, which often result in compromised performance and shortened lifespan of devices employing LEPs [10].

Moreover, one of the most promising solutions to these challenges is the integration of the LEPs with metal nanoparticles in one matrix. This innovative matrix has been shown to greatly enhance the performance of the optoelectronic devices [11].

In the case of the PFO and other photoactive polymers, integrating it with metal nanoparticles could mitigate some of its inherent weaknesses. Plasmonic metals such as silver or gold are able to improve the optoelectronic properties of the PFO by activating a special feature of plasmonic metals at certain frequencies of visible light called the surface plasmon resonance (SPR) [12,13]. This groundbreaking provides a promising solution to problems that limit the use of the PFO in optoelectronic devices, and also this approach could herald a new generation of more efficient and robust optoelectronic devices, indicating a future direction for research and development in this field [14,15].

This study examined the plasmon - exciton coupling between the PFO polymer and the SPR of silver nanoparticles (Ag NPs) to enhance the optical properties of the composite matrix. To achieve this, the Ag NPs were mixed with the PFO polymer dissolved in toluene in various concentrations. The SPR effect of Ag NPs, when coupled with the PFO, is expected to increase the efficiency of the optoelectronic devices. The aim of this study is to offer valuable insights

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that could guide future research and development of the photonics devices based on the light-emitting polymers.

MATERIALS AND METHODS

In this research, the poly (9,9-di-n-octylfluorenyl-2,7-diyl) polymer (PFO) is a type of light-emitting polymers with a molecular weight of 20,000 which was purchased from American Dye Source Company. The PFO dissolved in toluene (C7H8: with a molecular weight of 92.14) at three concentrations: $5*10^{-6}$ M, $3*10^{-6}$ M, and $1*10^{-6}$ M, as shown in Figure 1a.

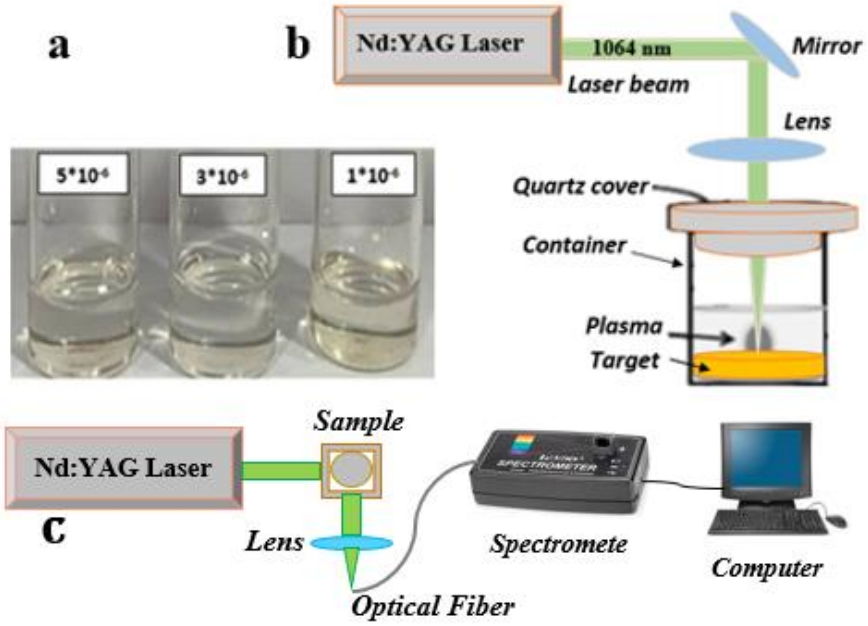

Figure 1: a) the image of the PFO polymer samples with different concentrations, b) the setup of the pulsed laser ablation in liquids, and c) the setup of the LIF technique.

Moreover, the Ag NPs experimentally generated using a pure silver target (with >99.9% purity and a thickness of 2 mm) via the pulsed laser ablation in liquids (PLAL) method. 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 pure silver target, the setup is shown in Figure 1b. The Ag NPs was experimentally generated by the PLAL at three distinct concentrations, using a different number of laser pulses (250, 500, and 750 pulses) directly focused on the target. Each of the three concentrations of the PFO and the Ag NPs was mixed with 50:50 ratios. Consequently, the nine samples were created with varying concentrations, they are used to complete the experiment.

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The optical spectroscopy of the samples was measured with a 190–900 nm UV–Vis spectrophotometer (model CECIL7100 Korea), also the Fluorescence spectrum (the emission and excitation spectra) of the samples were measured by a fluorescence spectrophotometer (model Scinco, FS-2). Then, it was measured excite fluorescent molecules by Laser-Induced Fluorescence (LIF) technique, this is done using 473 nm CW laser source, it works with power 30 *m watt*, the setting is as shown in Figure 1c. Finally, the morphology (shape and size) of the Ag NPs was measured using Field Emission Scanning Electron Microscopy (FE-SEM), its operated at an accelerating voltage of 10 kV. While the average size of the Ag NPs was calculated from FE-SEM images via Image J software.

RESULTS AND DISCUSSION

The results of optical spectra measurements of the all samples are shown in the Figure 2. The optical spectroscopy of the PFO polymer dissolved in toluene with different concentrations, it is observed that the absorption spectra increase with the PFO polymer concentration increasing, the behavior is depicted in the Figure 2a.

The absorption spectrum of the Ag NPs generated by PLAL method increases with increasing number of laser pulses focused on target (250, 500, and 750 pulse) with a minor red shift in wavelength, as in the Figure 2b. The absorption spectrums of the PFO polymer are improved, this is done by adding Ag NPs to the PFO polymer, to produce a matrix with different concentrations, as shown in the Figure 2c.

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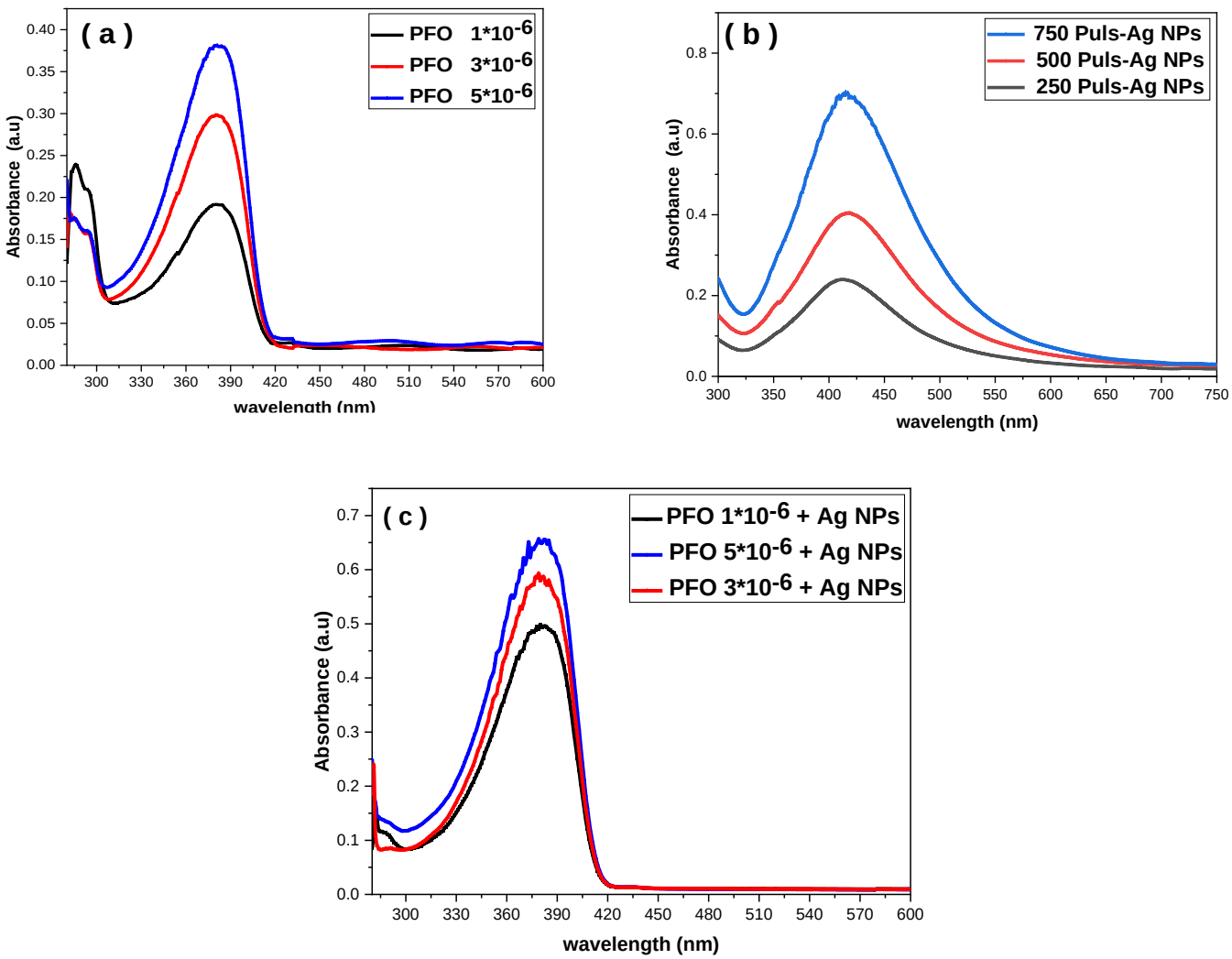

Figure 2: The absorption spectrum of a) the PFO polymer with different concentrations, b) the Ag NPs with different concentrations, and c) the matrix with different concentrations.

Notably, the improvement in the optical absorption spectra is due to the Ag NPs acting as thermal sources to absorb light, which leads to an increase in the absorption of the matrix, as the absorption spectrum increases when the concentration of the Ag NPs within the polymer increases, the result agrees with [16,17].

The results of the samples morphology are showed that all the Ag NPs that were produced by the method of laser ablation are spherical shape, the average size of the Ag NPs in the toluene solution is 26 nm, as shown in Figure 3.

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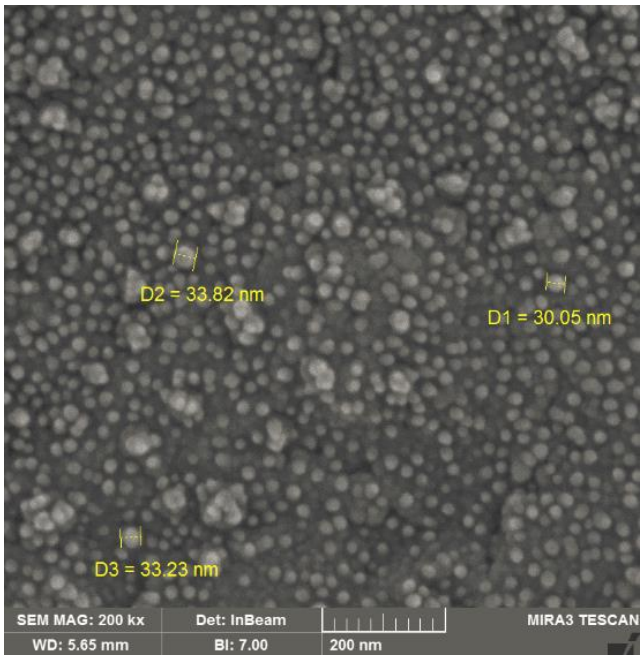

***Figure 3*: the FE-SEM image of the Ag NPs in the toluene solution.**

The results of the fluorescence spectra are shown in the Figure 4, the effect of adding the Ag NPs on improving the fluorescence spectra of the PFO polymer is observed, this improvement increases when the concentration of the Ag NPs increases, but an increase in the concentration of the Ag NPs for the number of pulses of 750 pulses, the fluorescence spectrum begins to decrease slightly due to the phenomenon of scattering that leads to suppression of the spectra, for all concentrations used in the work.

It can be clearly seen that the fluorescence spectra contain two peaks, likely due to distinct electronic transitions within the polymer molecules. The first peak is thought to represent the initial emission of the polymer, while the second peak could be associated with additional excited states or interactions within the material. When the Ag NPs are introduced into the PFO polymer, an increase in intensity is observed for both peaks in the fluorescence spectrum for all concentrations compared to the pure polymer. This improvement in fluorescence can be attributed to the well-known phenomenon of fluorescence intensification by metallic nanoparticles, which is typically associated with localized surface Plasmon resonance (LSPR)[16].

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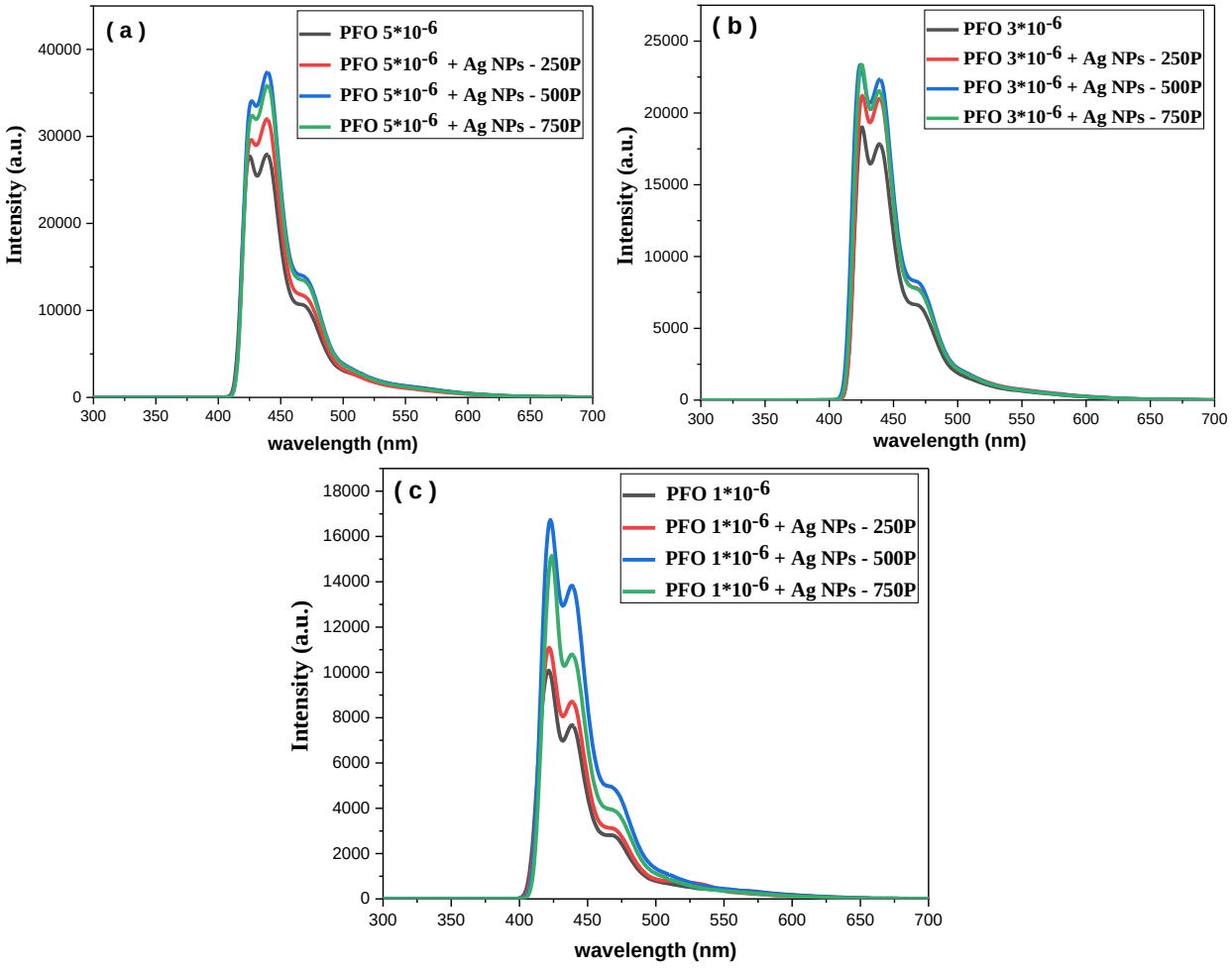

Figure 4: the fluorescence spectrum of the matrix (the PFO with Ag NPs) at different concentrations.

The LSPR amplifies the local electromagnetic field at the NPs surface, which leads to an increased Fluorescence spectra for all samples. In addition to this fluorescence intensification, the introduction of Ag NPs also induces a shift in the peak wavelengths. These shifts, commonly referred to as red or blue shifts, indicate changes in the photo-physical properties of the sample due to changing the energy states of the PFO polymer [17].

The Ag NPs are known for their strong interaction with light, a property frequently exploited in surface-enhanced luminescence applications. The Ag NPs should be added to the PFO polymer in calculated proportions.

In order not to suppress the polymer fluorescence spectrum due to the high concentrations of the silver NPs. For example, an increase in the Ag NPs concentration may lead to changes, such as a

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decrease plasmon-exciton interaction, this change can subsequently change optical energy levels of the polymer, resulting in the observed blue shift in fluorescence. This hypothesis, while plausible, is not definitive and would benefit from further investigation to confirm the exact mechanisms in this field of researches.

In the order, results of the effect of adding the Ag NPs to the PFO polymer on the LIF spectra are shown in the Figure 5. The noticeable improvement in the LIF spectra intensity as well as the redshift in wavelength that the Ag NPs causes to the matrix compared to the pure polymer, it is actually caused by the interaction between the plasmon-exciton.

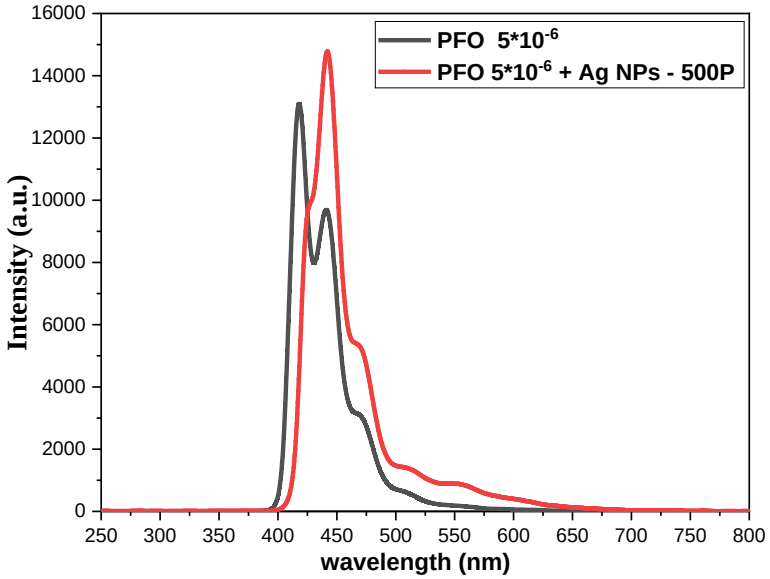

Figure 5: the LIF spectrum of the PFO polymer before and after adding the Ag NPs.

The presence of the Ag NPs can lead to enhanced light emission and a wider emission bandwidth, which indicates more efficient energy transfer between the excitons in the PFO polymer and the plasmons in the Ag NPs. The Ag NPs interact with excitons in the polymer, resulting in intense photoemission, the specific size, shape, and distribution of the Ag NPs within the polymer matrix can influence the strength of this coupling, which in turn affects the fluorescence properties of the PFO polymer. Attributed to changes in the local electromagnetic field caused by plasmonic coupling. These changes may lead to altered exciton energy levels or modified radioactive decay pathways within the polymer, leading to the observed spectral shift.

Overall, the results indicate that the incorporation of the silver nanoparticles into the light-emitting polymer (PFO) can enhance the fluorescence intensity and broaden the emission bandwidth, demonstrating the potential of the plasmon-exciton coupling as a means to improve the optical properties of the light-emitting polymers. Further investigations and optimizations of

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the silver nanoparticle concentration, size, and morphology can be explored to achieve more significant improvements in the fluorescence properties of the polymer.

CONCLUSION:

We conclude from the current experimental study that it is possible to obtain improved optical properties of the PFO polymer by doping with the Ag NPs at a certain concentration without reaching the scattering state. The pure PFO polymer has display two emission peaks due to two distinct electronic transitions occurring within its structure, when the Ag NPs are added, the intensity of these peaks increases significantly. In addition, the introduction of the Ag NPs causes a red shift at wavelengths, this wavelengths shift is most likely the result of the strong interaction of the Ag NPs with PFO polymer leading a change in the photo-activity. In turn, this interaction can lead to changes in the energy states of the PFO polymer as well as the emission and absorption of light. In addition, the study's analysis of the LIF spectra demonstrates the synergistic effect of the excitation of the plasmon on the photopolymer, which leads to increase the light emission efficiency and the elongated emission bandwidth, indicating more efficient energy transfer between the plasmon and exaction. This coupling can lead to improve the optical properties of the light-emitting polymers, increase the fluorescence intensity, and broaden the emission spectrum.

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Conflict of interests.

There are non-conflicts of interest.

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الخلاصة

المقدمة:

ركزت الدراسة التجريبية الحالية تأثير جسيمات الفضة النانوية على تحسين الخواص البصرية لبوليمرPFO الباعث للضوء هذا التحسين معتمد على اقتران البلازمون - الإكسيتون.

طرق العمل:

بوليمرPFO هو أحد البوليمرات الباعثة للضوء وله خصائص بصرية مميزة عندما يذوب بتركيزات مختلفة في التولوين. علاوة على ذلك، يتم تصنيع جسيمات الفضة النانوية تجريبيًا عن طريق تقنية الاستئصال بالليزر النبضي في السوائل ليتم خلطها لاحقًا مع بوليمر PFO بتركيزات مختلفة.

النتائج:

بناءا على النتائج, أدت الخصائص البلازمونية التي تمتلكها جسيمات الفضة النانوية إلى تحسين أطياف الامتصاص والفلورة لبوليمر PFO لجميع التركيزات. وبالإضافة إلى ذلك، تم تحسين أطياف الفلورة الناتجة من تقنية انبعاث الفلورة المحتثة باليزر.

الاستنتاجات:

الدراسة الحالية أظهرت أنه مع زيادة تركيز الفضة النانوية في محلول بوليمر PFO، ظهرت ازاحة حمراء في الطول الموجي لأطياف الامتصاص والفلورة. من المرجح أن تكون هذه الازاحة نتيجة للتفاعل القوي بين بلازمون وإكسيتون تحت تأثير ضوء الليزر. في المقابل، يمكن أن يؤدي هذا التفاعل إلى تغييرات في مستويات الطاقة لبوليمر PFO وبالتالي تحسين خصائصه البصرية.

الكلمات المفتاحية: اقتران البلازمون – الإكسيتون, البوليمرات الباعثة للضوء, طريقة الاستئصال بالليزر النبضي, جسيمات الفضة النانوية.

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