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Effect of plasmon resonance of metal nanoparticles on spectral-luminescent properties of polymethine dye

Spectral-luminescent properties of polymethine dye in ethanol solution were studied upon the addition of gold and silver nanoparticles. The absorption spectrum of Au nanoparticles has a large degree of overlap with the absorption and fluorescence spectra of the dye than the absorption spectrum of Ag. In the presence of plasmon nanoparticles, both the absorption and fluorescence of the polymethine dye was increased. The position of the maxima of the absorption and the fluorescence bands of the dye and their half-width were not changed. The growth of fluorescence in 4 times was recorded for the concentration of Ag nanoparticles, equal to $3*10^{-14}$ mol/l, and for the concentration of Au nanoparticles, equal to $7*10^{-11}$ mol/l. The greatest increase in the fluorescence intensity of polymethine was registered for solutions with gold nanoparticles. The enhancement of the fluorescence of the dye and the decrease in its lifetime can be connected with an increase in the rate of electronic transitions in dye molecules that are located in the near field of metallic nanoparticles with excited plasmons. The decrease in the intensity of the luminescence of the dye at high concentrations of nanoparticles can be the result of nonradiative energy transfer from polymethine molecules to metal particles, which leads to a decrease in the probability of radiative decay of excited molecules.

Keywords: polymethine, metal nanoparticles, plasmon, spectral-luminescent properties, plasmon-enhanced fluorescence.

Light technologies have promoted the improving of the quality of life over the centuries due to numerous achievements in the field of medicine, communications, culture and energy. In recent decades, efforts have been made to promote photonic devices through precise control over the materials used. In this context, a new field of research called «plasmonics» was appeared. Plasmonics is a section of nanophotonics that uses surface plasmons to control light at the nanoscale level by coherent coupling of photons with free electronic vibrations at the interface between the conductor and the dielectric. This area of researches has become extremely promising in connection with several key areas of application, including information technology, solar energy, high-density data storage, life sciences and safety.

One way to localize the optical radiation in a nanometer-sized volume can be realized by using the unique properties of plasmon metal nanoparticles (NPs). The physics of this phenomenon is based on the collective oscillation of conducting free electrons of metallic NPs that is called as localized plasmon resonance (LPR). The resonance frequency can be adjusted by changing both the size and shape of the NPs and the permittivity of the surrounding medium. Optical properties of nanoparticles are determined by a set of parameters that include the composition, particle size and shape, geometry, and local environment.

Despite a wide range of existing plasmon materials, gold and silver [1, 2] are most common used metals. Therefore, most of the existing works are devoted to the synthesis of NPs of noble metals with well-defined morphology and size [3], since the properties of the resulting material can be modulated with plasmon NPs in this way. LPR is more effective in silver, but gold nanoparticles have excellent chemical inertness and are simpler in synthesis [4, 5].

Polymethine dyes are now widely used in various fields of science and technology. They have high extinction coefficients and tunable absorption spectra in the entire visible and near infrared region. Because of their unique optical properties, they are used in nonlinear optics, in recording and storage devices like fluorescent probes in biomolecules or as contrast agents in optical images of tissues. Oxidation-reduction properties of polymethine dyes have also been studied from the point of view of their role as a sensitizer or desensitizer for silver halides. The combined advantages of optical and electronic properties make polymethines a promising class of materials for solar cells.

It is well known that the nature of the influence of LPR on the spectral-luminescent properties of organic dyes is determined both by the nature of the dye itself and by the degree of overlapping of the spectra of dye and plasmon particles. In this paper, we present the results of a study of the plasmon effect of gold and silver NPs on the spectral and luminescent properties of a polymethine dye. Despite the large number of

works devoted to the investigation of the plasmon effect on the luminescence of organic dyes, this effect on polymethine remains poorly illuminated.

The structural formula of the investigated polymethine dye (PD) is shown in Figure 1.

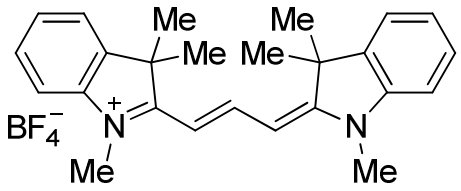


Figure 1. Structure of the polymethine dye

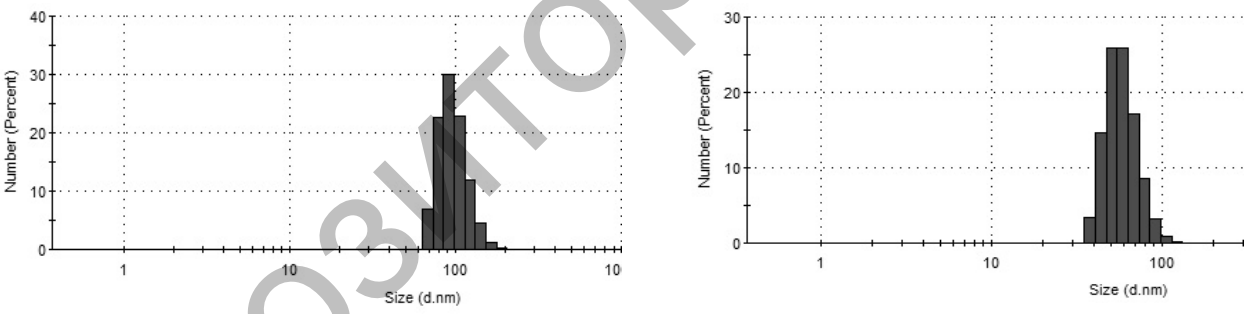
The absorption and fluorescence spectra of the dye solutions were measured on a Cary-300 spectrophotometer (Agilent). Fluorescence spectra were measured on a Cary Eclipse spectrofluorimeter (Agilent). The lifetimes of the excited state of the dye molecules were measured by using of pulsed spectrofluorimeter with a picosecond excitation with the registration in a time-correlated photon counting mode (Becker&Hickl, Germany).

The concentration of PD in all solutions was constant and equal to 10^{-5} mol/l. The concentration of NPs of silver or gold was varied in the range of 10^{-10} to $3*10^{-14}$ mol/l.

The NPs of Ag and Au in ethanol were obtained by ablating of the silver or gold target with the second harmonic of a solid-state Nd:YAG laser (SOLAR LQ 215, λ_{gen} = 532 nm, E_{pulse}= 90 mJ, τ = 10 ns). The concentration of NPs was determined from the change in the mass of the target before and after ablation and amounted to be equal to $6*10^{-11}$ mol/l for 10 minutes of ablation. The concentration of Au NPs was equal to $4*10^{-10}$ mol/l after 15 minutes of ablation.

The average sizes of Ag and Au nanoparticles were determined by the method of dynamic light scattering on the Zetasizer Nano ZS analyzer.

The measurements showed that Au nanoparticles in solution have an average diameter of about 60 nm. While for Ag, particles with a size of about 90 nm were obtained (Fig. 2).



a b

Figure 2. Size distribution of NPs of Ag (a) and Au (b)

The absorption spectrum of the synthesized NPs is shown in Figure 3. As can be seen from the figure, the absorption spectrum of silver NPs in ethanol exhibits as a broad band with a maximum of about 405 nm. The maximum of absorption band of gold NPs exhibits at 530 nm. The absorption band of the PD dye in ethanol solution was recorded ears in the region of 450-600 nm and has a maximum at 540 nm. Fluorescence spectra of dye with a maximum at a wavelength of λ_{max} = 565 nm and a half-width of the band of 54 nm was observed upon photoexcitation of the ethanol solution of the dye.

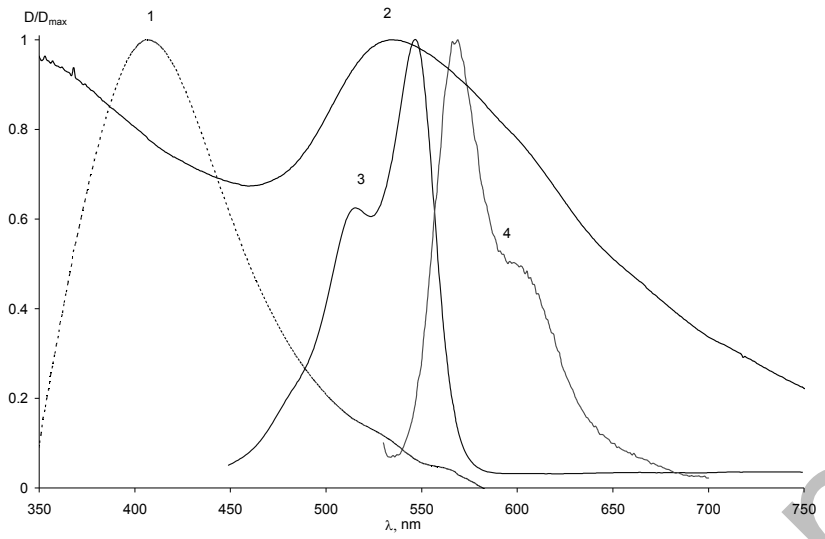


Figure 3. Absorption spectra of NPs of Ag (1), Au (2), PD (3, C=10^{-5} mol/l) and fluorescence of PD (4, λ_{ex}=530 nm)

As can be seen from the data obtained, the Au absorption band is almost completely superimposed on the absorption and fluorescence spectrum of the dye. The observed overlap is a necessary condition for the realization of plasmon resonance and electronic transitions in the dye molecule.

Next, the spectral-luminescent parameters of polymethine in solutions before and after addition of silver NPs were studied (Fig. 4).

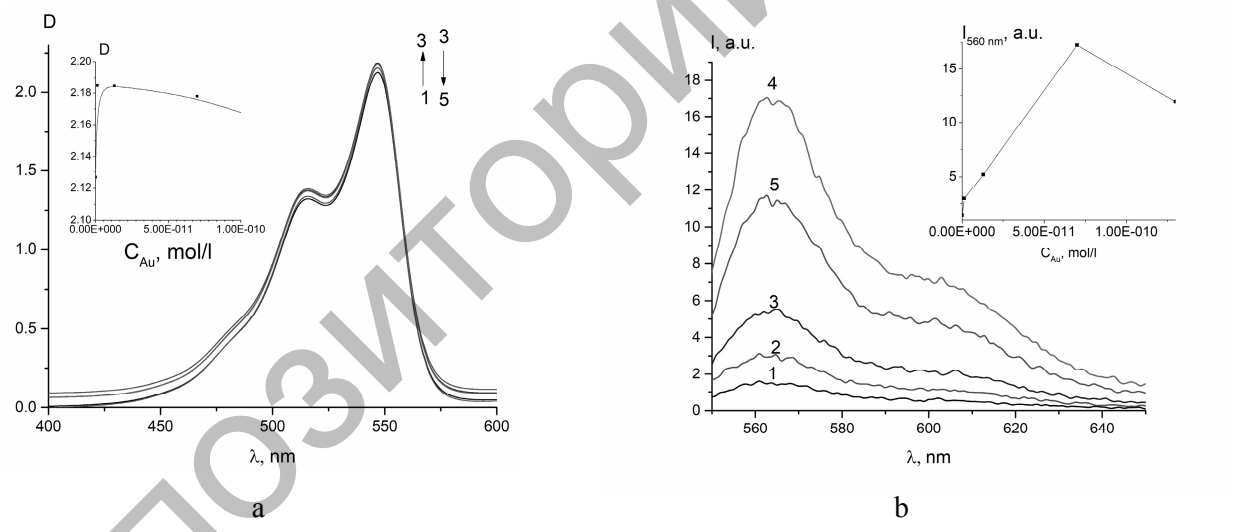


Figure 4. Absorption (a) and fluorescence (b) spectrum of PD in the presence and with Au NPs at concentrations of, mol/l: 1 – 0; 2 – 1.5*10^{-12}; 3 – 1.5*10^{-11}; 4 – 7*10^{-11}; 5 – 10^{-10}. On the inset – dependence of absorptivity and intensity of fluorescence of PD on Au NPs concentration

The measurements have shown that the addition of Ag NPs results in the slight increase of the absorptivity of the dye solution. The position of the maximum of the absorption band and its half-width were not changed (Table). In the presence of Au NPs, an insignificant increase in the optical density of the dye solution was also observed without changing of the position or shape of the spectrum. In contrast to Ag NPs, the maximum of growth of absorptivity was obtained at a plasmon NPs concentration of 1.5*10^{-12} mol/l.

The increase in the absorption of the dye at high concentrations of silver NPs (up to 3*10^{-12} mol/l) may be due to the fact that the dye molecules are in the near field of metallic NPs, in which plasmons are excited.

Table

Spectral parameters of PD at various concentrations of metal NPs in ethanol solutions

NPs concentration, mol/l	$\lambda_{ab\ max}$ (nm)	D	$\lambda_{fl\ max}$ (nm)	I (a.u.)	τ_{fl} (ns)	I/I_0	τ/τ_0
Ag							
0	547	2.88	564	5.51	0.36	-	-
$3*10^{-14}$	547	2.92	564	23.48	0.34	4.26	0.94
$3*10^{-13}$	547	3.04	564	21.60	0.34	3.92	0.94
$1.5*10^{-12}$	547	3.07	564	19.36	0.33	3.51	0.91
$3*10^{-12}$	547	3.04	564	14.00	0.33	2.5	0.91
Au							
0	547	2.12	564	1.54	0.36	-	-
$1.5*10^{-12}$	547	2.19	564	3.05	0.33	1.98	0.91
$1.5*10^{-11}$	547	2.19	564	5.44	0.33	3.53	0.91
$7*10^{-11}$	547	2.17	564	17.00	0.30	11.03	0.83
10^{-10}	547	2.16	564	11.00	0.31	7.14	0.90

Measurements have shown that the intensity of the dye fluorescence depends on the concentration of Ag NPs (Table). As can be seen from the Table, the maximal enhancement of fluorescence (4-fold) was recorded for the concentration of Ag NPs equal to $3*10^{-14}$ mol/l. A further increase in C_{Ag} results in quenching of the fluorescence. The position of the maximum of the band and its half-width were not changed. At the same time, the greatest increase in the fluorescence intensity of the dye with Au NPs was recorded at $C_{Au} = 7*10^{-11}$ mol/l, which agrees with the data obtained from the absorption spectra. It can be noted that in the presence of Au, the dye intensity is almost in 2.5 times was higher than for Ag NPs. Measurements of the kinetics of fluorescence decay of PD in the presence of plasmonic NPs and without them correlate with the obtained measurement data of intensity.

Thus, measurements have shown that both the absorption and fluorescence of the polymethine dye was increased in the presence of plasmon NPs of metals. The greatest increase in the fluorescence intensity of polymethine was registered for solutions with gold NPs.

An increase in the absorption of the dye can be attributed to the fact that the dye molecules are in the near field of nanoparticles in which resonant plasmon oscillations are excited [6]. Since the near field in the resonant nanoparticles is repeatedly amplified in comparison with the field of the incident wave, the dye molecules in solutions with NPs absorb more light than the dye molecules without metallic NPs.

The reason for the enhancement of the fluorescence of the dye and the decrease in its lifetime can be associated with an increase in the rate of electronic transitions in dye molecules that are in the near field of metallic NPs with excited plasmons [7, 8]. In this case, the near field of gold NPs is larger than the plasmon oscillations of Ag particles for dye molecules, so the plasmon effect for these NPs was differ. The decrease in the intensity of the dye luminescence at high concentrations of metal NPs can be the result of nonradiative energy transfer from PD molecules to NPs, which leads to a decrease in the probability of radiative decay of excited molecules [7].

The obtained results can serve as a basis for studying of photoinduced processes in hybrid materials such as organic dye-plasmon nanoparticles. The enhancement of optical absorption in dye molecules located near resonant metallic nanoparticles makes it possible to calculate the decrease in thresholds and increase the yield of photoinduced processes of rearrangement of dye molecules, which is of interest for applications in sensorics, laser technology, and for recording and storing information.

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Полиметинді боyғыштардың спектрлік-люминесценттік қасиеттеріне металл нанобөлшектерінің плазмондық резонансының әсері

Этил спиртіндегі полиметин боyғышының спектрлік-люминесценттік қасиеттері алтын және күміс нанобөлшектерді (НБ) қосқанда зерттелді. Au нанобөлшектерінің жұтылу спектрі, Ag жұтылу спектріне қарағанда, боyғыштың жұтылу және флуоресценция спектрімен үлкен көлемде қиылысады. Полиметин боyғышына металл плазмондық нанобөлшектерін қосу кезінде боyғыштың жұтылу және сәулелену қабілеті артады. Соған қарамастан, боyғыштың жұтылу және флуоресценция жолақтарының максимумы және жартылай ені өзгермейді. Флуоресценция қарқындылығының 4 есе артуы Ag НБ үшін $3*10^{-14}$ моль/л концентрация, ал Au НБ үшін $7*10^{-11}$ моль/л концентрация кезінде тіркелді. Полиметиннің флуоресценттік қарқындылығының ең көп ұлғаюы алтынмен қосылған ерітінділерде тіркелді. Боyғыш флуоресценциясының қарқындылығының артуы және оның өмір сүру уақытының азайғаны байқалды. Оның себебі металдың қозған плазмондық нанобөлшектеріне жақын өрісте орналасқан боyғыш молекулаларындағы электрондық өтулердің жылдамдығының артуымен түсіндіріледі. Металл НБ жоғары концентрациясы кезінде боyғыштың флуоресценция қарқындылығының азаюы полиметинді боyғыш молекулаларынан нанобөлшектерге сәулеленусіз энергия алмасуынан болуы мүмкін. Ол қозған молекулалардың сәулелік ыдырау ықтималдығын азайтады.

Кілт сөздер: полиметин, металл нанобөлшектері, плазмондар, спектрлік-люминесценттік қасиеттер.

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Влияние плазмонного резонанса наночастиц металлов на спектрально-люминесцентные свойства полиметинового красителя

Исследованы спектрально-люминесцентные свойства полиметинового красителя в этиловом спирте при добавлении наночастиц (НЧ) золота и серебра. Спектр поглощения наночастиц Au имеет большую степень перекрытия со спектрами поглощения и флуоресценции красителя, чем спектр поглощения Ag. В присутствии плазмонных НЧ металлов происходит увеличение как поглощательной, так и излучательной способности полиметинового красителя. При этом положение максимумов полос поглощения и флуоресценции красителя и их полуширина не меняются. Усиление флуоресценции в 4 раза было зарегистрировано для концентрации НЧ Ag, равной $3*10^{-14}$ моль/л, и концентрации НЧ Au, равной $7*10^{-11}$ моль/л. Наибольшее увеличение интенсивности флуоресценции полиметина было зарегистрировано для растворов с НЧ золота. Причиной усиления интенсивности флуоресценции красителя и уменьшения его времени жизни может быть увеличение скорости электронных переходов в молекулах красителя, которые находятся в ближнем поле металлических НЧ с возбужденными плазмонами. Уменьшение интенсивности свечения красителя при больших концентрациях НЧ металлов может быть результатом безызлучательного переноса энергии от молекул полиметинового красителя к НЧ, что приводит к уменьшению вероятности излучательного распада возбужденных молекул.

Ключевые слова: полиметин, наночастицы металлов, плазмоны, спектрально-люминесцентные свойства, плазмон-усиленная флуоресценция.