EFFECT OF SILVER AND GOLD NANOPARTICLES ON THE SPECTRAL AND LUMINESCENT PROPERTIES OF A MEROCYANINE DYE

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An increase in the concentration of silver nanoparticles (NP) initially causes an increase and then a decrease in the absorption and fluorescence intensities of a solution of tetramethinemerocyanine dye derived from indole and thiobarbituric acid. In the case of gold NP, the dye absorption remains unchanged, while fluorescence is reduced. The lifetime of the merocyanine fluorescent state does not change upon the addition of both types of nanoparticles. It is suggested that the observed effects are related to the action of plasmons in the metal nanoparticles on the electronic processes in the dye molecules.

Key words: *merocyanine, ablation, plasmon resonance, silver and gold nanoparticles, absorption and fluorescence spectra, fluorescence kinetics.*

Metal nanoparticles (NP) are capable of efficient interaction with light at a wavelength much greater than the size of the particles [1, 2]. The oscillation of free electrons in the NP arising upon the action of electromagnetic irradiation leads to a considerable increase in the absorption and scattering cross-section as well as the appearance of plasmon resonance when the distance between the nanoparticles is reduced [3]. These properties of plasmonic NP have found various applications, for example, for increasing the absorption cross-section of solar cells [4]. Significant theoretical and applied interest is found in the interaction of metal NP with typical organic chromophores since plasmons are capable of altering photophysical properties of dyes, in particular, considerably shortening the fluorescence lifetime due to nonradiative energy transfer from the chromophore to the NP [5]. This is the basis of highly-sensitive luminescent sensors [6], optoelectronic devices [7], and nanolasers [8]. The addition of metal NP to the active medium of dye lasers leads to a decrease in the generation threshold [9, 10].

Among organic chromophores, polymethine dyes have the greatest range of altering photophysical properties [11]. They are widely used in organic photovoltaics [12], laser technology [13], nonlinear optics [13, 14], biology, and medicine [11]. Special interest is found in merocyanines, which are neutral donor–acceptor polymethines [15]. These dyes have pronounced solvatochromism, high molecular polarizability, and pronounced nonlinear optical properties. In addition, their electronic state can be altered from the nonpolar polyene to the ideal polymethine and even the dipolar polyene by varying the

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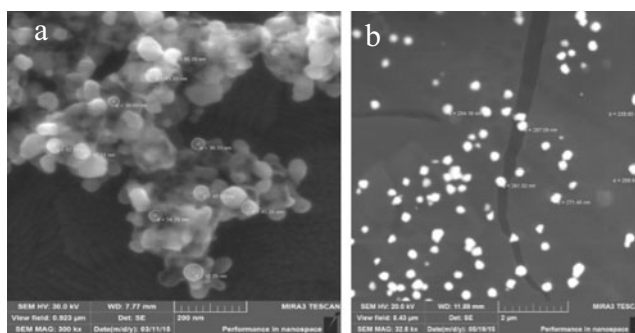
Fig. 1. Scanning electron microscopy images of silver NP (a) and gold NP (b).

donor–acceptor properties of the terminal groups and the polarity of the medium [15]. Thus, it was of interest to study the effect of plasmonic NP on the photophysical properties of merocyanines in solution.

The silver and gold NP were obtained by ablation of metal targets in ethanol using the second harmonic of a Solar LQ 215 solid-state Nd : YAG laser (λ_{gen} = 532 nm, E_p = 90 mJ, τ = 10 ns). The pulse repetition frequency was 20 Hz and the ablation time was 8 and 10 min for silver and gold, respectively. Each laser pulse packet was focused at different segments of the target surface. The volume of ethanol in the cell containing the target was V = 2 mL and the ethanol layer thickness above the target surface was 2.5 mm. The mean diameters of the metal NP obtained were determined by dynamic light scattering using a Zetasizer Nano ZS analyzer for submicron particles. The mean diameter of the silver NP was 27 nm, while the mean diameter of the gold NP was 95 nm. Images of the NP obtained by a Tescan Mira 3MLU electron microscope (Fig. 1) showed that the silver (Fig. 1a) and gold NP (Fig. 1b) are almost spherical in shape.

The amount of nanoparticles in the solutions obtained was found using the following equation:

$$\Delta N = \Delta m / m$$

where Δm is the difference in mass of the target before and after ablation, m is the mean mass of a single particle ($m = V\rho$, where V is the mean volume of a single nanoparticle and ρ is the density of the nanoparticle). Using this value and the solution volume, we calculated the number of nanoparticles in a unit of volume, which, for convenience of comparison with the dye concentration, was divided by Avogadro number to give the molar concentration of the nanoparticles. The concentrations of the silver and gold NP in the working solution were C_{Ag} = 2.4·10^{-11} mol/L and C_{Au} = 1.3·10^{-10} mol/L.

The inverse of the number of nanoparticles in a unit of volume is the volume of the solution per single nanoparticle. Assuming that the nanoparticles are equally distant from each other and the spheres, in which they are centrally located, are maximally dense-packed, we multiplied the volume per single nanoparticle by the coefficient 0.74048 to obtain the volume of an individual sphere [16] Then, the formula $r = \sqrt[3]{3V/4\pi}$ was used to calculate the radius of sphere. The mean distance between the nanoparticles in solution was obtained by multiplying the value obtained by 2.

As a consequence of the strong electron-withdrawing capacity of the thiobarbituric acid residue, merocyanines containing this residue have strong dipolarity and can achieve the electronic structure of the ideal polymethine with suitable polarity of the medium. The electronic structure of the ideal polymethine has narrow selective absorption bands, large absorption cross-sections (high molar extinctions), and fluorescence quantum yields even greater than those values for the corresponding cationic and anionic dyes [17, 18]. Merocyanine **ind4etb**, whose structure is based on 1,3,3-trimethylindole, which is a medium-strength electron donor group, has positive solvatochromism, reaching maximum molar extinctions and fluorescence quantum yield in polar solvents. This dye also has high photochemical stability [19]:
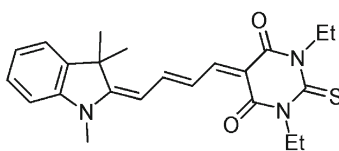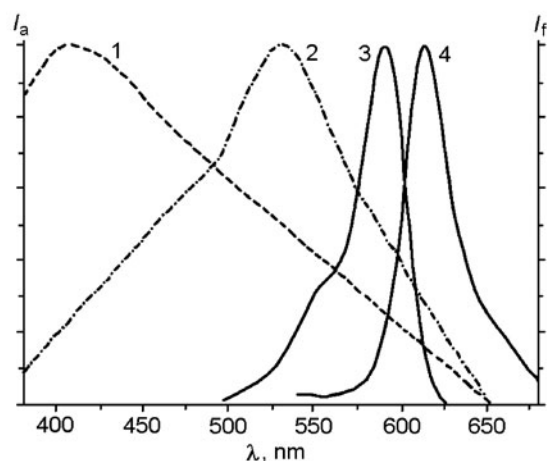
Fig. 2. Normalized absorption spectra of silver NP (1), gold NP (2), merocyanine **ind4etb** (3), and its fluorescence spectrum in ethanol (4).

The absorption spectra were recorded on an Agilent Cary 300 spectrophotometer, while the fluorescence spectra were taken on an Agilent Eclipse spectrometer.

The absorption spectrum of the silver NP in ethanol shown in Fig. 2 is a broad unstructured band with a maximum at 410 nm and long-wavelength edge at 650 nm. The plasmon band of the gold NP is narrower with a maximum at 532 nm. These values are similar to the literature data for the absorption maxima of spherical silver and gold NP taking account of their dimensions [20, 21].

The absorption (λ^a_{max} = 590 nm) and fluorescence bands (λ^f_{max} = 615 nm) of merocyanine **ind4etb** in ethanol are narrow, with half-widths of 720-740 cm^{-1}. These bands are highly intensive and have mirror-image shape. These findings indicate the similarity of the electronic structure of this dye in this solvent to the ideal polymethine structure [15]. The absorption bands of these silver and gold NP overlap with the absorption and fluorescence spectra of dye **ind4etb** (Fig. 2), indicating satisfaction of the conditions for plasmon resonance.

On addition of the silver NP, the optical density at the absorption band maximum of the dye increases relative to its initial value. When the nanoparticle concentration reaches $0.7 \cdot 10^{-12}$ mol/L, the optical density is enhanced by a factor of 1.45. Further increase in the nanoparticle concentration in solution leads to a decrease in the dye absorption (Fig. 3, curve 1). However, even at the maximum silver NP concentration studied ($1.4 \cdot 10^{-12}$ mol/L), the absorption intensity of merocyanine is greater than in the absence of these nanoparticles. The fluorescence spectrum of **ind4etb** depends similarly on the silver nanoparticle concentration (Fig. 3, curve 2).

The effect of gold NP on the spectral and luminescent properties of merocyanine **ind4etb** differs significantly from the effect for silver NP. Thus, in the presence of gold NP in solution, the dye absorption intensity remains virtually invariant (Fig. 4, curve 1). On the other hand, the fluorescence intensity of **ind4etb** decreases with increasing concentration of gold NP (Fig. 4, curve 2).

Measurements of the fluorescence kinetics by the time-correlation photon counting method upon excitation of the samples by a diode laser (λ_{gen} = 488 nm, τ = 150 ps) showed that the fluorescence decay of **ind4etb** proceeds exponentially with τ_{fl} = 0.6 ns. This parameter remains unchanged upon addition of the metal NP to the solution.

Merocyanine **ind4etb** has pronounced solvatochromism [17] and, thus, high sensitivity to the polarity of the microenvironment. However, the shape and position of its absorption and fluorescence bands are not altered in the presence of the metal NP. Therefore, despite the presence of a thione sulfur atom in the **ind4etb** molecule, which potentially can interact with the surface of gold and silver NP [22, 23], the observed spectral effects are not related to the adsorption of its molecules on the metal NP, i.e., these effects are dynamic rather than static.
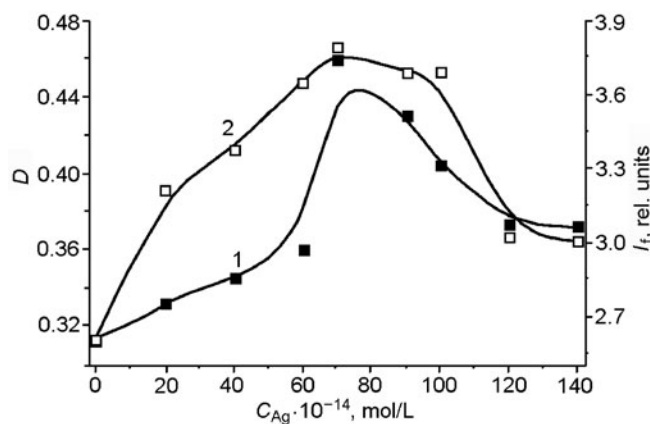
Fig. 3. Dependence of the optical density (1) and fluorescence intensity (2)
of merocyanine **ind4etb** on the concentration of the silver NP.
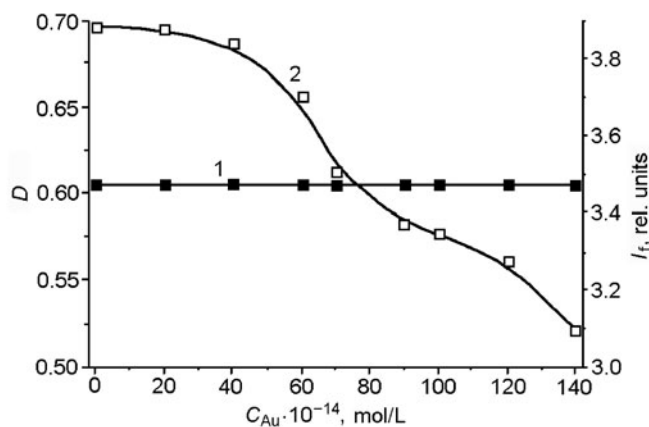

Fig. 4. Dependence of the optical density (1) and fluorescence intensity (2)
of merocyanine **ind4etb** on the concentration of gold NP.

This conclusion is supported by quantitative calculations for the possible adsorption of **ind4etb** molecules on the surface of the metal NP studied. We assumed a perpendicular arrangement of the merocyanine molecules relative to the nanoparticle surface since, firstly, this arrangement is denser relative to the number of molecules per unit of area and, secondly, the calculation is much simpler relative to other possible dense packings. In order to justify this model, we should note that polymethines, due to the planar structure of the chromophore and charge alternation along the polymethine chain, tend to form highly-ordered nanostructures (J- and H-aggregates) both in solution and on the surface of various substrates [11, 15]. The dye molecules in these aggregates form stacks, in which their long axes are parallel, providing for maximal dispersion and electrostatic interaction between them [11]. In this packing, the interaction of the dye molecules with the substrate is realized only through the atoms of the terminal groups.

The ratio of the concentrations of the dye and the nanoparticles is $\sim 1 \cdot 10^7$ for the silver NP and $1.9 \cdot 10^7$ for the gold NP, while the mean nanoparticle surface area, based on the mean diameter, is about $9 \cdot 10^3$ nm^2 for silver and $150 \cdot 10^3$ nm^2 for gold. Assuming that **ind4etb** molecules are arranged perpendicular to the nanoparticle surface, we can estimate the surface occupied by a single dye molecule as 0.5 nm^2 (the molecular thickness (0.5 nm) × width (1 nm)). The maximum adsorption density of 2-mercaptobenzimidazole with less steric requirements than **ind4etb** was 632 pmol/cm$^2 \approx 3.8$ molecules/nm^2, which indicates

that this estimate is reasonable [22]. Thus, about 0.2% and about 1.6% of the merocyanine molecules could be adsorbed on the silver and gold NP respectively under the experimental conditions.

The enhancement of dye absorption at low concentrations of the silver NP may apparently be attributed to the effect of the near field of the metal NP, in which plasmons are excited. Since the electromagnetic field near plasmonic NP is stronger compared with the field of the incident light wave [1, 2], the absorption cross-section of the dye molecules in the near field will be enlarged. We note that for nanoparticle concentration $0.7 \cdot 10^{-12}$ mol/L, at which there is the greatest change in the intensity of the dye absorption and fluorescence in the case of the silver NP, the calculation gives the mean distance between the nanoparticles equal to 15 μm, i.e., the radius of the imaginary sphere with a single nanoparticle in the center is 7.5 μm. This finding would exclude an action of short-acting (non-plasmonic) effects, such as Förster resonance energy transfer, on **ind4etb** spectra.

Anger et al. [24] have proposed that the major reason for the increased fluorescence of molecules near metal NP (metal-enhanced fluorescence (MEF)) is a reduction of the fluorescence lifetime of the molecules due to fast nonradiative energy transfer from the molecules to the nanoparticles with subsequent resonance fluorescence of the nanoparticles. This would lead to a decrease in the probability of competing nonradiative processes. However, at high nanoparticle concentrations and, thus, reduced distance between the dye molecules and nanoparticles, nonradiative deactivation of the excited state of the chromophore is considerably enhanced, which leads already to quenching of the fluorescence [24]. The observed dependence of the fluorescence intensity of **ind4etb** on the concentration of the silver NP might be interpreted by these factors. However, the similarity of the dependences of the absorption and fluorescence intensities on the nanoparticle concentration (Fig. 3) as well as the independence of the lifetime of the excited state of the dye studied on the presence of the metal nanoparticles show that the observed changes in the intensity of the fluorescence of merocyanine **ind4etb** in the presence of silver NP should be attributed primarily to change in the optical density of its solution at the excitation wavelength. The differences in the shapes of the curves in Fig. 3 may be related to the effect of plasmons on the fluorescent state of dye **ind4etb** as well as to scattering of both the exciting and emitted light on the nanoparticles, which leads to an increase in the amount of excited molecules at lower nanoparticle concentrations and a decrease in the fluorescence intensity incident on the detector due to its scattering at higher concentrations.

In order to interpret the spectral effects in the presence of gold NP, we should take into account that these NP, as a rule, are quenchers of the excited states of organic molecules [24]. Thus, in addition to scattering, there is a possible dynamic mechanism for the quenching of the fluorescence of merocyanine **ind4etb** at considerable distances. However, the shape of curve 2 in Fig. 4 shows that at low concentrations of gold NP, there is virtually no quenching of the fluorescence of this dye. The nanoparticles will be closer to each other as their concentration increases and this approaching will be accompanied by an increased probability of interaction between them with the formation of nanoparticle clusters [25]. An increase in the number of clusters should lead to an increase in the intensity of scattered light in the medium, decrease in the number of excited plasmonic particles, and, as a consequence, a decrease in the effect of the nanoparticles on the dye molecules. Thus, the weakening of the fluorescence of merocyanine **ind4etb** in this case should be attributed to greater light scattering on the gold NP, which are larger in size than the silver NP.

Therefore, the silver and gold NP obtained by the laser ablation method will have different effects on the spectral and fluorescent properties of merocyanine **ind4etb** in ethanolic solution. The silver NP at low concentrations up to $0.7 \cdot 10^{-12}$ mol/L cause an increase in the absorption cross-section of the dye and then its decrease at higher concentrations. The fluorescence intensity of the merocyanine shows similar change. These trends and the invariance of the lifetime of the fluorescent state of **ind4etb** in the presence of these metal NP indicate a dynamic mechanism for their effect on the spectral and fluorescent properties of this merocyanine. The observed effects are apparently related to plasmonic strengthening of the local electromagnetic field and the scattering of both the exciting and emitted light on the silver NP. Gold NP, in contrast to silver NP, do not affect the absorption of merocyanine **ind4etb**. However, increasing concentration of gold NP leads to a decrease in the dye fluorescence. It is indicative that the changes in the absorption and fluorescence spectra of this merocyanine are achieved at extremely low concentrations of the metal NP (10^{-13}-10^{-12} mol/L).

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