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Spectral-Luminescence and Lasing Properties of Merocyanine Dye Solutions in the Presence of Silver Nanoparticles

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Abstract—The effect of silver nanoparticles (NPs) on the spectral-luminescence and lasing properties of an ethanolic solution of positive solvatochromic merocyanine dye is studied. Increases in the absorption cross section, intensity, and duration of dye fluorescence are observed upon the addition of NPs to the solution. This leads to a decrease in the merocyanine lasing threshold. As a result, laser generation can be obtained in the presence of silver NPs ($C_{Ag} = 10^{-12}$ mol/L) at a dye concentration (10^{-4} mol/L) at which it cannot be achieved in the absence of NPs. It is noteworthy that the power density of laser pumping in the former case is lower than in the latter case.

Keywords: merocyanine dye, silver nanoparticles, plasmon effect, intensities of absorption and fluorescence, stimulated emission

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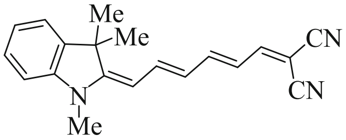
INTRODUCTION

Polymethine dyes are widely used as active and passive laser media [1, 2], since they have the greatest range of variation of the spectral-luminescence and nonlinear optical properties among organic dyes [3]. However, these applications concern mainly to cationic dyes [1, 2]. Based on them, ultrashort light pulses and lasing in the record-breaking long-wavelength region of the spectrum have been obtained [1, 4]. It was also found that the lasing threshold can be lowered and the quality of generation of laser radiation can be improved in cationic polymethines by using the localized plasmon resonance of noble metal nanoparticles (NPs) [5]. Nanoparticles can also have a significant effect on the photophysical properties of neutral polymethines, such as merocyanine dyes [6], as was shown recently [7, 8]. However, in spite of this, merocyanines have not been studied as active laser media in the presence of NPs.

In this work, we commit ourselves to study the effect of silver NPs on the spectral-luminescence and lasing properties of ethanolic solutions of positively solvatochromic merocyanine dye **1** (see formula below).



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The technique for its preparation and purification is described in [9]. The choice of this dye is determined by the fact that it has high photochemical resistance, is soluble in solvents with a wide range of polarity, and exhibits pronounced solvatochromy [10] and nonlinear optical properties [11].

EXPERIMENTAL

Silver nanoparticles in ethanol were obtained by ablation of a silver target with the second harmonic of a solid-state Nd:YAG laser ($\lambda_{gen} = 532$ nm, $\tau = 10$ ns, and $E = 90$ mJ). The methods for preparing NPs and determining their concentration in a solution are described in detail in [5, 7]. The size of nanoparticles in colloidal solutions was determined by dynamic light scattering using a Zetasizer Nano ZS size analyzer (Malvern) of submicron particles. The mean particle size of silver was 21 nm, and the standard deviation was 5 nm. The concentration of silver NPs in the working solution was $C_{Ag} = 2 \times 10^{-10}$ mol/L, and the concentration of dye **1** was constant and equal to 10^{-4} mol/L. The absorption spectra were recorded on a Cary 300 spectrophotometer (Agilent), and the fluorescence spectra were recorded on an Eclipse spectrofluorimeter (Agilent).

The fluorescence lifetime was measured by the method of time-correlated photon counting with excitation of specimens by a diode laser (λ_{gen} = 532 nm, τ = 150 ps) from Becker & Hickl GmbH [12]. The fluorescence decay curves were analyzed using the SPCImage software package [13].

Fluorescence quantum yield Φ_f was measured by the absolute method in accordance with the procedure described in [7, 14]. An AvaSphere 30-REFL integrating sphere and an AvaSpec-ULS2048 spectrometer were used in the measurement. An LCS–DTL–374QT laser (λ_{gen} = 532 nm, τ = 7 ns, and E = 20 μJ) was used as a monochromatic light source.

The properties of stimulated emission were studied using the setup described in [5]. The length of the active medium in the quartz cell was 1 cm. The power density of optical pumping was varied by means of neutral filters and was 15–35 MW/cm^2.

RESULTS AND DISCUSSION

A broad band with a maximum at 610 nm with a vibrational inflection at 575 nm (Fig. 1, curve *2*) is observed in the absorption spectrum of dye **1**, which is attributable to the long-wavelength π–π^* polarized along the long axis of the chromophore. The full width at half maximum of the absorption band is 3100 cm^{-1}. The fluorescence band with a maximum of 664 nm and a full width at half maximum of 980 cm^{-1} has a Stokes shift of 1330 cm^{-1}.

In the ground state, merocyanine **1** is characterized by a significant contribution of the structure of the neutral polyene [15]. A strong alternation of simple and double bonds in the polymethine chain is typical of it. These bonds are substantially aligned in the fluorescent state, as a result of which merocyanine **1** approaches the structure of an ideal polymethine [15].

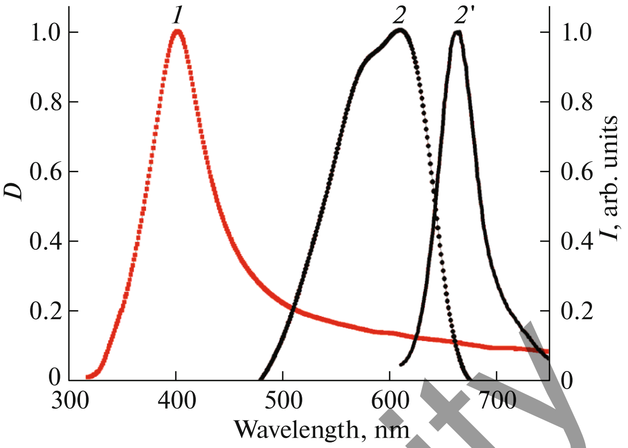

Fig. 1. Normalized absorption spectra of (*1*) Ag NPs and (*2*) dye **1**, and (*2*') the fluorescence spectrum of dye **1** in ethanol.

As a result, the long-wavelength electronic transition in the case of absorption is accompanied by a larger change in bond orders than the change in bond orders during fluorescence. Therefore, the absorption bands are broader than the fluorescence bands. The described difference in the electronic structure of the ground and excited states of merocyanine **1** causes its large Stokes shift.

The absorption spectrum of silver NPs in ethanol with a maximum at 400 nm overlaps with the absorption spectrum of merocyanine **1**, indicating the possibility of resonant energy transfer from NPs to the dye. The main spectral and luminescent properties of the ethanolic dye solution containing silver NPs are given in Table 1.

When silver NPs are added to an ethanolic solution of dye **1**, the positions of the absorption and fluorescence bands and their full widths at half maximum remain unchanged. This indicates the absence of aggregation of dye molecules and the absence of the formation of NP–dye complexes in solutions.

Table 1. Spectral-luminescence characteristics of dye **1** with different concentrations of silver NPs

Concentration of silver NPs, mol/L	$\lambda_{a\,max}$, nm	$\Delta\lambda_{1/2}$, nm	$\lambda_{f\,max}$, nm	$\Delta\lambda_{1/2}$, nm	D/D_0	I/I_0	τ, ns
0	610	116	664	43	1.00	1.00	0.37
3×10^{-13}	610	115	665	44	1.10	1.19	0.40
6×10^{-13}	610	115	665	45	1.21	1.55	0.41
10^{-12}	610	115	665	45	1.25	1.75	0.40
1.5×10^{-12}	611	115	665	44	1.51	1.45	0.40
3×10^{-12}	612	115	665	44	1.87	1.39	0.40
4.5×10^{-12}	612	115	665	44	1.38	1.12	0.40

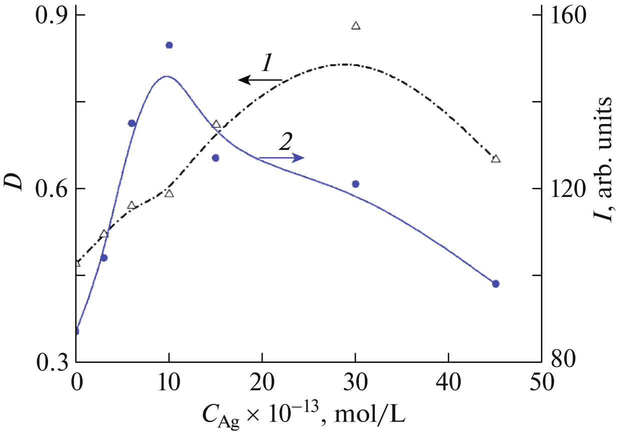

Fig. 2. Effect of the concentration of silver NPs on the (*1*) optical density and (*2*) fluorescence intensity of dye **1** in a solution.

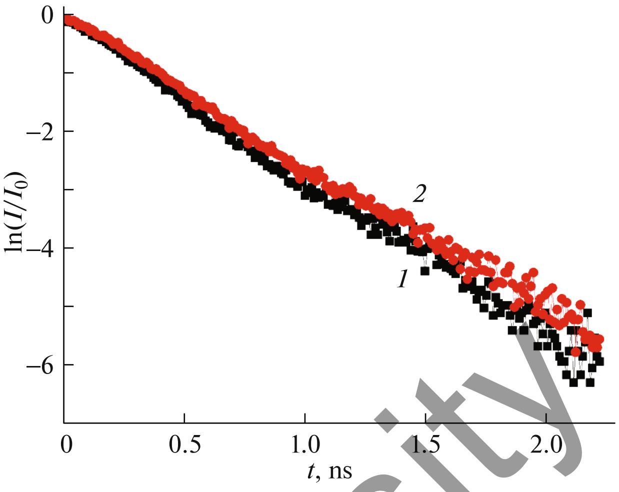

Fig. 3. Kinetics of fluorescence decay of dye **1** in the presence and absence of silver nanoparticles, namely, at concentrations of (*1*) 0 and (*2*) 10^{-12} mol/L.

As can be seen from Fig. 2, optical density D of merocyanine **1** nonmonotonically depends on the concentration of NPs in a solution. With low NP concentrations, an increase in the D value is observed. With an NP concentration of 3×10^{-12} mol/L, the optical density increases by a factor of 1.87. A further increase in the concentration of nanoparticles leads to a decrease in the optical density. An increase in the dye absorbance is associated with an increase in the absorption cross section under the influence of the local field strength near the NP metal surface [16]. With an increase in the number of NPs around the dye molecules, the effect of absorption enhancement should increase and reach saturation. However, an increase in the NP concentration leads to a decrease in the optical density of a dye solution, which may be due to an increase in the number of scattering events of the light incident on the cell [5].

The fluorescence intensity of dye **1** increases until reaching an NP concentration of $C_{Ag} = 10^{-12}$ mol/L and increases by a factor of 1.75 in comparison with a dye solution without NPs. An increase in the fluorescence intensity in this concentration range is stronger compared to an increase in the dye absorption intensity. A further increase in the C_{Ag} concentration leads to luminescence quenching. With a concentration of $C_{Ag} = 4.5 \times 10^{-12}$ mol/L, the fluorescence intensity decreases to the values observed for a dye solution without NPs (Fig. 2, curve *2*). An increase in the fluorescence intensity of the dye can be associated both with an increase in the number of singlet-excited molecules (S_1) and with an increase in the quantum yield of fluorescence (Φ_f) in the near field of the NP metal [5].

An analysis of the curves of fluorescence decay of the dye showed that it occurs exponentially with τ_{fl} = 0.37 ns. If NPs are added to the solution, then the fluorescence duration slightly increases (Fig. 3). The maximum lifetime, τ_{fl} = 0.41 ns, falls at an NP concentration of 6×10^{-13} mol/L (Table 1), with which an increase in the quantum yield of the dye luminescence is also observed. This value is close to the NP concentration value (10^{-12} mol/L), with which the maximum increase in the fluorescence intensity is observed.

The properties of stimulated emission of a solution of dye **1** in the presence of silver NPs were studied. Measurements of the emission spectra of dye solutions with $E_{DYE} = 10^{-4}$ mol/L showed that the generation of stimulated emission was not observed in the absence of silver NPs (Fig. 4, curve *1*). This can be explained by a significant decrease in the quantum yield of fluo-

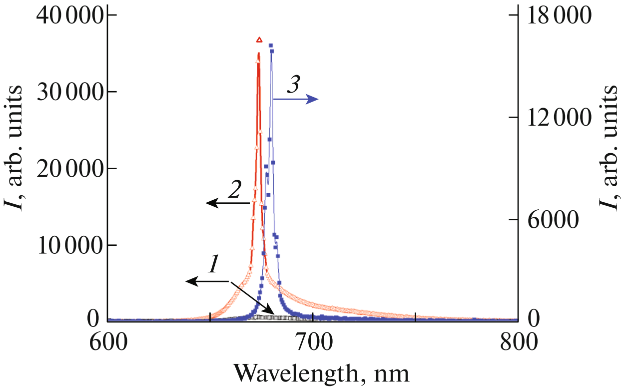

Fig. 4. Spectra of stimulated emission of dye **1** in an ethanolic solution: (*1*) $C_{DYE} = 10^{-4}$ mol/L, in the absence of NPs, P = 33.5 MW/cm^2; (*2*) $C_{DYE} = 10^{-4}$ mol/L, in the presence of NPs, P = 33.5 MW/cm^2; and (*3*) $C_{DYE} = 2.5 \times 10^{-4}$ mol/L, in the absence of NPs, P = 28 MW/cm^2.

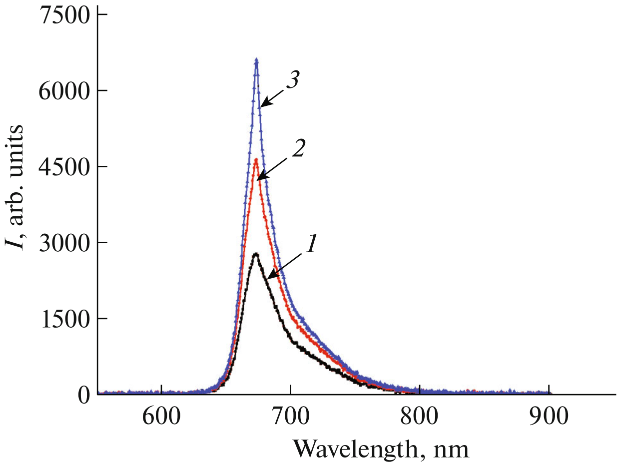

Fig. 5. Emission spectra of dye **1** ($C_{\text{DYE}} = 10^{-4}$ mol/L) in ethanol with NPs in a concentration of $C_{\text{Ag}} = 10^{-12}$ mol/L with different power densities P of optical pumping: (*1*) 15.75, (*2*) 25.25, and (*3*) 28.75 MW/cm^2.

rescence due to concentration quenching. The Φ_f value is 0.013 with this concentration and 0.061 with 10^{-6} mol/L [11]. The use of large concentrations for lasing is dictated by the need to ensure a high optical density at the pumping wavelength. The addition of NPs in a concentration of 10^{-12} mol/L to a solution of merocyanine **1** leads to generation of laser radiation (Fig. 4, curve *2*). The emission spectra of a dye solution with NPs are shown in Fig. 5. The stimulating role of silver NPs is most likely associated with increases in the dye absorption intensity and its fluorescence ability at the pumping wavelength, as noted above.

With a pumping source power density below 15 MW/cm^2, only the band of spontaneous fluorescence of the dye with a full width at half maximum of FWHM = 34 nm is observed (Fig. 5, curve *1*). A narrow band with a maximum at a wavelength of 673 nm appears in the laser-induced fluorescence spectrum when the pumping source reaches a power of about 29 MW/cm^2 (Fig. 5, curve 3), which is attributed to the lasing band. Stimulated emission of dye molecules was generated in a solution with nanoparticles at the maximum of the fluorescence band.

A further increase in the power density of the source of optical pumping leads to an increase in the lasing band intensity, as well as to a decrease in its full width at half maximum (Fig. 6). The narrowing of the emission band with an increase in the excitation intensity indicates the predominance of stimulated emission over spontaneous emission, i.e., the transition of the system to the lasing mode. The obtained data allowed us to determine the lasing threshold for stimulated emission. It was P_{thr} = 28.3 MW/cm^2 when a laser with λ_{gen} = 532 nm was used for optical pumping. The lasing threshold was determined by a sharp change in the growth rate of the dye emission intensity (Fig. 6). The threshold dye concentration at which stimulated emission was observed was also determined for a dye solution. It was found that the minimum concentration of dye **1** at which stimulated emission is observed in the absence of silver NPs is 2.5×10^{-4} mol/L (Fig. 4, curve *3*).

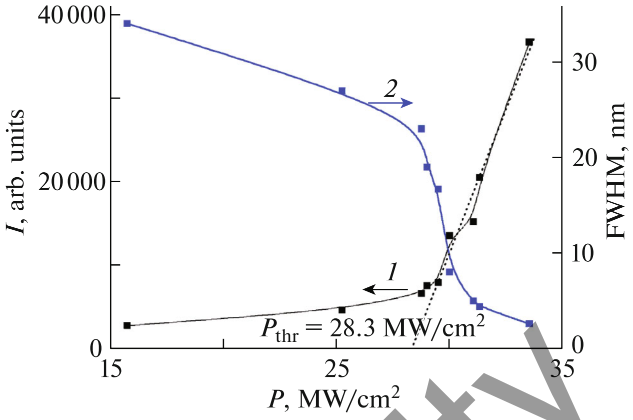

Fig. 6. Dependences of (*1*) the luminescence intensity and (*2*) the full width at half maximum of the luminescence band (FWHM) on the power density of optical pumping for a solution of dye **1**.

CONCLUSIONS

The addition of silver NPs to a solution of merocyanine dye leads to increases in its absorption cross section and in the intensity and lifetime of fluorescence. This creates the conditions for lowering the lasing threshold. It is noteworthy that the addition of silver NPs to a dye solution enables lasing even under the conditions, under which it cannot be achieved in their absence, namely, with the concentration of merocyanine **1** equal to $C_{\text{DYE}} = 10^{-4}$ mol/L. It should also be noted that it is widely accepted in the published studies that the presence of a chemical bond between NP atoms and dye molecules is a necessary conditions for the effect of NP plasmons on the photophysical properties of dyes [17]. It is noteworthy that this effect is achieved in our case in the absence of such bonds. Their absence is determined by the fact that there are no functional groups capable of coordinating with silver atoms in merocyanine **1**. Therefore, plasmons can be successfully used for the targeted control of the spectral-luminescence properties of a wide class of merocyanine dyes without functionalization of their molecules by anchor groups.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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