

## FEATURES OF THE DECAY OF EXCITED STATES OF IONIC DYES IN THE NEAR FIELD OF METAL NANOPARTICLES

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*The influence factor of silver nanoparticles on the intramolecular processes of deactivation of the electronically excited state of polymethine dyes (PD) of different ionicity has been studied. It has been demonstrated that the optical density for cationic 1 and anionic 2 dyes does not change under the action of the plasmon field of Ag nanoparticles. Whereas an increase in absorbance by almost 18% was observed for neutral dye 3. A decrease in the enhancement in fluorescence intensity in the series of anionic–cationic–neutral dyes was registered upon addition of Ag nanoparticles to their solutions. The fluorescence lifetime practically does not change for all PDs under study. Data processing within the framework of the model of the influence of a plasmonic nanoparticle on radiative transitions in a dye molecule showed that the values of plasmon-enhanced rates of radiative decay of molecules decrease from neutral to cationic and, finally, to anionic dye. The rates of energy transfer from PD to plasmonic nanoparticles decrease in the reverse sequence of dyes, i.e. anionic-cationic-neutral PD. This is expressed in a decrease in the proportion of neutral dye molecules that were deactivated by fluorescence.*

**Keywords:** polymethine dye, ionicity, localized plasmon resonance, silver nanoparticles, plasmon-enhanced fluorescence.

### Introduction

Over the last few decades, the phenomenon of localized plasmon resonance (LPR) of metal nanoparticles (NPs) has become a universal tool for studying the optical and electronic properties of various organic compounds [1, 2]. The LPR phenomenon is associated with the interaction of light and electrons on the NPs surface, which leads to strong oscillations of the electric field near the NPs. Such fluctuations are expressed in a significant increase in the local electromagnetic field around the NPs [3], which can be used for various applications, such as sensing, visualization, and energy conversion.

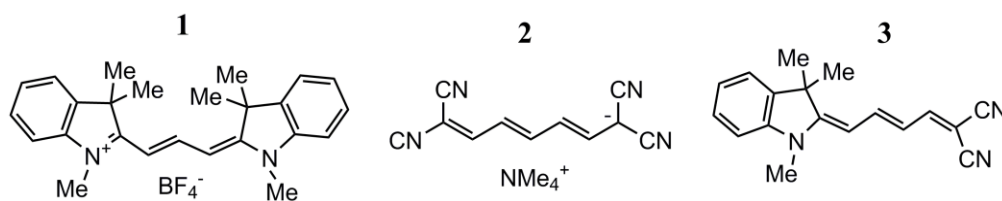
The size and shape of NPs play a decisive role in the LPR effect, since they determine the resonant frequency and strength of the plasmon resonance. The properties of the environment can also affect the LPR effect, for example, the refractive index of the environment or the presence of other molecules can change the plasmonic properties of metal NPs.

The application of plasmonic NPs of metal is currently very wide and ranges from optical technologies to biomedical applications and photovoltaic devices [2, 4]. In particular, they can be used in the development of optoelectronic devices [4, 5], nanolasers [6, 7], and photodynamic therapy [8, 9]. It was shown [10] that the addition of metal NPs to the active medium of dye lasers can lower their generation threshold. Also, in the presence of gold or silver NPs, the performance of solar [11-13] and photocatalytic [14-16] cells can be significantly increased.

Fluorophores located near the metal NPs can demonstrate both enhancement and quenching of luminescence. The magnitude and sign of the plasmonic effect of metal NPs depends on such factors as the distance between the fluorophore molecule and the plasmonic NP, the mutual orientation of their transition dipole moments, the permittivity of the medium, etc.

During the interaction between plasmonic NPs and a dye molecule, an electro-dipole interaction occurs [3, 17]. Due to the strong local electric field created by plasmonic NPs, the characteristics of the electronically excited states of organic fluorophores could be changed. This is expressed in the modification of the rates of intramolecular and intermolecular transitions with the participation of dye molecules [18, 19]. In this regard, it is reasonable to assume that the plasmonic effect of metal NPs will also depend on the ionicity of the dye.

Currently, there are practically no studies were found on the effect of the dye ionicity on the effectiveness of its interaction with plasmonic NPs. Meanwhile, the charge of metal NPs should have a strong effect on the charged molecule of dye. In this work, polymethine dyes (PDs) of various ionicity were selected: 1 – cationic, 2 – anionic, 3 – neutral dyes [20], the structural formulas of which are shown in Fig. 1.



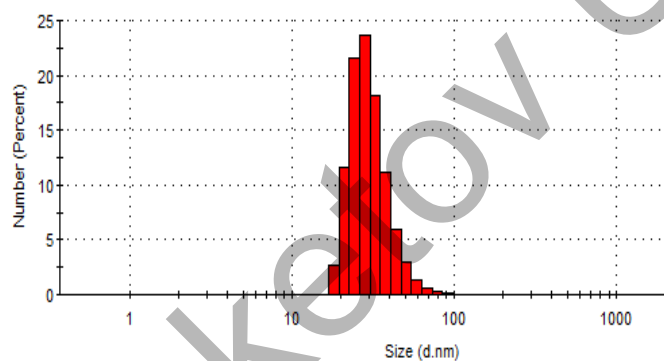
**Fig.1.** Structural formulas of PDs with different ionicity

## 1 Experimental part

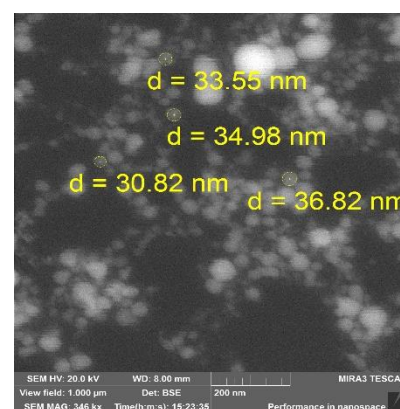
For the study, solutions of PD with a constant concentration (C) of dye 1, 2, or 3 equal to  $10^{-5}$  mol/L were prepared in ethanol. Silver NPs were used as plasmonic NPs. Their content in PDs samples was varied from  $5 \cdot 10^{-13}$  to  $10^{-12}$  mol/L.

Ag NPs were synthesized by laser ablation method. As the metallic silver target with 99.999% grade placed in ethanol (3 mL) was used. Ablation was carried out with an LQ 215 laser ( $\lambda_{\text{gen}}=532$  nm,  $E_p=90$  mJ,  $\tau=10$  ns), with a wavelength of 532 nm and a pulse repetition rate of 20 Hz. The ablation process was lasted for 10 minutes.

Zetasizer 90S (Malvern) was used to determine the size of the obtained nanoparticles. Measurements showed that the average radius of the synthesized Ag NPs is equal to  $31 \pm 9$  nm (Fig. 2a). According to the Mira 3MLU (Tescan) scanning electron microscope, they have a spherical shape (Fig. 2b). Zeta potential of Ag NPs is equal to  $-17.33$  mV (ZetaPALS, Brookhaven).



a)



b)

**Fig. 2.** Size distribution (a) and SEM image (b) of Ag NPs in ethanol.

Absorption spectra were registered on a Cary-300 spectrophotometer (Agilent), and fluorescence spectra of the samples were obtained with Eclipse spectrofluorimeter (Agilent).

The fluorescence duration of PDs molecules were measured with the TCPC system (Becker&Hickl). For the photoexcitation of solutions, lasers with picosecond pulse duration and a generation wavelength of 532 or 640 nm were used. Fluorescence decay kinetics was processed using the SPCImage program (Becker&Hickl). The fluorescence lifetime was estimated using the formula [21]:

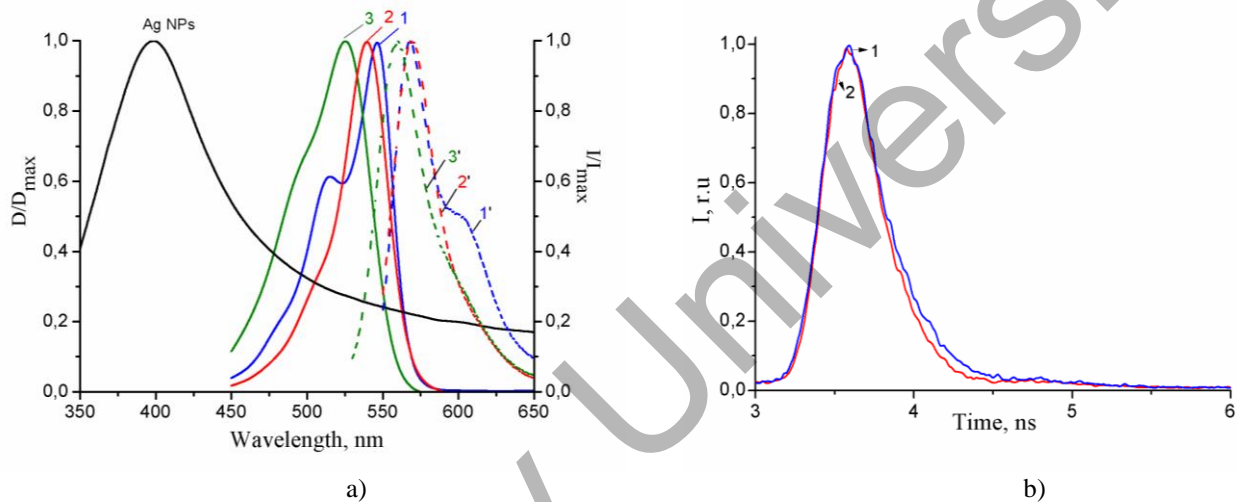
$$I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (1)$$

where  $\tau_i$  – is the decay time,  $\alpha_i$  – is the amplitude (contribution fraction) of  $i$ -th component ( $\sum_i \alpha_i = 1.0$ ) and  $t$  – is the time.

Spectral-luminescence measurements were carried out at atmospheric pressure and room temperature. To obtain reliable data, all measurements were carried out at least 3 times, and the obtained data were averaged.

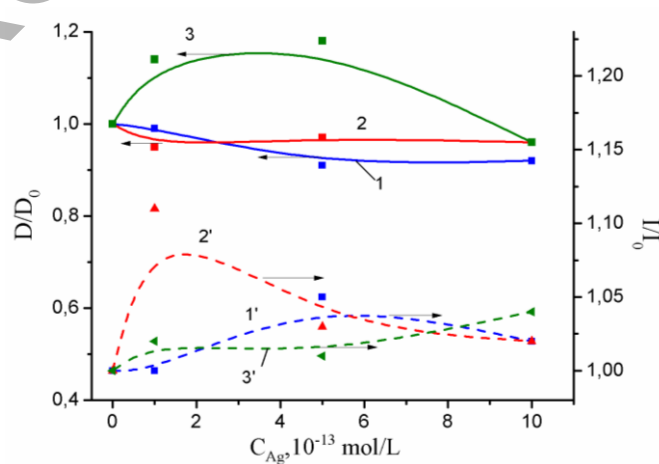
## 2 Results and discussions

The absorption bands of dyes 1, 2 or 3 (curves 1, 2, or 3, respectively) and their fluorescence (curves 1', 2', or 3', respectively) without the addition of NPs, as well as the absorption spectrum of NPs in an undiluted solution (curve Ag NPs, concentration of NPs is  $C_{Ag}=1.5 \cdot 10^{-10}$  mol/L) are shown in Fig. 3a. The maximum of the absorption spectrum of Ag NPs is located at 405 nm, and its absorption band has a significant overlap with the absorption and fluorescence bands of the PDs under study. On Fig. 3b the fluorescence decay kinetics of dyes 1 and 2 are shown.



**Fig. 3.** (a) Normalized spectra of absorption (1, 2, 3, solid curves) and fluorescence (1', 2', 3', dashed curves) of dyes 1 (1, 1', blue), 2 (2, 2', red), 3 (3, 3', green) at  $C=10^{-5}$  mol/L without addition of NPs and absorption spectrum of Ag NPs (Ag NPs curve, black); (b) decay kinetics of fluorescence for dyes 1 and 2.

It was found that no changes in the spectral characteristics of the PDs under study were observed upon addition of plasmon NPs. The absorptivity ( $D$ ) did not change for 1 and 2 dyes when Ag NPs were added (Table 1, Fig. 4).



**Fig. 4.** Effect of Ag NPs concentration ( $C_{Ag}$ ) on optical density (1, 2, 3, solid curves) and fluorescence intensity (1', 2', 3', dashed curves) of dyes 1 (1, 1', blue), 2 (2, 2', red) and 3 (3, 3', green)

For neutral dye, an increase in the  $D$  of solutions by almost 18% is observed (Table 1) upon the plasmon effect of Ag NPs. The observed increase in the absorptivity may be result of growth in the excitation rate and the transition of the dye 3 molecules to the  $S_1$ -state [22, 23]. Fluorescence becomes more intense for all dyes when Ag NPs were added to their solutions. The concentration of Ag NPs ( $C_{Ag}$ ) on the order of  $\sim 10^{-13}$  mol/L is the most suitable for both cationic dye 1 and anionic dye 2. Further growth in  $C_{Ag}$  leads to the reducing of the fluorescence intensity. It is noteworthy that the largest enhancement in the fluorescence intensity is observed for PD 2 and the smallest for PD 3. At the same time, fluorescence lifetime  $\tau_f$  practically was not changed (Table 1). For neutral PD 3, no noticeable changes in fluorescence intensity and lifetime were registered.

**Table 1.** Spectral-luminescent parameters of 1, 2 and 3 dyes at different concentrations of silver NPs\*

Silver concentration, mol/L	$\lambda_{\text{abs max}}$ , nm	$D$	$D/D_0$	$\lambda_{\text{fl max}}$ , nm	$I$ , r.u	$I/I_0$	$\tau_f$ , ns	$\tau/\tau_0$
1 (cationic) dye								
0	546	1.450	1.000	568	280	1.000	0.290	1.000
$1 \cdot 10^{-13}$	546	1.440	0.990	568	279	1.000	0.286	0.986
$5 \cdot 10^{-13}$	546	1.320	0.910	568	292	1.050	0.287	0.989
$1 \cdot 10^{-12}$	546	1.330	0.920	568	284	1.020	0.285	0.983
2 (anionic) dye								
0	540	1.230	1.000	569	287	1.000	0.253	1.000
$1 \cdot 10^{-13}$	540	1.170	0.950	569	319	1.110	0.251	0.992
$5 \cdot 10^{-13}$	540	1.190	0.970	569	295	1.030	0.250	0.996
$1 \cdot 10^{-12}$	540	1.180	0.960	569	294	1.020	0.248	0.988
3 (neutral) dye								
0	525	0.630	1.000	560	157	1.000	0.245	1.000
$1 \cdot 10^{-13}$	525	0.720	1.140	560	160	1.020	0.243	0.992
$5 \cdot 10^{-13}$	525	0.740	1.180	560	159	1.010	0.241	0.983
$1 \cdot 10^{-12}$	525	0.600	0.960	560	158	1.000	0.230	0.938

\*where,  $\lambda_{\text{abs max}}$  – is the wavelength of the absorption maximum,  $D$  – is the optical density,  $\lambda_{\text{fl max}}$  – is the wavelength of the fluorescence maximum,  $I$  – is the fluorescence intensity and  $\tau_f$  – fluorescence lifetime.

The mathematical model used in [18, 23] was used to analyze the data obtained. Calculations have shown (Table 2) that the  $w_{\text{sp}}^0$  fluorescence rate of PD in the absence of Ag NPs decreases in the series of 1–2–3 dyes. Since the radiation decay rate  $w_{\text{sp}}^0$  depends on the third power of the radiative transition frequency  $\omega$ , the observed difference in the value of  $w_{\text{sp}}^0$  is a consequence of a decrease in the frequency  $\omega$  in the series of dyes 3–2–1 (Table 1). However, large values of the transition dipole moment were obtained for molecules 1 and 2, which causes a greater value of  $w_{\text{sp}}^0$  for them. This is also clearly noticeable for the dependence of the plasmon-enhanced fluorescence rate  $w_{\text{sp}}$ , where its values decrease in the series of 1–3–2 dyes.

**Table 2.** Values of the estimated oscillator strength  $f$ , transition dipole moments  $p$ , plasmon-enhanced fluorescence rate of dye molecules  $w_{\text{sp}}$ , fluorescence rate of PD molecules without the metal NPs  $w_{\text{sp}}^0$ , FRET rate  $U(\omega|\mathbf{r})$  from PD to Ag NPs

Dye	$p$ , D	$I/I_0^*$	$w_{\text{sp}}^0$ , $s^{-1}$	$w_{\text{sp}}$ , $s^{-1}$	$w_{\text{sp}}/w_{\text{sp}}^0$	$U(\omega \mathbf{r})$ , $s^{-1}$
1 (cationic)	11.70	1.05	$2.3 \cdot 10^8$	$3.50 \cdot 10^9$	14.90	$0.35 \cdot 10^9$
2 (anionic)	11.80	1.11	$2.2 \cdot 10^8$	$3.26 \cdot 10^9$	14.80	$0.24 \cdot 10^9$
3 (neutral)	10.70	1.04	$2.1 \cdot 10^8$	$3.30 \cdot 10^9$	15.70	$1.60 \cdot 10^9$

Thus, the value of the transition dipole moment  $p$  is one of the main parameters that has influence on the magnitude of the plasmonic effect of metal NPs on a fluorophore molecule. Calculations showed that the

maximum enhancement in the radiative decay rate  $w_{sp}/w_{sp}^0$  of fluorophore molecule is observed for a neutral dye and it was equal to 15.7 times. However, due to the fact that the spectrum of the fluorescence band of PD 3 has a large overlap with the absorption spectrum of Ag NPs, the effect of fluorescence enhancement is leveled by the process of energy transfer (FRET) from dye molecules to metal NPs.

As were shown in [23, 24], FRET from dye molecules to NPs is a competing process with respect to fluorescence. For dye molecules 1 and 2, the rate  $U(\omega|\mathbf{r})$  is about 5–6 times lower than for neutral dye 3 that results in the growth of the fraction of molecules that decay through fluorescence. The values of  $w_{sp}$  for dyes 2 and 3 have similar values. Whereas the FRET rate  $U(\omega|\mathbf{r})$  to Ag NPs for dye 2 has the lowest value. In turn, this leads to large fluorescence enhancement factors observed in the experiment.

## Conclusion

The role of the ionicity of the dye in the efficiency of their interaction with plasmonic NPs of silver is considered.

It has been demonstrated that the optical density for cationic 1 and anionic 2 dyes does not change with the addition of Ag NPs. Whereas for neutral dye 3, an increase in absorbance by almost 18% is observed, which is a consequence of an increase in the rate of excitation of PD3 molecules from the  $S_0$  state to the  $S_1$  state.

At the same time, the plasmonic effect of Ag NPs has a greater effect on the fluorescence of the anionic dye. It was found that under the action of LPR of silver NPs, the fluorescence intensity increases in the series of dyes 3–1–2 (neutral–cationic–anionic). In this case, the duration of the luminescence of the considered dyes remains almost constant.

Consideration of the obtained experimental results within the framework of the model of the influence of a plasmonic NPs on radiative transitions in a dye molecule showed that the values of plasmon-enhanced rates of molecules fluorescence decrease with the transition from neutral to cationic and, finally, to anionic dye.

The rates of energy transfer from PDs to plasmon NPs decrease in the reverse sequence of dyes, i.e. anionic–cationic–neutral PD. The plasmon Ag NPs synthesized in this work and the anionic dye for which the greatest intensity enhancement was recorded have a negative charge. Therefore, it can be concluded that this prevents the PD 2 molecules from approaching the Ag NPs at the distances necessary for effective energy transfer from the dye 2 to the Ag NPs, which results in the observed greatest increase in fluorescence.

The results obtained can serve as a scientific basis for the development of new methods of plasmon modulation of signals in devices of molecular photonics, photovoltaics, photocatalysis and detectors. The ability to control the conditions of such interaction will allow us to form and study new phenomena and properties associated with the «light-matter» interaction.

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