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Plasmon enhancement of fluorescence of phthalocyanines metallocomplexes in solutions of silver nanoparticles

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Abstract. A method of creation of aqueous solutions with silver nanoparticles for studying of fluorescence of hydrophobic compounds has been proposed for metallocomplexes of phthalocyanines. The effect of silver nanoparticles on the fluorescence of phthalocyanines metallocomplexes at room and low temperatures was studied. The addition of silver nanoparticles leads to plasmonic enhancement of signals in fluorescence and fluorescence excitation spectra of the compounds of interest from 1,5 to more than 7 times. The lifetimes and quantum yield of fluorescence were measured for solutions of metallophthalocyanines in binary mixtures and in binary mixtures with the addition of silver triangular nanoplates with shells of silicon dioxide.

Fluorescence for a number of chromophores can be enhanced upon their interaction with nanoparticles of various noble metals. Such types of effects are called plasmon enhanced fluorescence and such methods have a lot of interesting analytical applications as optical sensors in colloidal solutions or in the solid state [1]. It is well known, that phthalocyanines have been widely used in organic solar cells or as effective photosensitizers in cancer treatment. The parent phthalocyanines possess hydrophobic properties and cannot be dissolved in water. The main idea of our concept was to create a methodology for observation of the effects of plasmon enhancement of fluorescence for hydrophobic organometallic compounds using aqueous solutions of silver nanoparticles (AgNPs).

In this report we presented the data on the conventional and surface-enhanced fluorescence and excitation of fluorescence spectra of Mg-phthalocyanine (Mg-Pc) and Zn-phthalocyanine (Zn-Pc), the structures of which are shown in Fig. 1. The above mentioned compounds were preliminary dissolved in dimethyl sulfoxide (C_2H_6OS) or ethanol (C_2H_5OH) with concentration about 10^{-8} M. After that, 600 µl of prepared solutions was mixed with 2400 µl of deionized water (for recording of the conventional spectra) or water solution of AgNPs. AgNPs of two types have been used: 1. triangular Ag nanoplate (average edge length - 52 nm, thickness -3 .8 nm); 2. silver triangular nameplate’s of Ag

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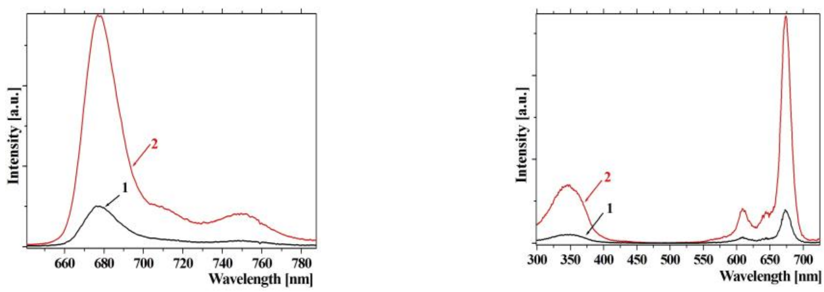
isolated in shell of SiO_2 (AgNPs-SiO_2) with using the following method. The solution of 3.1 ml AgNPs were mixed at stirring with 6,9 ml of H_2O and 0,66 ml of 0,3 M Na_2SiO_3. Then pH was adjusted to 6,8-7,2 acetic acid. After several hours AgNPs-SiO_2 were triply washed with 10 ml of H_2O at centrifugation/

a b

Fig. 1. Chemical structures of Mg-Pc (a) and Zn-Pc (b)

The fluorescence and excitation of fluorescence spectra of Mg-Pc in various solutions are shown in Fig. 2. Upon using of AgNPs-SiO_2, a plasmonic enhancement of fluorescence signals by more than 7 times of signals has been recorded in fluorescence and excitation of fluorescence spectra.



a b

Fig. 2. Fluorescence spectra (a) at $\lambda_{exc.}$ = 350 nm and excitation of fluorescence (b) spectra at $\lambda_{em.}$ = 750 nm of Mg-Pc in binary mixture of H_2O-C_2H_6OS (4:1): 1 - without AgNPs-SiO_2;2 - with AgNPs-SiO_2 at 293 K

The growth of fluorescence signals with factor more than 7 times is difficult to explain, because the quantum yield of fluorescence for Mg-Pc in tetrahydrofuran (THF) is 0.54 (absolute measurements) and cannot exceed 1 when using of AgNPs-SiO_2. In order to interpret the above mentioned data, the lifetimes and relative fluorescence quantum yields for Mg-Pc and Zn-Pc solutions in binary mixtures without and with AgNPs-SiO_2 were measured. The lifetime of the singlet state of Mg-Pc in THF is 6.6 ns, in H_2O-C_2H_6OS mixture - 5.8 ns, and in the mixture with AgNPs-SiO_2 decreases to 4.9 ns. For Zn-Pc, similar values are 3.8, 3.2, and 2.9 ns, respectively. The fluorescence quantum yields was decreased from 0.54 (in THF) to $1.4 * 10^{-3}$ in the H_2O-C_2H_6OS mixture and reached $1*10^{-2}$ for the mixture with the addition of AgNPs-SiO_2.

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References

1. E. Priyadarshini, N. Pradhan, Sensors Actuat. B: Chemical **238**, 888 (2017)