

**DEPENDENCE OF PHOTOLUMINESCENCE OF NANOPARTICLE ENSEMBLES OF STANNUM (IV) COMPLEXES IN SILICA POROUS MATRIX ON CONCENTRATION OF SATURATING SOLUTION**<sup>1</sup>I. I. Mechnikov National University of Odessa, Dvoryanska St., 2, Odessa, 65026, Ukraine<sup>2</sup>Institute of Physics, Wrocław University of Technology, W. Wyspińskiego 27, 50-370 Wrocław, Poland

Dependence of photoluminescence of high-molecular nanoformations of dyes on the basis of stannum (IV) complexes in porous glass on concentration of saturating solution has been researched. The results have been compared with photoluminescence of corresponding solutions, in which the effect of concentration quenching, was due to the Franck-Condon principle, was observed. It was found that intensity of luminescence for nanoparticle ensembles was always higher than in solution. At that, decrease of luminescence intensity alongside with concentration growth of saturating solution was observed as well. However, the observed dependence was more complicated than in solution. It can be explained by the fact that the pores with maximal sizes are filled at large concentrations of saturating solution of dye. The dye particles act almost the same as in solution, where photoluminescence is fainter, in such pores.

**1. Introduction**

It is known [1-2] that the dyes on base of the 4-valence stannum complexes are most sensitive to the gas composition of environment, therefore they can be used for construction of gas sensors, used for the ecological monitoring [3]. It is a big group of dyes, which are close structurally and differ with some details of their molecular composition only. Previous investigations show [4] that the luminescence centra in specified dyes are probable concentrated on the surface of molecules. So surface development of particles of this substance by creating of nanoparticles ensemble inside matrix of porous glass may result in increase of luminescence. We created such ensemble by soak glass with corresponding solution. At that concentration of the soaking solution is its most importable characteristic. Dependence of luminescence properties of nanoparticle ensemble on concentration of the soaking solution and also comparison of this result with luminescence of the solution itself are the subject of present pa-

per. Such research will permit to elaborate ways of affecting their optic and photoluminescence features that will considerably widen the sphere of functional hybrid nanomaterials. An important factor, affecting the effectiveness of dye luminescence, is interaction of separate dye molecules when its concentration in solution grows [5-6]. In this case aggregating takes place, i.e. formation of molecular assemblies (clusters) [7]. As centers of dye luminescence are concentrated on surface of molecule [4], aggregating causes self-passivating of dye [8] that must considerably decrease luminescence. Use of porous glass minimizes interaction between molecules and aggregations and also among molecules of dye inside assemblies, weakening this effect and strengthening luminescence [9]. Quantity of nanoparticles, formed in pores, must depend on concentration of solution, saturating glass [10].

Two dyes on the basis of complexes of four-valent stannum [11]: 4-amic-benzoyl hydrazone of tetra-dimethyl aminobenzaldehyde (hereinaf-

ter – dye **(I)**) and 4-hydroxyl-benzoyl hydrazone of tetra-dimethyl aminobenzaldehyde (hereinafter – dye **(II)**) was studied in the present paper. Dependence of luminescence spectra of nanoparticle ensembles of specified dyes in porous glass on their concentration in dimethyl formamide (DMFA) solution, which was soaked glass, was researched. Results of research were compared with photoluminescence of solutions these dyes having correspondent concentration [12].

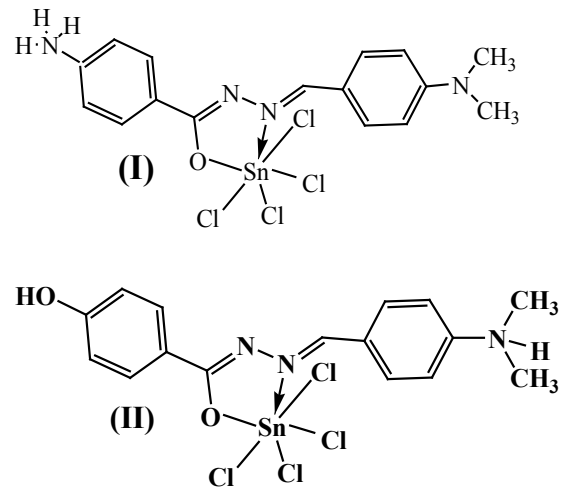
## 2. Materials and methods

Ensemble of nanoparticles of dye was formed by way of saturation of *A*-type porous silica glass with corresponding solution in DMFA. The porous glass *A* is obtained from sodium boro-silicate glass. The glass is heated at the temperature of 763K at 165h in order to separate phases rich in silica and sodium-boron. Then it is immersed in 0.5N hydrochloric acid and deionized water. The porosity determined from the mass decrement after etching was: 38%. The texture parameters of investigated glasses were determined by adsorption poroscopy method. The average diameter of pores was 30 nm, total average pore volume was 292 mm<sup>3</sup>/g and the average surface area was 54,7 m<sup>2</sup>/g. The residual fine dispersed secondary silica gel presents in pores of glass after this chemical treatment.

Duration of saturation process was 10-12 hours and its end was fixed in accordance with visual changes in the system. After the end of saturation the sample was keeping by room temperature during a day (so called low temperature annealing) in order to secure uniform enough dimensional distribution of nanoparticles in the glass [1, 10].

For experimental research of influence of saturating solution concentration on photoluminescence of nanoparticle ensemble of dye in porous matrix, porous glass was saturated by two types of dye solutions on the basis of complexes of four-valent stannum: dye **(I)** or dye **(II)**. Structural formulas of both types of dyes are shown in *Fig.1*. One can see, that both substances are very much similar as to their structure: they have the same tautomeric form «4», the same substituent type (benzoyl) and almost the same coordination set (there is “extra” hydrogen atom in dye **(II)**, se-

curing electrical neutrality of the molecule). They differ in substituent: it is amic in dye **(I)** and hydroxyl in dye **(II)**.



**Fig.1. Structural formulas of dyes, for which dependence of luminescence on solution, saturating matrix, was researched: dye (I) – 4-amic-benzoyl hydrazone of tetra-dimethyl aminobenzaldehyde, dye (II) – 4-hydroxyl-benzoyl hydrazone of tetra-dimethyl aminobenzaldehyde**

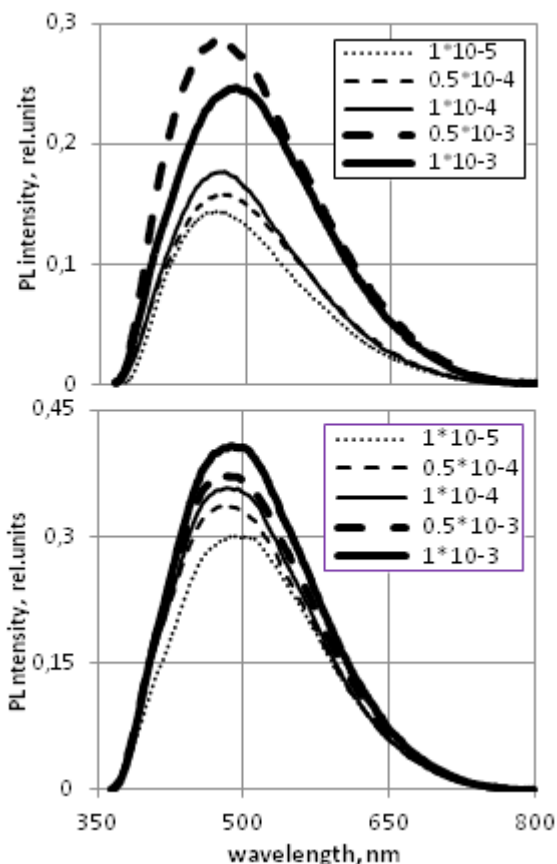
Saturating solutions were of five concentrations ( $10^{-5}$ ,  $5 \times 10^{-5}$ ,  $10^{-4}$ ,  $5 \times 10^{-4}$  and  $10^{-3}$  gMole/l). The first one can be considered rather low, and the last one is close to limiting concentration of solution.

Photoluminescence spectra were excited with UV laser LCS-DTL-374QT (wavelength  $\lambda=355$  nm, power 15 mW) and were recorded by standard set-up [13].

## 3. Experimental results

*Fig.2* shows the groups of luminescence spectra for nanoparticle ensembles of dye **(I)** and dye **(II)**, obtained at different concentrations of corresponding saturation solutions. One can see, that the spectra have one maximum at all concentrations of saturating solution for both dyes. The glow intensity of dye **(II)** with hydroxyl substituent is more than for dye **(I)** with amic substituent at any concentration of saturating solution. Maxima of glow intensity of glow intensity are situated rather close to each other for all cases. However, whereas photoluminescence spectrum for dye **(II)** remains practically hyperchromic at

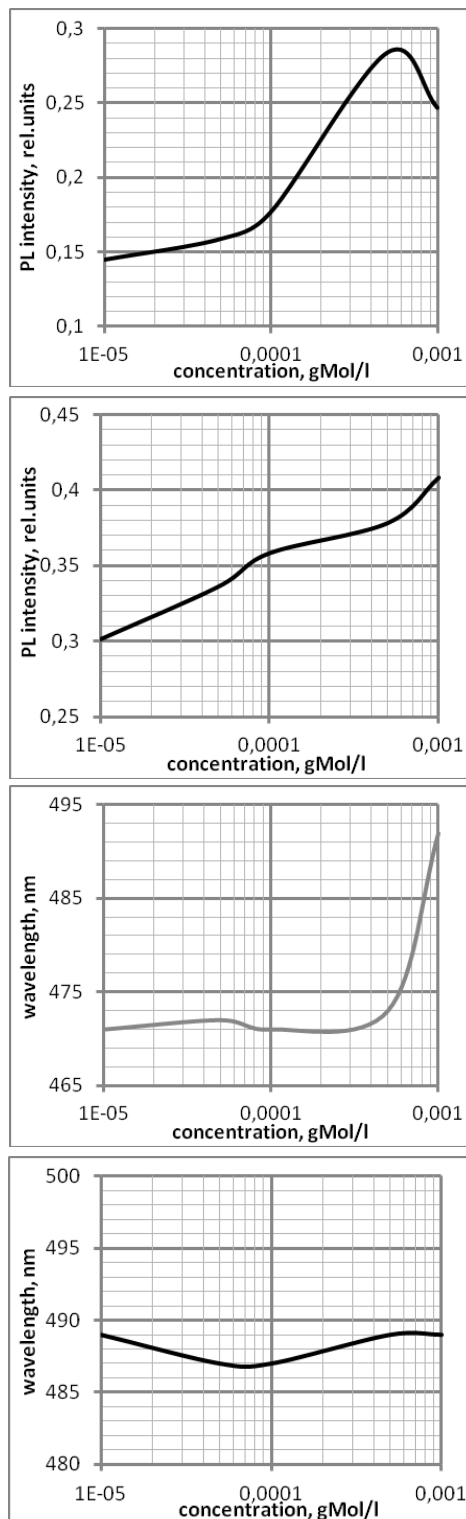
all concentrations of saturating solution, a small, but noticeable, bathochromic shift takes place for dye (I) if the concentration of saturating solution is maximal. Decrease of photoluminescence intensity corresponds to this shift.



**Fig. 2. Photoluminescence spectra of nanoparticle ensemble of dye (I) (on the top) and dye (II) (on the bottom) in porous matrix at different concentrations of saturating solution**

Fig.3 shows the experimental concentration dependence of photoluminescence parameters of nanoparticle ensemble for dye (I) (on the left) and for dye (II) (on the right) in silica porous glass matrix. Upper part of the figure corresponds to dependence of glow intensity on concentration of saturating solution, and its lower part corresponds to its maximum position of concentration of saturating solution. One can see in Fig.3 that the increase of photoluminescence intensity accords with “piecewise-linear” law, when concentrations of saturating solution are low. Photoluminescence intensity reduces for nanoparticles of dye (I), if

the concentration of saturating solution is almost limiting one. At that, such reducing is not observed, if the concentration of saturating solution is high, for nanoparticles of dye (II).



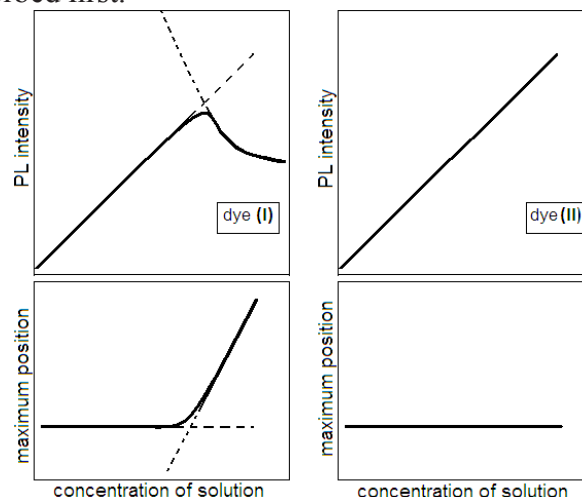
**Fig. 3. Experimental concentration dependence of parameters of photoluminescence of nanoparticle ensemble of dye (I) (on the left) and dye (II) (on the right) in silica porous glass matrix**

#### 4. Discussion

«Piecewise-linear» law of increase of luminescence intensity of nanoparticle ensemble of dye (I), when concentration of saturating solution grows, is associated, evidently, with nonuniformity of filling different sizes of pores [13] when nanoparticles of dye are formed in porous glass. When concentrations of saturating solution are low not many molecules of dye penetrate into pores, and they either penetrate into the smallest pores one by one, or stay on surfaces of larger pores as a quantity of small dye particles (such as “dew”). The silica gel particles, which gather round these dye particles, will prevent merging of them [14]. Photoluminescence intensity at that slowly increases with concentration growth. Similar processes take place, when concentration of saturating solution reaches “middle” values. However, the surface of nanoparticles, appearing inside pores, turns out to be more developed due to increase of quantity of dye molecules. That leads to faster increase of glow intensity [15-16]. When concentration of saturating solution comes close to limiting one, luminescence intensity reduces.

It's interesting to compare these results with dependence of luminescence of dye (I) solution in DMFA on its concentration in solution (left part of Fig.4, see [12]). Intensity of glow increased linearly with concentration growth, when concentrations are low. When solution concentration comes close to limiting value, effect of concentration quenching was observed, and intensity of photoluminescence started decreasing almost parabolically. Concentration quenching of luminescence for dye (I) solution in DMFA is explained by presence of two competing processes in the system: light radiation and light absorption, which take place simultaneously [17] in according with the Franck-Condon principle. If concentration of solution is low, number of radiation transitions increases with its grow, and glow intensity increases too. When concentration of solution is rather high, the process of absorption of the light, which radiated by the solution, starts to prevail, obviously, that causes concentration quenching. This supposition is supported by concentration dependence of photoluminescence maximum position:

when concentrations are low, spectrum is hyperchromic, and when they are high, bathochromic shift takes place. This shift indeed accords with supposition on prevalence of absorption process, as high energetic quanta of light are always absorbed first.



**Fig. 4. Model concentration dependence of photoluminescence parameters of dye in solution [12]: when concentrations are low, both types of dye act similarly, but for dye (II) parabola, which corresponds to concentration quenching, is beyond the figure bounds**

Our results for nanoparticles ensemble are in accord with this statement. However, reduce of luminescence intensity is not associated with concentration quenching, in contrast to solution, but with the fact that the largest pores (about hundreds of nanometers) turn out to be filled in this case. There would be so many small particles in the large pores, that they would merge in aggregation already at the stage of their formation and silica gel particles would passivate surface of dye molecules partially only wrapping around already formed aggregations [7, 9, 14]. That is why the most part of dye, which penetrated into the large pores, acts as in solution, i.e. decrease of photoluminescence intensity, which has almost the same value as that for solution, is observed. This process is also followed by intensive absorption of high energy light quanta (as the lower part of Fig.3 shows). That leads to additional decrease of dye glow intensity.

For DMFA solution of dye (II) when concentration of solution was high, glow intensity continued to increase linearly and no concentration

quenching took place (right part of *Fig.4*, see [12]). Apparently, limiting concentration for this dye is achieved before this effect appears. At that spectrum remained hyperchromic at all concentrations of the solution. These results reasonably accord with regularities, were found in our works [18-19]. Deviations of concentration dependence of photoluminescence intensity from linearity also take place for ensemble of dye (**II**) nanoparticles, as in the case with dye (**I**), on comparing it with solution. They also are associated with non-uniformity of filling with dye molecules various sizes of pores. At that, decrease of glow intensity is not observed, when concentration of saturating solution is high, as there was no concentration quenching in solution, too. This assertion is supported by absence of bathochromic shift of spectra, is typical when absorption processes in the system prevail. Photoluminescence spectrum remains hyperchromic practically, when concentration of saturating solution grows, as the lower part of *Fig.3* shows.

### 5. Conclusions

Photoluminescence spectra of formed nanoparticle ensembles have one maximum and differ only in glow intensity and position of its peak for all concentrations of dye solutions on the basis of complexes of four-valent stannum, saturating porous matrix. At that, both in solution and for nanoparticle ensemble, first increase of photoluminescence intensity is observed, when concentration of solution grows, and when it comes to solubility limit, its decrease takes place, which is associated with prevalence of the process of photons' absorption over their radiation. This is supported by the fact that intensity increase is followed by hyperchromic spectrum, and its decrease is followed by bathochromic shift.

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**Abstract**

Dependence of photoluminescence of high-molecular nanoformations of dyes on the basis of stannum (IV) complexes in porous glass on concentration of saturating solution has been researched. The results have been compared with photoluminescence of corresponding solutions, in which the effect of concentration quenching, was due to the Franck-Condon principle, was observed. It was found that intensity of luminescence for nanoparticle ensembles was always higher than in solution. At that, decrease of luminescence intensity alongside with concentration growth of saturating solution was observed as well. However, the observed dependence was more complicated than in solution. It can be explained by the fact that the pores with maximal sizes are filled at large concentrations of saturating solution of dye. The dye particles act almost the same as in solution, where photoluminescence is fainter, in such pores.

**Key words:** photoluminescence, porous glass, dyes on base of stannum complexes, nanoparticle ensembles, concentration of saturating solution

**ЗАЛЕЖНІСТЬ ФОТОЛЮМІНЕСЦЕНЦІЇ АНСАМБЛІВ НАНОЧАСТИНОК  
КОМПЛЕКСІВ 4-ВАЛЕНТНОГО СТАНУМУ ВСЕРЕДИНИ ШПАРИСТОЇ  
СИЛКАТНОЇ МАТРИЦІ ВІД КОНЦЕНТРАЦІЇ НАСИЧУЮЧОГО РОЗЧИНУ**

**Резюме**

Досліджено залежність фотолюмінесценції високомолекулярних формувань барвників на базі комплексів чотиривалентного стануму всередині шпаристого скла від концентрації насичуючого розчину. Результати порівняно із фотолюмінесценцією відповідних розчинів, у яких спостерігається ефект концентраційного гасіння, зумовлений принципом Франка-Кондома. Виявлено, що інтенсивність люмінесценції ансамблю наночастинок завжди вища, аніж у розчині. При цьому, теж спостерігається зменшення інтенсивності люмінесценції при наближенні концентрації насичуючого розчину до границі розчинності. Проте, залежність, що спостерігається, є складнішою, аніж у розчині, і може пояснюватися заповнюванням шпарин максимальних розмірів у випадку великих концентрацій насичуючого розчину. Тож барвник поводить себе всередині таких шпарин майже, наче у розчині, де фотолюмінесценція слабша.

**Ключові слова:** фотолюмінесценція, шпаристе скло, барвники на базі комплексів стануму, ансамблі наночастинок, концентрація насичуючого розчину

**ЗАВИСИМОСТЬ ФОТОЛЮМИНЕСЦЕНЦИИ АНСАМБЛЕЙ НАНОЧАСТИЦ  
КОМПЛЕКСОВ 4-ВАЛЕНТНОГО ОЛОВА В ПОРИСТОЙ СИЛИКАТНОЙ МАТРИЦЕ  
ОТ КОНЦЕНТРАЦИИ НАСЫЩАЮЩЕГО РАСТВОРА**

**Резюме**

Исследована зависимость фотолюминесценции высокомолекулярных нанообразований красителей на основе комплексов четырёхвалентного олова в пористом стекле от концентрации насыщающего раствора. Результаты сравниваются с фотолюминесценцией соответствующих растворов, в которых наблюдается эффект концентрационного гашения, связанный с принципом Франка-Кондома. Обнаружено, что для ансамблей наночастиц интенсивность люминесценции всегда выше, чем в растворе. При этом так же наблюдается уменьшение интенсивности фотолюминесценции при приближении концентрации насыщающего раствора к пределу растворимости. Однако, наблюдаемая зависимость более сложная, чем в растворе, и может быть объяснена тем, что при больших концентрациях насыщающего раствора красителя оказываются заполненными поры максимальных размеров, в которых краситель ведёт себя почти, как в растворе, где фотолюминесценция слабее.

**Ключевые слова:** фотолюминесценция, пористое стекло, красители на основе комплексов олова, ансамбли наночастиц, концентрация насыщающего раствора