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PHOTOLUMINESCENCE OF TAUTOMERIC FORMS OF NANOPARTICLE ENSEMBLES OF DYES BASED ON THE 4-VALENCE STANNUM COMPLEXES IN POROUS SILICA GLASS

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Luminescence of tautomeric forms of dyes based on the 4-valence stannum complexes was researched. Symmetry of photoluminescence spectra of different tautomeric forms relative to direction of reading of atom positions in the hydrazide fragment was found clockwise or anti clockwise. It was determined that the illumination of nanoparticle ensembles of dyes in A-type porous silica glass is always more intensive than in appropriate solution. It was shown that the luminescence intensity of tautomeric forms increases, if the substituent comes nearer to the coordination set irrespective of type and nature of substituent and type of coordination set. At the same time, change of illumination energy of tautomeric forms depends on both type and nature of substituent and coordination set. The results were explained by the development of inner surface of matrix and also by the features of atom disposition in dye molecule and by interaction between them.

1. INTRODUCTION

Interest to the dyes on base of the 4-valence stannum complexes is non-random, as far as it is known [1-3] that such dyes are most sensitive to the gas composition of environment, therefore they can be used for construction of gas sensors, used for the ecological monitoring [4]. It is a big group of dyes, which are close structurally and differ with some details of their molecular composition only. So arise an opportunity to research the influence of these details on the optical properties of dyes. Investigation of the mechanism of optical processes in such systems will make it possible to improve the luminescence efficiency of new nanostructures. It would give the opportunity to create new generation of microelectronic devices, such as new classes of luminophores and photosensitive optoelectronics elements, which would promote expansion of potential resources of optoelectronics.

It is known [5] that the dyes usually luminesce only in the solutions, which provide formation of electron-vibration sublevels in the system, so its illumination is a result of transitions among them. We managed to find luminescence of nanoparticle ensembles of dyes formed in A-type porous silica glass. Illumination intensity of such system considerably exceeds luminescence intensity of appropriate solution.

The photoluminescence spectra of all the feasible tautomeric forms of dyes based on the 4-valence stannum complexes with coordination sets of 2 types and with the substituent in hydrazide fragment of both nicotinoyl (HN⁺) and benzoyl types were researched in the present paper. The last ones were of 2 sorts: hydroxyl (OH) and amine (NH₂). We studied 4-dimethylaminobenzaldehydes {SnCl₄ON} and 2-hydroxynaphthaldehydes {SnCl₃O₂N}. Fig.1 shows the structural formulas of appropriate coordination sets (e.g., see [6]).

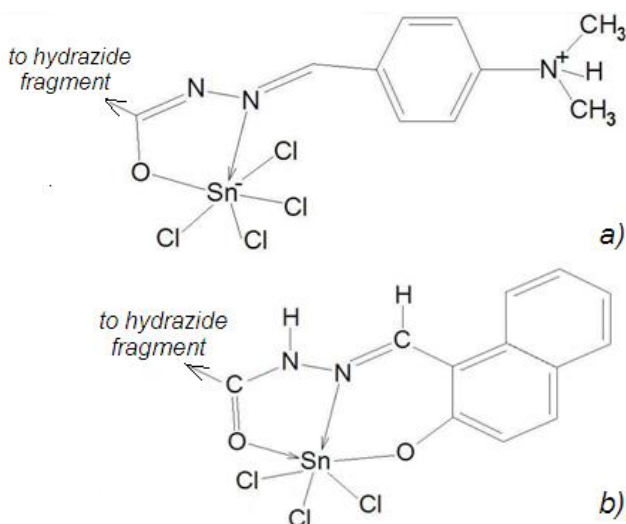


Fig. 1. Structural formulas of coordination sets of 4-dimethylaminobenzaldehydes (a) and 2-hydroxynaphthaldehydes (b) in the case of hydroxyl substituent. Loss of hydrogen atom on nitrogen atom occurs for providing electroneutrality for amine substituents

Hydrazide fragment represents usual benzene ring with substituent (*A*). The substituent can be of nicotinoyl or benzoyl type. In the first case some nitrogen group incorporates into the benzene ring directly (i.e. in fact a substitution of carbon atom with nitrogen one takes place), in the second case one of the hydrogen atoms in some position of hydrazide fragment is substituted with hydroxyl or amine group. The isomeric dyes, which differ only in substituent (*A*) position relative to the hydrazide fragment, are called the dyes with different tautomeric forms. Substituent position in current tautomeric form is designated by number. The bond, connecting the hydrazide fragment with the coordination set, is marked as «1». One indicates the other positions with the natural numbers anticlockwise from «2» to «6» by increase. Fig.2 shows the nicotinoyl substituent in position «5», and benzoyl one in position «3».

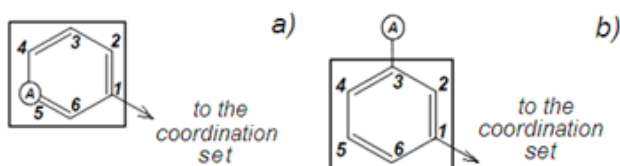


Fig. 2. Hydrazide fragment with constituent of nicotinoyl (a) and benzoyl (b) types

2. MATERIALS AND METHODS

The porous glass *A* is obtained from sodium boron-silicate glass. The glass is heated at the temperature of 763 K at 165 hours 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 mm³ g⁻¹ and the average surface area was 54.7 m² g⁻¹. The residual fine dispersed secondary silica gel presents in pores of glass after this chemical treatment.

Nanoparticle ensembles of dyes in porous silica glass were formed by soaking glass, embedding it directly into dimethylformamide (DMFA) solution of appropriate dye with concentration 1×10⁻³ gMole l⁻¹. We have selected particularly this solvent because it adsorbs the light in radiated range minimally, and so all dyes fluoresced most intensively in it. Storage duration of glass in the solution of each concrete dye was verified visually and usually formed more than 12 hours. After finish of soaking the specimen was exposed to low-temperature anneal that was necessary in order to provide sufficiently uniform space distribution of nanoparticles in glass.

Composition and structure of the investigated dyes were determined by the complex of spectroscopic and X-ray methods. Fig.1 and Fig.2 show these results.

Photoluminescence spectra were excited with UV laser LCS-DTL-374QT (wavelength λ=355 nm, power 15 mW) and were recorded by standard set-up [7].

3. EXPERIMENTAL RESULTS

Fig.3 shows photoluminescence spectra for three dyes on the basis of complexes, molecular structures of which are the most alike. They all have similar coordination set (depicted in Fig.1,a), shortened {SnCl₄} and similar tautomeric form «2». They differ only in substituent. The spectra, marked with thick and dash line are for dyes with substituents of benzoil type OH or NH₃, correspondingly, and spectrum, marked with

thin line belongs to dye with substituent of nicotinoil type NH^+ . The left part of Fig.3 corresponds to solutions of the specified dyes in DMFA, and the right one – to ensemble of nanoparticles in porous matrix. One may see from the figure that similar dyes in porous matrix glow considerably more intensively than in solution.

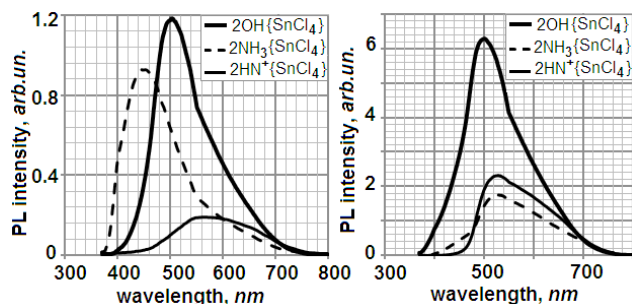


Fig. 3. Photoluminescence spectra for some dyes, which have similar molecular structure, in DMFA solution (on the left) and as nanoparticles ensemble in porous glass (on the right)

A comparison of the photoluminescence spectra of DFMA-solutions of dyes based on the 4-valence stannum complexes and *A*-type silica porous glass matrixes, soaked in same solution, showed [8] that they have one maximum for all the considered dyes. These spectra only differ in glow intensity and spectral position of this maximum. Taking it into account and as the coordination set preserves its original for isomeric dyes with different tautomeric forms we have compared the histograms, which correspond with the intensity and maximum position of photoluminescence spectrum depending on the complex's tautomeric forms for further research.

Fig.4 shows the histograms of dependences of intensity and maximum position of photoluminescence spectra of dyes with benzoyl type hydroxyl (OH) substituent on its position in tautomeric form for the complexes with coordination sets $\{\text{SnCl}_4\text{ON}\}$ and $\{\text{SnCl}_3\text{O}_2\text{N}\}$. One can see that the glow intensity of nanoparticle ensemble of dye always exceeds the glow intensity of its solution. Dye with coordination set $\{\text{SnCl}_3\text{O}_2\text{N}\}$ illuminates more intensively both in solution and in porous matrix. However, the photoluminescence intensity for the dye with coordination set $\{\text{SnCl}_4\text{ON}\}$ increases almost sixfold by transition from solution to the nanoparticles ensemble,

whereas for the dye with coordination set $\{\text{SnCl}_3\text{O}_2\text{N}\}$ it increases roughly threefold only.

One can see from histograms, which describe the change of luminescence maximum position, that all the photoluminescence spectra are hyperchromic ones by transition from solution to the nanoparticle ensemble irrespective of tautomeric form and coordination set for the dyes with benzoyl type

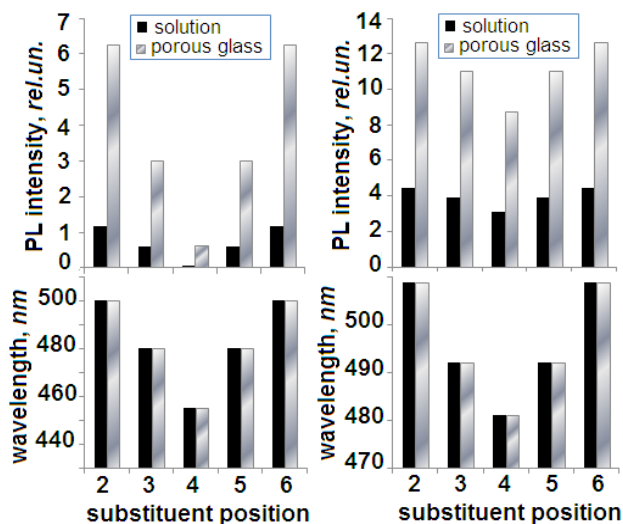


Fig. 4. Dependence of photoluminescence intensity and maximum position of its spectrum for dye with coordination set $\{\text{SnCl}_4\text{ON}\}$ (on the left) and $\{\text{SnCl}_3\text{O}_2\text{N}\}$ (on the right) on position of benzoyl type OH substituent in tautomeric form

hydroxyl (OH) substituent. We also can mark that the wavelength of illumination differs by the change of the coordination set insignificantly for each tautomeric form. In all the cases the illumination energy of current tautomeric form of dyes based on 2-hydroxynafaldehyde $\{\text{SnCl}_3\text{O}_2\text{N}\}$ is a little less than of those based on 4dimethylaminbenzaldehyde $\{\text{SnCl}_4\text{ON}\}$. Besides, one can conclude from histograms that the illumination of dyes with tautomeric form «4», in which the substituent is most distant from the coordination set in it, has maximal energy.

Fig.5 shows the histograms of dependences of intensity and maximum position of photoluminescence of dyes with benzoyl type amine (NH_3) substituent on it position in tautomeric form for the complexes with coordination sets $\{\text{SnCl}_4\text{ON}\}$ and $\{\text{SnCl}_3\text{O}_2\text{N}\}$. One can observe for such dyes the same regularity as for ones with hydroxyl substituent.

ent: illumination of nanoparticle ensemble of dye in the porous glass is more intensive than in its solution irrespective of tautomeric form. The illumination of dye with coordination set $\{\text{SnCl}_3\text{O}_2\text{N}\}$ in solution is about 2.5-fold fainter than that with coordination set $\{\text{SnCl}_4\text{ON}\}$, which has the same tautomeric form. Intensity of photoluminescence for the dye with coordination set $\{\text{SnCl}_3\text{O}_2\text{N}\}$ increases by almost ten times by transition from solution to the nanoparticle ensemble, whereas for the dye with coordination set $\{\text{SnCl}_4\text{ON}\}$ it increases less than 2-fold (while for the tautomeric form «4» it doesn't change practically in this case).

Researching change of maximum position of photoluminescence spectrum for dyes with benzoyl type amine (NH_2) substituent on its position in tautomeric form shows bathochromic shift of photoluminescence spectra for all tautomeric forms of dyes with coordination set $\{\text{SnCl}_4\text{ON}\}$ by transition from solution to the nanoparticle ensemble, whereas in the case of coordination set $\{\text{SnCl}_3\text{O}_2\text{N}\}$ they remain hyperchromic. Herewith the wavelength of illumination, when tautomeric form changes for the case of coordination set $\{\text{SnCl}_3\text{O}_2\text{N}\}$, changes to a very little degree (within 10 nm). Same effect occurs also for the solution of dyes with coordination set $\{\text{SnCl}_4\text{ON}\}$. However, wavelength of illumination changes more considerably (up to 50 nm) by transition to the nanoparticle ensemble in this case. Illumination of dyes with tautomeric form «4», in which substituent is the most distant from coordination set, also has maximal energy for this substituent.

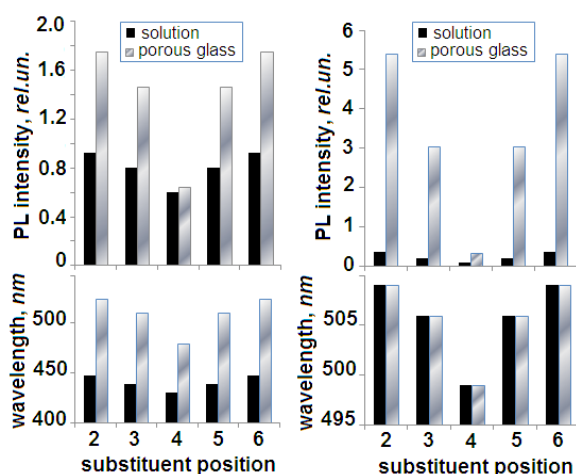


Fig. 5. Dependence of photoluminescence intensity and maximum position of its spectrum for dye with coordination set $\{\text{SnCl}_4\text{ON}\}$ (on the left) and $\{\text{SnCl}_3\text{O}_2\text{N}\}$ (on the right) on position of benzoyl type NH_2 substituent in tautomeric form

The dyes with nicotinoyl type amine (HN^+) substituent behave somewhat in a different way. Fig.6 shows that the histograms of dependences of photoluminescence intensity on the substituent position in tautomeric form are very similar for both types of coordination sets for the dyes with such substituent. In both cases the illumination intensity changes to a little degree for different tautomeric forms in solution, but by transition from solution to the nanoparticle ensemble it increases about by ten times (for the tautomeric form «4» this increment is a little less). The difference is only that the dyes based on 2-hydroxynafthaldegyde $\{\text{SnCl}_3\text{O}_2\text{N}\}$ glow about 4-fold more intensively than those based on 4dimethylaminbenzaldehyde $\{\text{SnCl}_4\text{ON}\}$. However quite notable difference in dependences of photoluminescence spectra of dyes with nicotinoyl type amine (HN^+) substituent on the substituent position in tautomeric form deduces from histograms of change of maximum position of photoluminescence spectrum of dyes with such substituent as against similar spectra of dyes with benzoyl substituent. As distinct from dyes with benzoyl type substituents radiant energy decreases for these dyes when substituent moves away from coordination set (irrespective of its type), and thus it turns out to be minimum for tautomeric form «4». Besides, hypsochromic shift of photoluminescence spectra takes place for all tautomeric forms by transition from solution to nanoparticle ensemble for dyes on the basis of 4-dimethylaminbenzaldehyde $\{\text{SnCl}_4\text{ON}\}$, whereas spectra remain hyperchromic for the dyes on the basis of 2-hydroxynafthaldegyde $\{\text{SnCl}_3\text{O}_2\text{N}\}$ irrespective of tautomeric form.

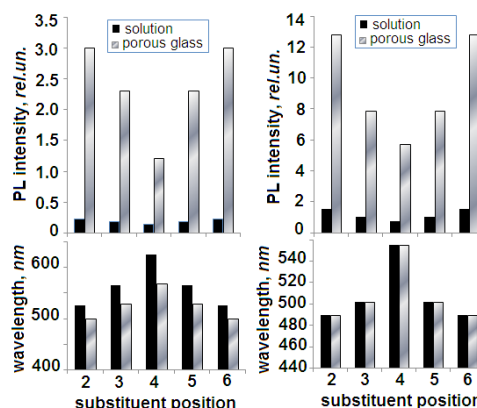


Fig. 6. Dependence of photoluminescence intensity and maximum position of its spectrum for dye with coordination set $\{\text{SnCl}_4\text{ON}\}$ (on the left) and $\{\text{SnCl}_3\text{O}_2\text{N}\}$ (on the right) on position of nicotinoyl type HN^+ substituent in tautomeric form

4. DISCUSSION

The nature of occurrence of nanoparticle ensemble glow in pores of porous silica glass is the same as in solution: luminescence occurs as consequence of transition between level, situated close to bottom of first excited dye molecule state, and set of electron-vibration sublevels of its ground state. Intensity of photoluminescence at that increases on the account of development of inner matrix surface and due to insignificant probability of aggregations' appearance because of presence of residual silica gel in pores of A-type matrix, it always exceeds intensity of glow of appropriate solution. The silica gel prevents aggregation of dye in big pores by covering the formed dye nanoparticles [9-10]. It is known [11-13] that aggregation would lead to dye bleaching. Effect of increasing of photoluminescence intensity of dye in porous glass takes place irrespective of type of their coordination set and tautomeric form of dyes based on 4-valence stannum complexes.

Invariability of photoluminescence spectra occurs relative to direction of reading of positions of atoms in hydrazide fragment clockwise or anti clockwise for tautomeric forms of all the dyes based of 4-valence stannum complexes both in solution and in the case of nanoparticle ensemble. That is, tautomeric forms with substituents in positions «2» and «6» or «3» and «5» turn out to be equivalent. This conclusion seems trivial at first, as all connections of benzoyl ring are equivalent. Nevertheless, on account of possible intramolecular hydrogen bondings the specified tautomeric forms are not necessarily equivalent. The obtained results show that intramolecular hydrogen bondings are not formed in the researched complexes for any coordination sets, tautomeric forms or substituents.

Glow intensity increases when substituent in hydrazide fragment moves closer to coordination set for all tautomeric forms both in dye solution and in its nanoparticle ensemble. This effect can be considered as direct consequence of symmetry of tautomeric forms relative to direction of reading of atom positions in hydrazide fragment. Indeed, as tautomeric forms are equivalent to substituents in positions «2» and «6» additional rotation symmetry occurs in dye molecule. It causes formation of additional electron rotational levels, fit for radiative transition.

In order to explain the dependence of dye radiative energy on substituent position in tautomeric form one should assume presence of two competing mechanisms in the system. One is connected with interaction of substituent with coordination set, and the other is connected with the degree of freedom of the substituent in relation to benzoyl ring of hydrazide fragment. Let us recall that at substitution nicotinoyl type substituent incorporates into benzoyl ring of hydrazide fragment, substituting carbon therein. At that no additional degree of freedom appears in the substituent. On account of interaction of substituent and coordination set some energy is radiated, and the closer the substituent to coordination set is, the higher the energy is. And that is why histogram, represented in the lower part of the Fig.6, shows that maximal radiative energy corresponds to tautomeric forms with the closest to coordination set substituent «2» (or «6»), and minimal energy corresponds to tautomeric form with the most distant from coordination set substituent «4», as one may see from maximum position of photoluminescence spectra. In the case of benzoyl substitution small hydrogen atom in benzoyl ring of hydrazide fragment is substituted by bulky group of atoms, which can vibrate relative to benzoyl ring. The further from coordination set benzoyl type substituent is, the more intensively it can vibrate, and the more electron-vibration states, fit for radiative transition, occur in the system, that, as follows from histograms shown in the lower part of Fig.4 and Fig.5, with a vengeance compensates losses, connected with substituent's moving away from coordination set. Thus, at benzoyl substitution maximal radiative energy corresponds to tautomeric form with maximally distant from coordination set substituent «4».

5. CONCLUSIONS

Illumination intensity of nanoparticle ensembles of dyes based on the 4-valence stannum complexes in the pores of porous silica glass is always more than illumination intensity of appropriate solution. Herewith the luminescence intensity of dyes of such type with hydroxyl substituent was always more than in case with the amine one.

Symmetry of photoluminescence spectra relative to clockwise or anti clockwise reading of

atom positions in the hydrazide fragment takes place for the tautomeric forms of all the dyes based on the 4-valence stannum complexes both in solution and for nanoparticle ensemble. Here-with the illumination intensity increases if the substituent in the hydrazide fragment moves closer to the coordination set for all the tautomeric forms both in dye solution and in its nanoparticle ensemble. Probably this effect was connected with appearance of additional electron-rotational states, which would suit for radiative transition. It's a consequence of the degeneration due to abovementioned symmetry. At the same time, it was shown that the change of illumination energy of tautomeric forms depends on both type and nature of substituent and on coordination set.

Radiative energy at nicotinoyl substitution is minimal for the tautomeric form with substituent, which is most distant from coordination set. However, at benzoyl substitution radiative energy will be maximal for such tautomeric forms.

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Summary

Luminescence of tautomeric forms of dyes based on the 4-valence stannum complexes was researched. Symmetry of photoluminescence spectra of different tautomeric forms relative to direction of reading of atom positions in the hydrazide fragment was found clockwise or anti clockwise. It was determined that the illumination of nanoparticle ensembles of dyes in A-type porous silica glass is always more intensive than in appropriate solution. It was shown that the luminescence intensity of tautomeric forms increases, if the substituent comes nearer to the coordination set irrespective of type and nature of substituent and type of coordination set. At the same time, change of illumination energy of tautomeric forms depends on both type and nature of substituent and coordination set. The results were explained by the development of inner surface of matrix and also by the features of atom disposition in dye molecule and by interaction between them.

Key words: photoluminescence, porous glass, dyes on base of stannum complexes, tautomeric forms, nanoparticle ensembles

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ФОТОЛЮМИНЕСЦЕНЦІЯ ТАУТОМІРНИХ ФОРМ АНСАМБЛІВ НАНОЧАСТИНОК БАРВНИКІВ НА БАЗІ КОМПЛЕКСІВ 4-ВАЛЕНТНОГО СТАНУМУ В СЕРЕДИНІ ШПАРИСТИХ СИЛКАТНИХ СТЕКОЛ

Резюме

Досліджено люмінесценцію таутомірних форм барвників на базі комплексів чотиривалентного стануму. Виявлено симетрію спектрів фотолюмінесценції різних таутомірних форм відносно напрямку відліку позицій атомів у гідрозидному фрагменті за стрілкою годинника або проти неї. Виявлено, що світіння ансамблю наночастинок барвника у шпаристому силікатному склі типу А є завжди більш інтенсивним, ніж у відповідному розчині. Продемонстровано, що інтенсивність люмінесценції таутомірних форм зростає, якщо замісник наближається до координаційного вузла, незалежно від типу і природи замісника і типу координаційного вузла. Натомість, змінення енергії випромінювання таутомірних форм залежить як від типу замісника, так і від його природи і координаційного вузла. Результати пояснено розгорнутістю внутрішньої поверхні матриці, а також особливостями розміщення атомів всередині молекули барвника та взаємодії між ними.

Ключові слова: фотолюмінесценція, шпаристі стекла, барвники на базі комплексів стануму, таутомірні форми, ансамблі наночастинок

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ФОТОЛЮМИНЕСЦЕНЦІЯ ТАУТОМЕРНИХ ФОРМ АНСАМБЛЕЙ НАНОЧАСТИЦ КРАСИТЕЛЕЙ НА ОСНОВЕ КОМПЛЕКСОВ 4-ВАЛЕНТНОГО ОЛОВА В ПОРИСТЫХ СИЛИКАТНЫХ СТЕКЛАХ

Резюме

Исследована люминесценция таутомерных форм красителей на основе комплексов четырёхвалентного олова. Обнаружена симметрия спектров фотолюминесценции разных таутомерных форм относительно направления отсчёта позиций атомов в гидрозидном фрагменте по, либо против часовой стрелки. Установлено, что свечение ансамбля наночастиц красителя в пористом силикатном стекле типа А всегда интенсивнее, чем в соответствующем растворе. Показано, что интенсивность люминесценции таутомерных форм возрастает при приближении заместителя к координационному узлу, независимо от типа и природы заместителя и типа координационного узла. Вместе с тем, изменение энергии излучения таутомерных форм зависит как от типа заместителя, так и от его природы, и от координационного узла. Результаты объяснены развитостью внутренней поверхности матрицы, а также особенностями расположения атомов в молекуле красителя и взаимодействия между ними.

Ключевые слова: фотолюминесценция, пористое стекло, красители на основе комплексов олова, таутомерные формы, ансамбли наночастиц