

Spectral properties of nanoporous SiO₂ matrices with polymethine dye molecules

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SiO₂ matrices with PM1, PM2 and PM3 polymethine dyes are synthesized. The dyes PM2 and PM3 are found to form *H*-aggregates and dimers, respectively, in aqueous solutions. PM1 dye forms neither *H*-aggregates nor dimers due to peculiarities of its structure. The luminescence maximum of PM1 dye in the matrix is shown to be hypsochromically shifted with respect to that in the solution. A rigid structure of SiO₂ matrix suppresses rotation of PM1 dye molecules, that increases the lifetime of the excited states of the dye molecules by 1.6 times in comparison with the one in the solutions.

Синтезовані SiO₂ матриці з поліметиновими красителями PM1, PM2 і PM3. Установлено, що в водних розчинах красители PM2 і PM3 утворюють, відповідно, *H*-агрегати і димери, а краситель PM1 не утворює, що обумовлено особливостями структури PM1. Внаслідок цього композити SiO₂:PM2 і SiO₂:PM3 практично повністю обесцвечуються, а композит SiO₂:PM1 зберігає окраску довгий час. Максимум люмінесценції красителя PM1 в матриці зсунуто гіпсохромно відносно розчинів. Жорстка структура SiO₂ матриці призводить до пригнічення обертання молекул красителя PM1, що збільшує час життя збудженого стану молекул цього барвника в 1,6 рази.

Спектральні властивості напористих SiO₂ матриць з молекулами поліметинових барвників. О.Н.Безкровна, І.М.Питула, А.Г.Плаксії, В.М.Пузіков, Ю.А.Гуркаленко, Д.Качковський, Ю.Л.Сломінський, А.Канаєв.

Синтезовано SiO₂ матриці з поліметиновими барвниками PM1, PM2 і PM3. Встановлено, що у водних розчинах барвники PM2 і PM3 утворюють, відповідно, *H*-агрегати та димери, а барвник PM1 їх не утворює, що обумовлено особливостями структури PM1. Спостерігається гіпсохромний зсув максимуму люмінесценції барвника PM1 у матриці щодо розчинів. Жорстка структура SiO₂ матриці призводить до пригнічення обертання молекул барвника PM1, що збільшує час життя збудженого стану молекул цього барвника у порівнянні з розчинами в 1,6 рази.

1. Introduction

Recent years have seen considerable interest in creation of effective and reliable limiters of the intensity of dangerous laser radiation. High radiation intensity of widely used laser facilities leads to destruction of the elements of optical devices located in the vicinity of laser radiation focusing. Moreover, high-power coherent radiation in the visible spectral region gives rise to thermal burn of retina and vascular tunic of human eye [1, 2]. The optical limiters are produced on the base of such materials which essentially weaken high-intensity optical beams and have higher transmission coefficients at low radiation intensities.

The media used as limiters of high-power laser radiation intensity comprise liquid solutions of organic dyes, disperse systems and films of metal and semiconductor particles, liquid and KDP crystals with incorporated nanoparticles [1, 3, 4]. Squarilium and polymethine dyes with delocalized π -electron systems are promising light energy converters for the visible and near-IR spectral region to be used for creation of nonlinear optical materials [2–8]. Polymethine dyes are characterized by intense absorption from excited states in the visible region with a cross-section of approximately $7 \cdot 10^{-16} \text{ cm}^2$ comparable with the absorption cross-section from the ground state [9].

Nanoporous sol-gel SiO_2 matrices have high mechanical and radiation strength in combination with high absorption ability and chemical stability. Therefore, they may be an ideal medium for incorporation of active molecules [4,10]. The obtaining of composite materials on the base of SiO_2 matrices possessing laser [11] and nonlinear optical properties was discussed in a number of papers [2, 4]. There were considered the properties of the composite materials SiO_2 /polymethine dyes [12–14], in particular, of thin composite films for the IR region [14, 15]. The semiorganic thin films based on silicon and zirconium oxides containing the polymethine dye IR1051 were shown to emit in the IR region at wavelengths up to $1.3 \mu\text{m}$ [14].

However, though the composites SiO_2 /polymethine dyes are promising for the use in the capacity of components of devices for quantum electronics and optoelectronics, the influence of SiO_2 matrix on the properties of the incorporated dyes has not been studied sufficiently so far. It should be

noted that the micro-environment of the dye molecules in the nanoporous matrix differs from the one in the solutions, since the incorporated dye contacts with the xerogel surface.

In the present paper we report the data on the synthesis of SiO_2 matrices with a number of polymethine dyes, and consider the effects connected with the influence of the medium of the matrix on the spectral and luminescent properties of the incorporated dyes.

2. Experimental

To synthesize the silica gel, we used tetraethoxysilane (TEOS; Aldrich), ethanol, formamide (FA, chemically pure) and twice distilled water. In the capacity of active molecules there were applied polymethine dyes (Fig. 1) synthesized at the Institute of Organic Chemistry (Kyiv, Ukraine) by the conventional method, as described in [16]. The dimethylformamide (DMFA), ethanol and twice distilled water were used as solvents for the dyes.

SiO_2 matrices were obtained using the sol-gel method by the hydrolysis of TEOS, with the addition of citric acid as a reaction catalyst [11, 17–19]. TEOS and ethanol were mixed by a magnetic stirrer during 30 min. Then we added twice distilled water, a few drops of water solution of citric acid and FA, the latter being used to control separation of moisture from the xerogel. After the addition of the solution of the dye in FA, the resulting mixture was stirred during two hours. The obtained sol was placed into plastic cuvettes which then were hermetically sealed and stored till the gel was formed. Afterwards they were opened, and the samples were dried during 3–4 weeks at room temperature and at 60°C during the next 7–10 days. The geometric size of the finished SiO_2 matrices was $0.5 \times 0.5 \times 1.5 \text{ cm}^3$.

The absorption spectra of the samples were measured by Lambda 35 UV/Vis Spectrophotometer (Perkin-Elmer, USA) in 200–1100 nm region. The luminescence spectra were obtained using fluorimeter FluoroMax-4 (Horiba Jobin Yuon, USA). The lifetime of the excited state of luminescence was estimated using Fluo-Time 200 picosecond spectrofluorimeter (PicoQuant, Germany) and FluorFit software (PicoQuant, Germany).

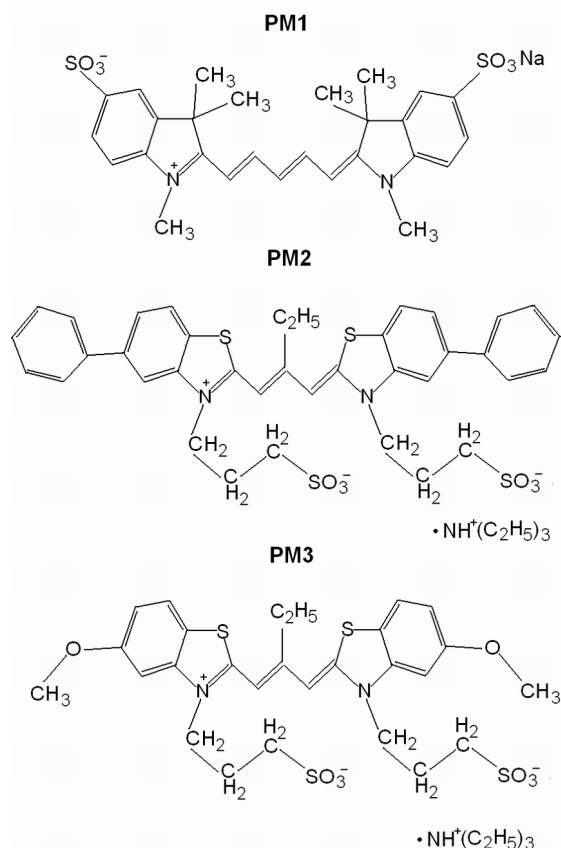


Fig. 1. Structural formulas of PM1, PM2 and PM3 polymethine dyes.

3. Results and discussion

We studied the influence of SiO₂ matrix and the structure of the dye molecules on the behavior of the properties of the dyes in the matrices. As is known, the dyes with the structure similar to that of PM2 and PM3 form associates in water [20], whereas the dyes which structure is similar to the one of PM1 do not form associates. The absorption and luminescence spectra of the dyes PM1, PM2 and PM3 were measured in ethanol, DMFA, water, SiO₂ sol and SiO₂ matrix. The shapes of the absorption bands of PM1, PM2 and PM3 in ethanol and DMFA were similar. The solutions of these dyes in ethanol and DMFA were stable for a long time. A bathochromic shift of the maxima of the absorption and luminescence spectra of PM1 with respect to those of PM2 and PM3 was observed both in the solvents and in SiO₂ matrix (Table) [13]. Such a shift is caused by the increase of the effective length of polymethine chain (the quantity of CH=CH groups) in PM1 in comparison with those in PM2 and PM3 dyes [2, 13]. The

Table. Absorption and luminescence maxima of polymethine dyes (PM1, PM2 and PM3) in different media

Medium	Absorption maxima, nm	Luminescence maxima, nm
PM1 ($\lambda_{ex} = 600$ nm)		
SiO ₂ matrices, 60°C	650	668
DMFA	648	679
ethanol	650	674
H ₂ O	642	668
PM2 ($\lambda_{ex} = 520$ nm)		
SiO ₂ gel	556	581
DMFA	558	588
ethanol	556	588
H ₂ O*	449	574, slightly
PM3 ($\lambda_{ex} = 560$ nm)		
SiO ₂ gel	563	587
DMFA	568	598
ethanol	565	596
H ₂ O**	522	584, slightly

The concentrations of the dyes were: 1·10⁻⁵ M (PM1, PM2 and PM3) in the solutions; 8.6·10⁻⁶ mole/dm³ (PM1) and 1.3·10⁻⁵ mole/dm³ (PM2 and PM3) in SiO₂ matrices;

* $\lambda_{ex} = 400$ nm, ** $\lambda_{ex} = 520$ nm.

spectral and luminescent properties of polymethine dyes are mainly defined by their long-wavelength π - π^* transition which dipole moment is directed along the chain of conjugation from one heteroradical to the other [6].

It is found that the maxima of the absorption bands of PM2 and bands PM3 are shifted from 556 nm (for PM2) and 565 nm (for PM3) in ethanol to 449 nm and 522 in water, respectively (Fig. 2, Table). The maximum of the absorption of PM2 in water is shifted hypsochromically with respect to the one in alcohol by 107 nm, that is typical of the formation of *H*-aggregates of PM2 in water. The absorption band of PM3 water solution is characterized by redistribution of the intensities of the short- and long-wavelength maxima with respect to its ethanol solution. In particular, the intensity of the former maximum rises, whereas the intensity of the monomer band absorption reduces. This shift that may be caused by the formation of PM2 dimers is characteristic of

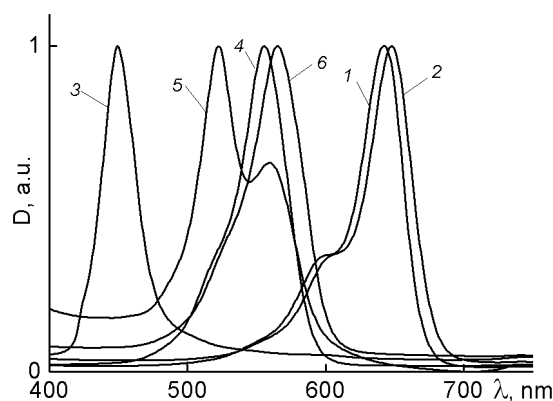


Fig. 2. Absorption spectra of PM1 (1, 2), PM2 (3, 4) and PM3 (5, 6) polymethine dyes in water (1, 3, 5) and ethanol (2, 4, 6) with a dye concentration of $1 \cdot 10^{-5}$ M.

water solutions of cyanine, rhodamine and xanthene dyes [21]. At the same time, PM1 dye does not form aggregates in water (Fig. 2), obviously due to peculiarities of its structure. The behavior of the intensities of the short- and long-wavelength maxima in the absorption spectra of PM1 dye in alcohol and water solution does not change. The intensity of its color remains unchanged, and its water solutions are stable for a long period of time, whereas the water solutions of PM2 and PM3 dyes bleaching with time. Luminescence of these dye in water is weak (Table 1) due to the absence of emission from *H*-aggregates [6, 13, 21].

As is seen, the luminescence maxima of PM2 and PM3 dyes in SiO_2 gel are hypsochromically shifted with respect to those in ethanol and DMFA (Table). This is explained by higher viscosity of the gel in comparison with that of the solutions, as well as by the formation of aggregates of PM2 and PM3 molecules in water at the matrix synthesis. The intensity of PM2 and PM3 color gradually reduces while the gel undergoes ageing. After drying at 60°C the matrices containing these dyes become practically completely colorless (Fig. 3).

At the same time, the color of PM1 is retained both in the gel and in SiO_2 matrix dried at 60°C . As distinct from PM2 and PM3 polymethines, the dye PM1 in SiO_2 matrix is in the monomer form (Table). The Stokes shift of this dye in the matrix is 437 cm^{-1} (the maxima of the absorption and luminescence bands are 650 nm and 668 nm, respectively). This is characteristic of symmetrical polymethine dyes (where such a shift may reach 700 cm^{-1}) and leads to an essential overlapping of the absorp-

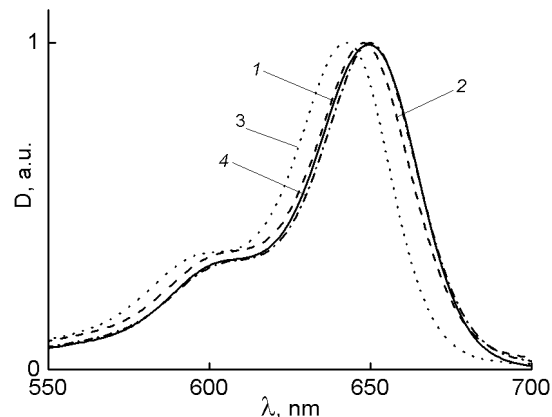


Fig. 3. Absorption spectra of SiO_2 matrices (60°C) with polymethine dyes: PM1 (1), PM2 (2) and PM3 (3). The dye concentration in sol is $1 \cdot 10^{-6}$ mole/ dm^3 .

tion and luminescence spectra [9]. In the luminescence spectrum of PM1 in SiO_2 matrix the intensity in the vicinity of 720 nm diminishes in comparison with that in the solutions. This is obviously caused by a reduced quantity of conformations of the dye molecules in the rigid matrix in comparison with that in the dye solutions, due to disturbance of the planar structure.

The influence of the micro-environment also becomes evident in the shifts of the maxima of the absorption and luminescence bands by several nanometers for PM1 dye in the sequence ethanol-DMFA-water (Table, Fig. 4). Their absorption maxima in the matrix and in ethanol solution are the same (650 nm). The observed hypsochromic shift of the absorption maximum in water solution with respect to the maxima in DMFA and ethanol solutions may be caused by the rise of the polarity of the medium in the sequence ethanol-DMFA-water which is defined by the value of dielectric permittivity: 78.3 for water, 24.3 for ethanol [22] and 36.7 for DMFA [23].

It is found that the lifetime of excited state (τ) of PM1 molecules in SiO_2 matrix exceeds the one in the solvents. For FA, ethanol and water this value is equal to 1.094 ns ($\lambda_{ex} = 600\text{ nm}$; the dye concentration is $8 \cdot 10^{-5}$ mole/ dm^3). For the matrix SiO_2 with the same dye concentration τ rises up to 1.78 ns. The rise of τ almost by two fold for molecules of polymethine dyes in solid polyurethane matrix in comparison with the corresponding value in ethanol solutions reported in [2] is explained by limited movement of dye molecules in polymer medium. As is known, excitation of dye

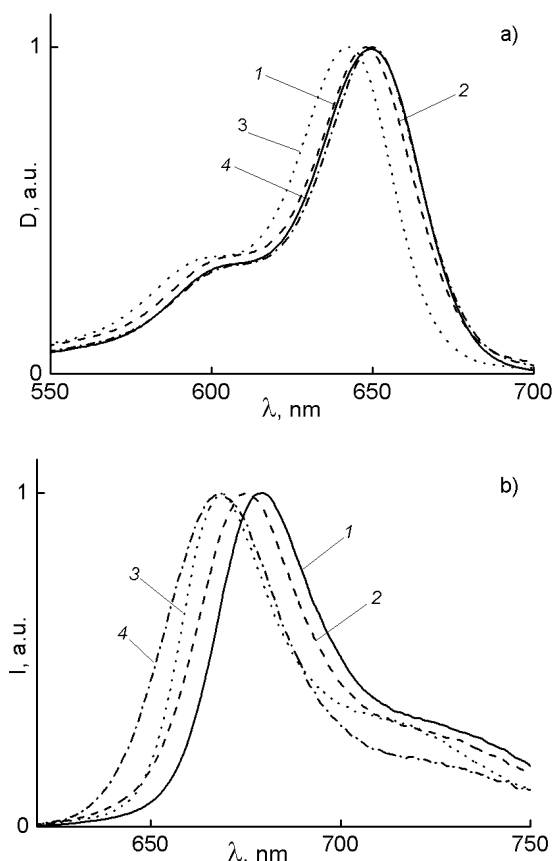


Fig. 4. Absorption (a) and luminescence (b) spectra of PM1 polymethine dye in different media: 1 — DMFA, 2 — ethanol, 3 — water, 4 — SiO₂, 60°C. The concentrations of PM1 are $9.5 \cdot 10^{-7}$ mole/dm³ in SiO₂ matrix and $1 \cdot 10^{-6}$ M in the solutions.

molecules leads to re-orientation of their dipole vectors. Thereat, the molecules may start rotating as a whole, or a new state of the molecules with new coordinates of the nuclei may be formed due to intramolecular rotation of the molecule fragments. There may also occur *cis-trans*-isomerization of polymethine dye molecules followed by twisting of polymethine chain [2]. In SiO₂ matrix the dye molecules are distributed in the pores, and the rigid xerogel skeleton which surrounds the molecules blocks their movement and conformation changes, that influences the rise of τ .

4. Conclusions

SiO₂ matrices with PM1, PM2 and PM3 polymethine dyes using FA in the capacity of DCCA and citric acid were synthesized. The absorption and luminescence spectra of PM1, PM2 and PM3 dyes were measured in

ethanol, DMFA, water solutions and SiO₂ matrices. The dyes PM2 and PM3 are found to form *H*-aggregates and dimers, respectively, in aqueous solutions. In ethanol and DMFA their form remains monomeric. For PM1 such an effect is not observed due to peculiarities of its structure. Consequently, the composites SiO₂:PM2 and SiO₂:PM3 become practically colorless, whereas SiO₂:PM1 preserves its color for a long time. A rigid skeleton of the xerogel structure suppresses rotations of the molecules of the polymethine dye PM1. As a result, the lifetime of excited state of the dye molecules increases by 1.6 times in comparison with the corresponding value for the solutions. The obtained data testify that the composites SiO₂:PM1 may be used in devices for quantum electronics and optoelectronics.

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