

Composite Materials on the Base of Nanoporous SiO₂ Matrices with Polymethine Dyes Molecules

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Sol-gel SiO₂ matrices with Polymethine dyes (PM1, PM2 and PM3) were synthesized using citric acid as a catalyst. There were measured the absorption and luminescence spectra of PM1, PM2 and PM3 dyes (with a concentration of 1·10⁻⁵ mole/dm³) in different solvents (ethanol, dimethylformamide, formamide and water) and in sol-gel SiO₂ matrices. The said dyes were found to be present in monomeric form in ethanol, dimethylformamide and formamide. PM1 dye did not form dimers in water and in matrices and retained its color. PM2 and PM3 dyes aggregated into the network of SiO₂ matrices and in water solution, and the intensity of their coloration reduced in the course of time.

Keywords: Sol-gel SiO₂ matrices, Nanopores, Luminescence, Polymethine dyes, Non-linear optical materials.

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1. INTRODUCTION

The development of laser technologies has aroused considerable interest in the creation of optical limiting materials used to protect solid-state sensors and eyes from intense laser beams [1, 2]. Nonlinear absorptive organic dyes are among the most widely studied optical limiting materials. The creation of optical limiting devices that protect sensitive optical involves the use of active components with high RSA (reverse saturable absorption) [1]. High values of RSA in the visible spectral region are characteristic of organic dyes including Polymethine and Squarylium dyes [1]. The necessary condition for the existence of RSA-mechanism for dye molecules – is the excess (at the excitation wavelength) of the absorption cross-section of the excited state above the cross-section of linear ground state absorption [2-4]. RSA is one of the most low-threshold and effective physical mechanisms leading to nonlinear decrease of radiation intensity.

Presented in [2] were the results of the investigations of the optical limiting behavior of acid blue 29 ethanol solutions under the influence of a low-power CW He-Ne laser irradiation at 632.8 nm. Polymethine dyes as donor-acceptor conjugated compounds which have highly polarizable π -electron systems, are of interest in the capacity of non-linear optical (NLO) materials [1, 4]. In [1] the non-linear properties of Polymethine and Squarylium dyes were studied in the elastopolymeric material polyurethane acrylate and in ethanol solutions. In [4] the NLO properties of solutions a series of asymmetric cyanine dyes were investigated. However, the solutions of these dyes lose their color with time.

Different NLO materials are prepared using the sol-gel method as the most preferable, since it allows

to obtain optical elements of various forms, e.g. monoliths, thin film and fibers. SiO₂ matrices do not possess NLO properties, but with their low optical losses they serve as ideal matrices for nonlinear materials. Into SiO₂ matrices there can be incorporated various active nano-objects, in particular, nanocrystals such as PbS [5] and the dye molecules having laser [6] and NLO properties [1]. Reported in [7] is the use of the sol-gel method for the synthesis of three types of nanocomposites with NLO properties: semiconductor-glass, metal cluster-glass, and organics-glass nanocomposites.

A special position among solid materials belongs to nano-porous silicate glasses synthesized by the sol-gel method, as their properties are widely needed for modern scientific and technological developments. In particular, such materials possess high mechanical and radiation strength in combination with high absorption capacity and chemical stability, as well as and high transparency in the visible and near-infrared spectral regions.

Limited space in the pores of SiO₂ matrix and efficient contact of the dye molecules with the walls of the pores make the micro-environment of the dye molecules different from that in the case when these molecules are contained in the solution. In our study, we examined the effect of the microenvironment of the dye molecules incorporated into the matrices, on their absorption and luminescence spectra. There were synthesized SiO₂ matrices with three different Polymethine dyes (Fig. 1), and the effect of the water environment on the dimerization of the dye molecules and discoloration was studied.

2. EXPERIMENTAL

For the silica gel synthesis we used tetraethox-

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ysilane (TEOS; Aldrich), ethanol, dimethylformamide (DMFA), formamid (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 (Kiev, Ukraine).

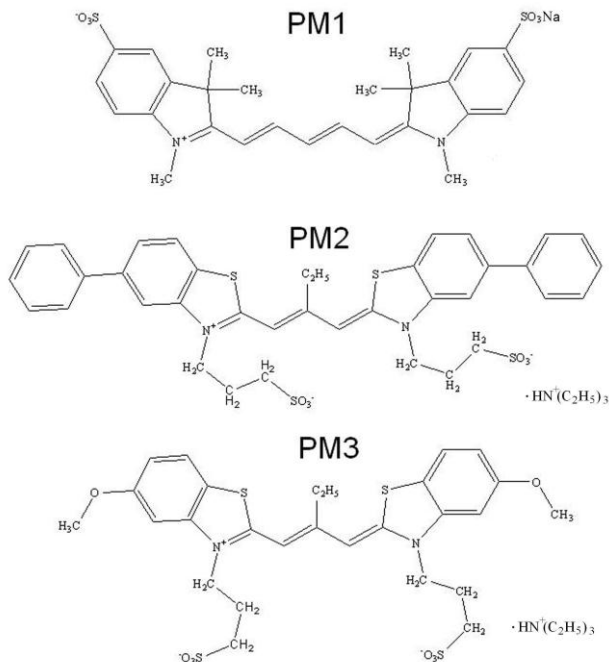


Fig. 1 – Structural formulas of PM1, PM2 and PM3 Polymethine dyes

SiO₂ matrices were synthesized using the sol-gel method by the hydrolysis of TEOS with the addition of citric acid as a reaction catalyst [6, 8]. It is known that the use of acid as a catalyst of the hydrolysis reaction leads to the formation of a three-dimensional network consisting of SiO₂ particles of nanometer size [6, 9]. TEOS and ethanol were stirred with a magnetic stirrer during 30 minutes. Then we added twice distilled water, a few drops of citric acid water solution and FA as a DCCA (the additive controlling separation of moisture from the xerogel). Then the solution of the dye in FA was added to the mixture, and the resulting mixture was stirred during two hours. The obtained sol was placed into plastic cuvettes; the latter were hermetically sealed and stored till the gel was formed. Then the cuvettes 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 densities of the SiO₂ matrices with FA (1.5 – 1.6 g/cm³) were determined by the method of hydrostatic weighing and from their geometric size (0.5 × 0.5 × 1.5 cm) and weight.

3. RESULTS AND DISCUSSION

We measured the absorption and luminescence spectra of PM1, PM2 and PM3 dyes in ethanol, DMFA, FA solutions and in SiO₂ matrices (dried at

60°C). The absorption spectra of Polymethine dyes are presented in Fig. 2. The positions of the absorbance and luminescence maxima of the long-wavelength bands of PM1, PM2 и PM3 dyes are shown in Table 1. As seen from Fig. 1, the shapes of the absorption bands of PM1-PM3 dyes in ethanol, DMFA and FA solutions are similar. The position of the absorption and luminescence maxima differ slightly (Table 1). The solutions of these dyes were found to be stable in FA, DMFA and ethanol solutions. At the change-over from the solutions of PM1, PM2 and PM3 dyes in ethanol, DMFA and FA to SiO₂ matrix there was observed hypsochromic shift of the luminescence peaks. This shift is due to changes in the microenvironment of the dye, the presence of minor amounts of water, as well as to the interaction of the dye molecule with the surface of the pores formed by the three-dimensional network of the xerogel consisting of the chains of SiO₂ nanoparticles.

The absorption maximum of PM1 dye in aqueous solution shifts hypsochromically only by 8 nm relative to ethanol solution (650 nm in ethanol solution and 652 in water), the coloration intensity remains unchanged (Fig. 2). At the same time, the color of the dyes PM2 and PM3 noticeably changed in aqueous solution. For PM2 dye in an aqueous medium there was observed hypsochromic shift of the absorption maximum by 31 nm with respect to ethanol solution. For the dye PM3 the absorption maximum shifted by 20 nm.

The appearance of a short-wave absorption maximum in aqueous solutions and a decrease of the intensity of the molecular band (as for PM3 dye, Fig. 2) is observed for many classes of dyes including cyanine, rhodamine, xanthene and other dyes [10]. At aggregation of the dye the formation of dimers is followed by a hypsochromic shift of the maximum of the bandwidth from the dimer band and its expansion. Such a change in the absorption spectrum is due to the formation of polymolecular structures of H-aggregates. Typically, the H-like aggregates do not luminesce similar to the dimers [10].

A few days later, aqueous solution of PM1 dye was stable, but PM2 and PM3 dyes gradually changed their color and became colorless.

For all the three dyes (PM1, PM2 and PM3) the absorption maxima in SiO₂ matrices are shifted hypsochromically relative to the dye solution in ethanol, DMFA and FA (Fig. 2). This is connected with a the reduced interaction of the dye molecules in the xerogel network. It should be noted that these dyes became colorless in SiO₂ gels at the use of nitric acid as a catalyst, probably due to their degradation. At the substitution of the strong nitric acid by the weak citric acid the dyes PM2 and PM3 retain their colors in the gels, and the dye PM1 does not lose the color in the SiO₂ matrices dried at 60°C. Dyes PM2 and PM3 in the matrices dried at 60°C lose their color almost completely (Fig. 3). The observed effect seems to be caused by dimerization of the dyes PM2 and PM3 in the porous matrices however, in the case of PM1 dye dimerization is absent. The tendency of PM2 and PM3 dyes to aggregation may be caused by

their conformation features [10].

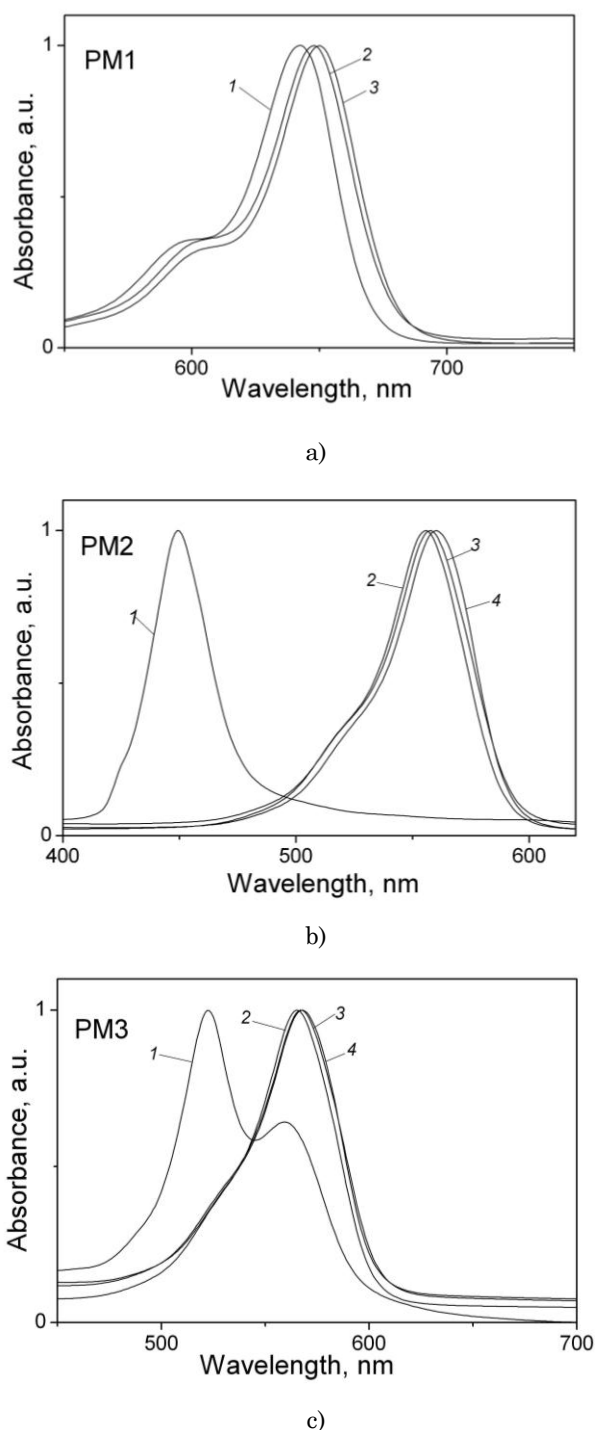


Fig. 2 – Absorption spectra of PM1 (a), PM2 (b) and PM3 (c) Polymethine dyes in various solvents: water (1), ethanol (2), DMFA (3) and FA (4) with dyes concentration of $1 \cdot 10^{-5}$ M

At the concentration of the dye PM1 in the matrix higher than $3 \cdot 10^{-5}$ mole/dm³ there was observed quenching of the dye luminescence caused by reabsorption due to a small Stokes shift characteristic of Polymethine dyes.

Table 1 – Absorbance and Luminescence maxima of Polymethine dyes (PM1, PM2 and PM3) in different media.

Medium	Absorbance 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
FA	560	588
DMFA	558	-
ethanol	558	588
H ₂ O*	449	574, slightly
PM3 ($\lambda_{Ex} = 560$ nm)		
SiO ₂ gel	563	587
FA	568	-
DMFA	568	598
ethanol	565	596
H ₂ O**	522	584, slightly

The concentrations of the dyes were: $1 \cdot 10^{-5}$ M in the solution; $8.6 \cdot 10^{-6}$ mole/dm³ (PM1) and $1.3 \cdot 10^{-5}$ mole/dm³ (PM2 and PM3) in SiO₂ matrices; * $\lambda_{ex} = 400$ nm, ** $\lambda_{ex} = 520$ nm.

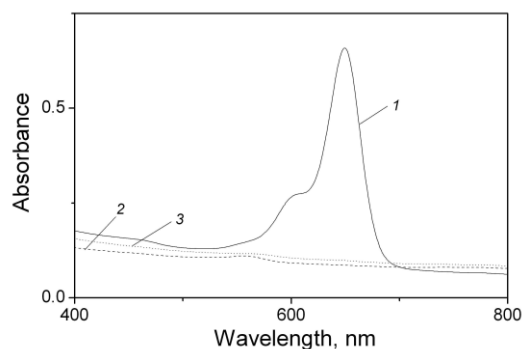


Fig. 3 – Absorption spectra of Polymethine dyes PM1 (1), PM2 (2) and PM3 (3) in SiO₂ matrices (60°C) with a dye concentration of $1 \cdot 10^{-6}$ mole/dm³ – in sol, and $8.6 \cdot 10^{-6}$ – $1 \cdot 10^{-5}$ mole/dm³ – in matrices, respectively.

4. CONCLUSIONS

There were synthesized SiO₂ matrices with PM1, PM2 and PM3 Polymethine dyes using FA in the capacity of DCCA and citric acid as a catalyst for the hydrolysis reaction TEOS were synthesized. The absorption and luminescence spectra of PM1, PM2 and PM3 dyes were measured in ethanol, DMFA, FA, water solutions and SiO₂ matrices. The dye PM1 was found not to form dimers in water and in the matrices and to retain its color. The dyes PM2 and PM3 form aggregates in the matrix and in water. When the concentration of the dye in the matrix is higher than $3 \cdot 10^{-5}$ mole/dm³ there is observed quenching of its luminescence. The obtained dates testify to the possibility to use SiO₂ matrices with PM1 Polymethine dye for the creation of optical limiting materials.

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