

Cyanine dye excimer formation in nanoporous SiO₂ matrices

B.A. Gnap, I.I. Bespalova, S.L. Yefimova, A.V. Sorokin

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin ave., 61001 Kharkiv, Ukraine

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Novel red-shifted band has been observed in luminescence spectra of a cyanine dye embedded into nanoporous SiO₂ matrix. That band is concentration dependent and disappears at cooling to low temperature. It has been associated with the dye excimer formation due to strong interaction with the pores surface.

В спектрах люмінесценції ціанінового красителя, введеного в нанопористу SiO₂ матрицю, обнаружена новая полоса, смещенная в красноволновую область. Данная полоса является концентрационно-зависимой и исчезает при охлаждении до низкой температуры. Она приписана образованию эксимеров красителя в результате сильного взаимодействия с поверхностью пор.

*Формування ексимерів ціанінового барвника в нанопористих SiO₂ матрицях.
Б.А. Гнап, І.І. Беспалова, С.Л. Єфімова, О.В. Сорокін*

У спектрах люмінесценції ціанінового барвника, що введено до нанопористої SiO₂ матриці, спостерігається нова смуга, яка зміщена у червонохвильову область. Ця смуга є концентраційно-залежною і зникає при охолодженні до низької температури. Вона асоційована з формуванням ексимерів барвника внаслідок сильної взаємодії з поверхнею пор.

1. Introduction

Nanoporous materials are very attractive due to their wide abilities to adsorb and interact with atoms, ions and molecules on their large interior surfaces and in the nanometer sized pore space [1,2]. Particularly, they could be used as a host for fluorescent molecules providing them novel properties like for example enhanced photostability [3], supramolecular organization and so on [4-6]. Nanoporous SiO₂ matrices are very promising hosts for organic and inorganic molecules via their quite gentle synthetic conditions, rigidity, transparent glass formation and so on [4,7-10].

Recently we have published effective embedding cyanine dyes into nanoporous SiO₂

matrix (10-20 nm pore diameter) with Förster resonant energy transfer realization [10].

In present article we report peculiarities of one of these dye accumulation in the matrix. It results in intense red-shifted band appearance in the dye luminescence spectrum associated with excimer formation.

2. Experimental

The SiO₂ sol-gel matrices synthesis was describe elsewhere [9]. In result we obtained round SiO₂ transparent plates with ~ 2 cm diameter and 1 mm thickness. After polycondensation finishing matrices was annealed at 750 °C. To work with the same matrix within experiment series each matrix was divided on several pieces. DiD (1,1'-dioctadecyl-3,3,3',3'-tetramethylindod-

icarbocyanine perchlorate, Fig. 1a) dye was obtained from Sigma-Aldrich (USA) and used as received. To embed dyes into SiO_2 matrix its pieces was placed into the dye chloroform solution for at least one hour. After that sample was dried at temperature 60°C for at least three hours.

Luminescence spectra were recorded using fluorescence spectrometer Lumina (Thermo Scientific, USA) equipped with solid sample holder. For luminescence measurement $\lambda_{exc} = 600\text{ nm}$ has been used. Absorption spectra was registered using a microspectrometer USB4000 (Ocean Optics, USA) supplied with an incandescent lamp. Luminescence spectra at low temperature were recorded using cryostat, in which samples was cooled down to liquid nitrogen temperature, a diode-pumped YAG:Nd³⁺ laser ($\lambda = 532\text{ nm}$) for excitation and monochromator MDR-23 for registration. Luminescence decay spectra were registered using FluoTime 200 fluorescence lifetime spectrometer (PicoQuant, Germany) equipped with 531 nm picosecond pulsed laser diode head. An instrument response function (IRF) full width at half maximum (Δ_{FWHM}) for the whole setup was about 100 ps. Decay time analysis has been performed using FluoFit software (PicoQuant, Germany).

3. Results and discussion

DiD dye well dissolves in many solvents excluding aqueous ones revealing quite narrow intense absorption ($\lambda_{max} = 650\text{ nm}$ in dimethylformamide (DMF)) and luminescence ($\lambda_{max} = 675\text{ nm}$ in DMF) bands (Fig. 1b). The dye is highly accumulates in nanoporous SiO_2 matrix with a very strong unresolved absorption at matrix thickness 1 mm and more [10]. The best solvent for matrix impregnation found to be the chloroform [10]. At low dye concentration used in our previous experiments the dye mainly preserves its luminescent band with $\lambda_{max} = 670\text{ nm}$ (Fig. 2a, curve 1) hereafter referred to as the monomer band. The dye concentration increasing results in novel red-shifted band with $\lambda_{max} = 720\text{ nm}$ appearing and became dominant (Fig. 2a, curve 4). Such situation could be achieved both by the dye concentration enhancement in stock solution and by successive a several times matrix immersion into the solution with low dye concentration (Fig. 2a). Using specially obtained a very thin matrix with thickness less than 1 mm lets us to record absorption spectra of the dye accumulated sample (Fig. 2b). Fig. 2b

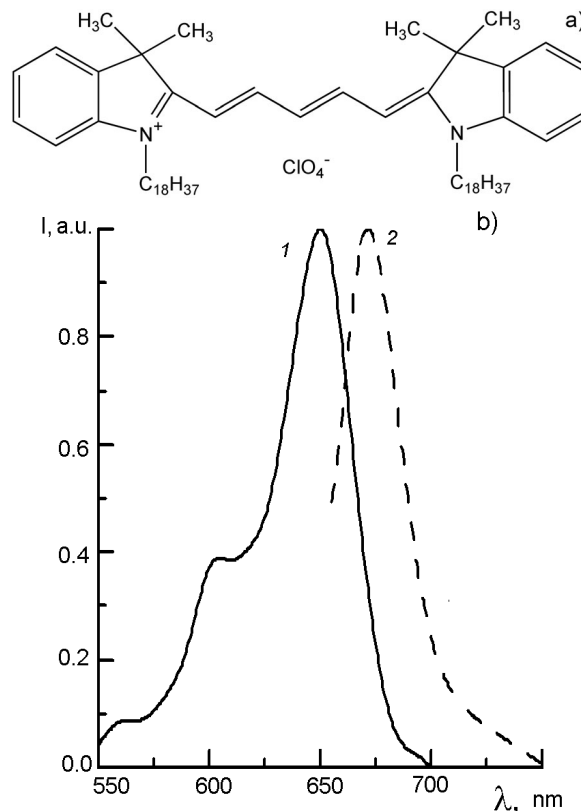


Fig. 1 a) Structural formula of DiD dye, b) its absorption (1) and luminescence (2) spectra in DMF solution.

clearly shows only one band with $\lambda_{max} = 645\text{ nm}$ which form and maximum spectral position are not concentration dependent.

Appearing in luminescence spectrum of red-shifted band, which is structureless, wider ($\Delta_{FWHM} = 1130\text{ cm}^{-1}$ with Lorentzian fitting) comparing with monomer one ($\Delta_{FWHM} = 715\text{ cm}^{-1}$ with Gaussian fitting for main electronic transition) and lacking an analogue in absorption spectrum, could be associated with the dye excimer formation [11]. Hereafter the red-shifted band referred to as the red band. Indeed, well-known pyrene dye easily forms excimers in silica gels [8,12]. But typically excimer band is strongly shifted relatively monomer absorption band with Stokes shift $\sim 5000\text{ cm}^{-1}$ and more [11,12] while in our case the Stokes shift for the red band is only 1650 cm^{-1} . The reason could be steric hindrance for the dye dimer formation caused by methyl groups and long hydrophobic tail (Fig. 1a). According our experience DiD is hardly associated in well-ordered form and only in aqueous solutions it is organizing in sandwich-like non-fluorescent aggregates [13].

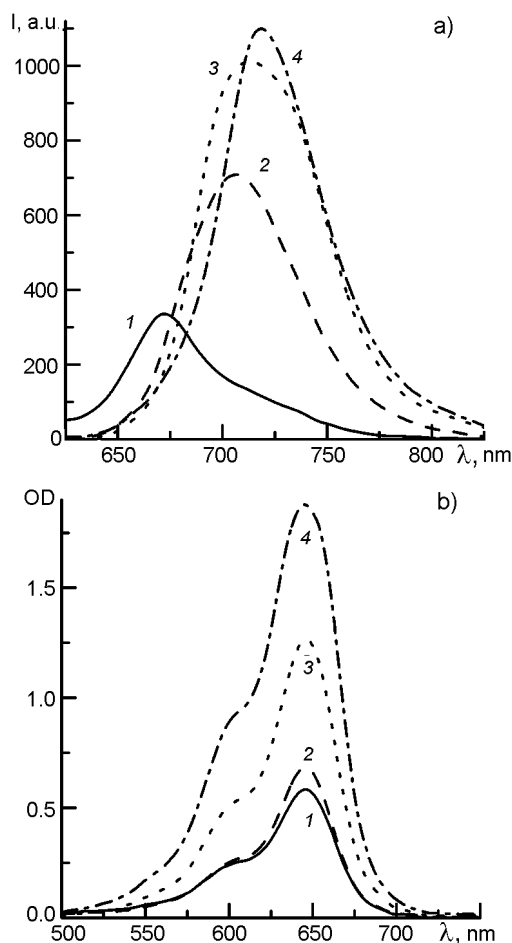


Fig. 2 Luminescence (a) and absorption (b) spectra of DiD dye in SiO_2 matrix (thickness less than 1 mm) after successive matrix immersion into the 10^{-6} M dye chloroform solution: 1 - after first impregnation, 2 - after second impregnation and so on.

To verify an excimeric nature of the red band we got luminescence decay curves for monomeric and red bands (Fig. 3). Luminescence decay of monomer band (Fig. 3, curve 1) is well fitted by single exponential law with lifetime $\tau = 2.75$ ns. Comparing DiD monomer luminescence decays for solutions with different polarity one could find lifetime increasing with polarity decrease in series: ethanol ($\tau = 1.35$ ns) \rightarrow DMF ($\tau = 1.75$ ns) \rightarrow chloroform ($\tau = 2.2$ ns). In SiO_2 matrix DiD dye reveals the largest lifetime. There are two reasons possible: the dye molecules fixation due to interaction with pore surface and non-polar environment or most probably combination of both. Indeed, high adsorption degree supposes interaction with pore surface. On the other hand, as SiO_2 matrices were annealed at 750°C adsorbed molecules most of surface silanol groups,

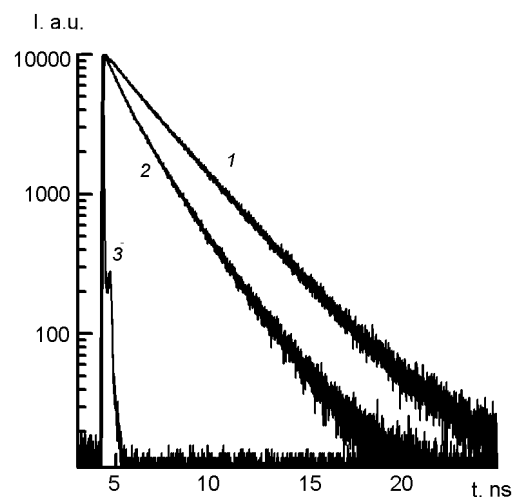


Fig. 3 Luminescence decay curves for the dye impregnated matrices at different dye concentrations and registration wavelengths: 1 - $\lambda_{\text{reg}} = 675$ nm, low dye concentration (corresponds to curve 1 on Fig. 2a); 2 - $\lambda_{\text{reg}} = 720$ nm, high dye concentration (corresponds to curve 4 on Fig. 2a); 3 - IRF.

with which usually interact [8,12], turned to nonreactive siloxane bridges [8]. That is causes nonpolar microenvironment of DiD molecules.

Luminescence in the red band reveals nonexponential decay (Fig. 3, curve 2) similarly to luminescence decay curve of the pyrene excimers in [12]. The latter was fitted by two-exponential law and such multiexponentiality explained by inhomogeneous interaction (a) between pyrene and the adsorbing surface [12]. Indeed, the best fitting in our case has been obtained using three-exponential decay. Note that in such case using Gaussian distribution of lifetimes is more appropriate [8,14]. Applying Gaussian lifetime distribution for the red band luminescence decay (Fig. 3, curve 2) gives us the average lifetime $\tau_{av} = 1.45$ ns and $\Delta_{\text{FWHM}} = 1.9$ ns. Lifetime decreasing compared to monomer lifetime is typical for excimers [11,12]. Wide distribution of lifetimes for DiD red band luminescence could be caused by steric hindrance for the dye dimer formation and different distances between molecules in pores.

It is known that excimers are dimers of molecules one of which is in excited state [11]. One of reason for excimer formation is thermal movement of molecules. So, excimer luminescence band should be temperature dependent. We examine behavior of the red band at cooling down to liquid nitrogen

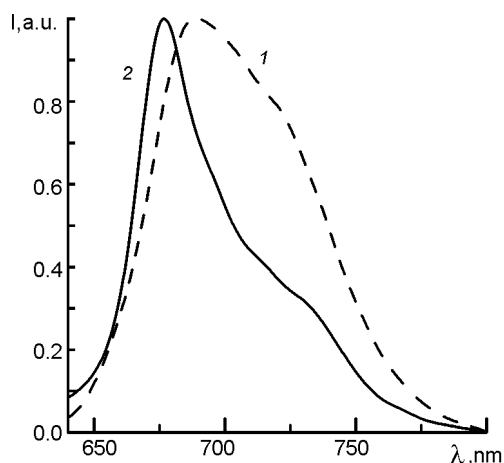


Fig. 4 Luminescence spectra of the dye impregnated matrix at different temperatures: 1 – 295 K, 2 – 80 K.

temperatures (Fig. 4). For this procedure samples with medium DiD concentration and presence of both luminescence bands has been chosen to get a situation with rather big distances between the dye molecules. As clearly seen from Fig. 4 cooling results in disappearing the red band accordingly to our expectations. So, we could conclude that the red band is result of excimer formation between the dye molecules adsorbed on nanopore surfaces.

4. Conclusions

DiD cyanine dye accumulation within nanoporous SiO₂ matrix leads to the red-shifted, structureless, wide band appearing in luminescence spectrum. This band is concentration and temperature dependent. No changes was found in absorption spectrum. Luminescence of the red-shifted band decays nonexponentially and well fitted using Gaussian lifetime distribution model with

average lifetime smaller than monomer one and wide lifetime distribution. The red-shifted luminescence was associated with the dye excimer formation dye to interaction with the pores surface. Excimer formation hasn't been observed for DiD dye before.

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