

Interface interactions and optical properties of novel photonic nanocomposites consisting of porous glasses doped with organic luminophore molecules

TATIANA V. ANTROPOVA¹, JAN BARAN², TATIANA GAVRILKO³, IVAN GNATYUK³,
TERESA MORAWSKA-KOWAL², VOLODYMYR MELNIK³,
GALYNA PUCHKOVSKA³, VOLODYMYR VOROBYEV³

¹Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, 24/2 Odoevskii Str.,
199155 St. Petersburg, Russia

²Institute of Low Temperature and Structure Research, PAS, PO Box 1410, 50-950 Wrocław 2, Poland

³Institute of Physics, National Academy of Sciences of Ukraine, 03028 Kyiv, Ukraine

Absorption and luminescence spectra of nanocomposites consisting of photonic molecules rhodamine 6G, trishydroxyquinoline aluminum (Alq₃) complex and benzophenone adsorbed on soda-borosilicate porous glasses from ethanol and dichloromethane (DCM) solutions are investigated. The effect of sorption interactions at the interface between the glass pore surface and the organic media on luminescent and optical characteristics of the nanocomposites was investigated by NIR spectroscopy. It was shown that spectral changes observed in the absorption and emission spectra of the luminophores in the porous glasses are determined by the balance between physical interaction of the organic molecule with different adsorption centers on the pore walls and solvation effect.

Keywords: soda-borosilicate porous glasses, rhodamine 6G, trishydroxyquinoline aluminum (Alq₃), benzophenone, luminescence, interface interactions, NIR spectroscopy.

1. Introduction

Photonic nanocomposites consisting of porous glasses doped with organic luminophore molecules are now in the focus of attention of materials science due to their remarkable emission and optical properties. They are widely used as active media for tunable dye lasers, elements for non-linear optics and second harmonic generation, solar batteries and so on. From many studies [1–9] it is known that incorporation of photoactive molecules into the porous matrix affects all their absorption and luminescent properties. The matrix effect is revealed, for example, in increased Stokes shifts, high migration stability and photostability, increased fluorescence decay time, *etc.*

In our research, we concentrated on problems that need to be studied for the development of more stable and efficient nanocomposites based on porous systems. First, it is necessary to clarify the effect of surface properties on photophysics and dynamics of incorporated molecules. Another question is connected with incorporation of organic molecules into the porous matrix. Most often, this is done by sorption process from solution, and therefore the role of solvent nature in the character and efficiency of interaction between the introduced luminophore molecules and matrix absorption centers should be clarified, too.

2. Experimental

2.1. Materials

The porous glasses with controllable pore size were produced by leaching initial alkali borosilicate glasses according to the synthesis procedure described elsewhere [10]. They are characterized by strongly interconnected and randomly oriented pores with narrow pore size distribution, high porosity and specific surface area. The porosity and density parameters of the glasses are listed in the Table. Glasses of different pore diameter were used. The pore size was selected in such a way as to fit the dimensions of the luminophore molecules to be incorporated and to allow their sorption by the porous glass. Before filling with organic luminophores, the porous glass matrices were activated by heating them up to 600°C during 1 hour.

Table. Composition (wt%) and pore diameter of the porous glass samples.

Sample	Na ₂ O	B ₂ O ₃	SiO ₂	K ₂ O	Al ₂ O ₃	P ₂ O ₅	PbO	Pore diameter [nm]
PG(3.0)	0.16	3.22	96.60	—	—	—	—	3.0
PG(6.6)	0.42	2.90	96.68	—	—	—	—	6.6
PG(10.0)	0.09	6.29	93.49	0.13	—	—	—	10.0
PG(5.6)	0.25	3.15	96.60	—	0.1	—	—	5.6

For our research we used three families of luminophore molecules with well studied structure and optical properties. Two of them – rhodamine 6G (R6G) and tris-hydroxyquinoline aluminum (Alq3) complex – were selected due to their efficient fluorescence from singlet state. As the third family of organic molecules we used benzophenone to study the influence of porous matrix on the emission from triplet state. All these molecules contain active functional groups capable of strong interaction with porous glass surface. All chemicals were commercial products obtained from Merck (pro-analysis) and used without additional purification. For incorporation of the organic molecules into the porous glasses, we used both aprotic (dichloromethane (DCM)), and protolytic (ethanol) solvents. Sorption of R6G and Alq3 molecules was carried out from their 10⁻³ mol/l solutions by dipping the porous glass samples into the solution and soaking them for 24–48 hours at controlled temperature of 25°C. Then

the solvent was slowly evaporated by heating the samples to 80°C and storing them at this temperature for 12 hours. The loading of PG with benzophenone was carried out directly from the melt kept at controlled temperature of 60°C for 24 hours. After adsorption, the samples were put onto a filter paper to remove residual solution or melt. The samples thus prepared were kept in dry atmosphere in the exsiccator.

2.2. Methods

The measurements of luminescence spectra were performed in the spectral range 280–760 nm with a resolution of 2 cm⁻¹ on MPF-4 Hitachi spectrofluorometer. The luminescence spectra were excited with monochromatic lines of 100 W Hg lamp spectrum. The front-face fluorescence collection technique was employed to eliminate self-absorption and secondary emission. The measurements were done in 4.2–180 K temperature interval. For low temperature measurements, a home-made (IOP NASU, Kyiv, Ukraine) closed-cycle helium cryostat equipped with a temperature controller was used. The temperature was controlled with accuracy of 0.1 K.

Spectra in the NIR (4000–10000 cm⁻¹) range were measured at room temperature with “Cary-5E” (Varian) UV–VIS–NIR spectrophotometer with resolution of 2 cm⁻¹ (32 scans).

3. Results and discussion

3.1. UV–VIS absorption and luminescence spectra

Figure 1 shows the luminescence spectra of R6G in porous glasses. In the matrix, the luminescence spectrum of the dye is broadened and shifted, but in general, it is similar to fluorescence spectrum of the dye in solution. However, the spectral characteristics observed are different for different solvents. If the dye is introduced into the porous glass from ethanol solutions, the spectrum is blue shifted by 3 nm. For

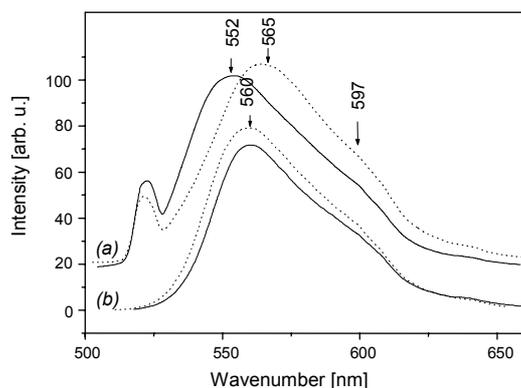


Fig. 1. Fluorescence spectra ($\lambda_{\text{ex}} = 525$ nm) of R6G adsorbed on PG(10.0) (solid line) and PG(5.6) (dotted line) from 10⁻⁴ mol/l ethanol (a) and DCM (b) solution at $T = 300$ K. The spectra are normalized to a sample thickness and shifted in intensity for clarity.

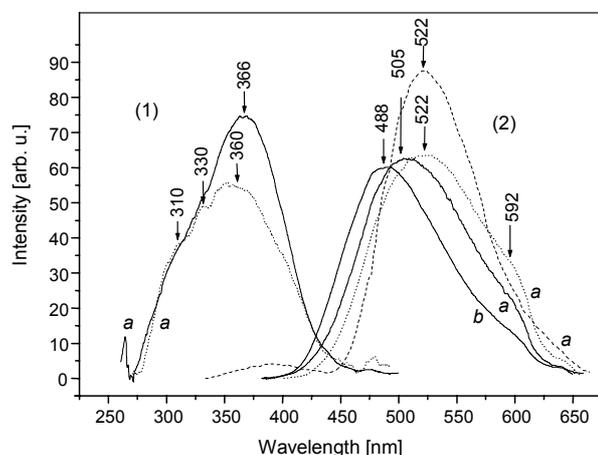


Fig. 2. Absorption (1) and fluorescence (2) spectra ($\lambda_{\text{ex}} = 365$ nm) of Alq3 adsorbed on PG(6.6) from ethanol (solid line) and DCM (dotted line) solutions compared to fluorescence of its 10^{-3} mol/l ethanol solution (dashed line) registered at 300 K (a) and 4 K (b).

DCM solution, the fluorescence band maximum is red-shifted by 5 nm. It is interesting that a decrease of the pore size does not lead to substantial changes in the luminescence spectrum of the dye in the case of adsorption from DCM solution, and cause red-shift of the spectrum, if ethanol is used as a solvent.

These results suggest that the luminescence properties of the dye in porous glasses are determined by the balance between the solvation effect and interaction of the dye molecules with different adsorption centers on the pore surface. The efficiency of this interaction depends both on the adsorption strength and the amount of the respective surface active sites in the matrix.

Similar results were obtained with another family of the nanocomposites. Figure 2 shows absorption and luminescence spectra of Alq3 in porous matrix. Here again, the introduction of Alq3 molecules into the matrix from ethanol solution is accompanied by blue-shift and broadening of the luminescence spectra. The shape and temperature dependence of the spectra demonstrate features characteristic of luminescence of Alq3 in ethanol solution. This suggests that due to strong solvation of Alq3 molecules, only small part of them is interacting with the strongest adsorption sites on the pore walls, whereas the major part of the luminophore molecules as a whole remain in the solvent. When Alq3 is adsorbed from DCM solution, the emission maximum is red-shifted by 33 nm compared to its position in solution (555 nm). The red-shift observed for Alq3 fluorescence maximum in porous matrix indicates relatively strong interactions of its molecules with the different adsorption centers on the porous glass surface.

For comparison, Fig. 3 illustrates the phosphorescence spectra of the nanocomposite consisting of benzophenone directly adsorbed on the porous glass from the melt.

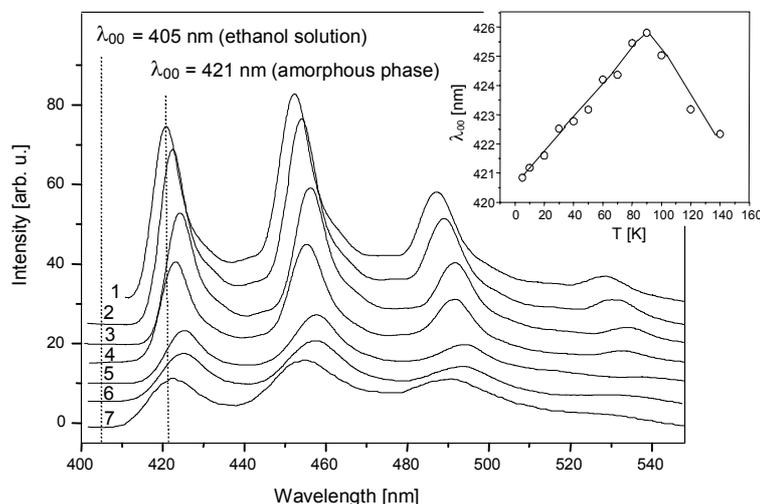


Fig. 3. Phosphorescence spectra ($\lambda_{\text{ex}} = 360$ nm) of benzophenone adsorbed from the melt on PG (3.0) at $T = 5$ (1), 30 (2), 50 (3), 60 (4), 80 (5), 100 (6), and 140 K (7). The insert shows the shuttle-like temperature dependence of λ_{00} emission band characteristic of amorphous benzophenone.

The spectrum is red-shifted in comparison with the phosphorescence spectrum of benzophenone in ethanol solution, and its structure is characteristic of the phosphorescence spectrum of strongly distorted conformation of benzophenone molecules existing in its amorphous phase [11]. This is also confirmed by the temperature dependence of zero-zero peak position as illustrated by the insert in Fig. 3. Such a behavior is expected for strong host-guest interactions in the nanocomposite that results in strong distortion of the adsorbed molecules. This indicates that in the absence of solvent benzophenone molecules are directly interacting with the adsorption sites on the porous glass surface.

3.2. NIR absorption spectra

To clarify the interface interaction in our systems, we use infrared spectroscopy in the near infrared region, which is known to be the most sensitive tool to study the adsorption mechanisms in porous structures [12, 13]. It is known [14] that the main adsorption sites on the porous glass surface are silanol groups. There are also hydroxyl groups associated by hydrogen bonds, which are also regarded as adsorption sites of lesser strength. The most important absorption bands of our systems and their interpretation were published elsewhere [13]. Here, we concentrate on the first overtone $2\nu(\text{OH})$ and combination $\nu(\text{OH}) + \delta(\text{OH})$ of stretching and bending vibrations of silanol and hydroxyl groups, and first overtone $2\nu(\text{CH})$ of CH stretching vibrations.

NIR absorption spectra of R6G adsorbed on porous glass from different solvents are shown in Fig. 4a together with the initial glass spectra and the spectrum of the dye

in solution. As is seen from the spectra, in the case of R6G adsorption from ethanol solution the band of stretching vibrations of surface hydroxyl groups centered at 7327 cm^{-1} completely disappears, and new broad absorption band of OH stretching vibrations appears at 7085 cm^{-1} shifted to lower frequencies; at the same time, the band of CH stretching vibrations at 5897 cm^{-1} moves in opposite direction to 6001 cm^{-1} . This behavior, together with the increased intensity of combination OH absorption band related to associated OH groups at 5128 cm^{-1} , strongly proves that ethanol molecules themselves are strongly interacting with surface hydroxyl groups by hydrogen bonds, thus shielding the dye molecules from these adsorption sites. The dye molecules therefore can interact only with stronger binding adsorption sites (probably with boron complexes $\text{B}(\text{OH})_2$), which leads to the blue shift of

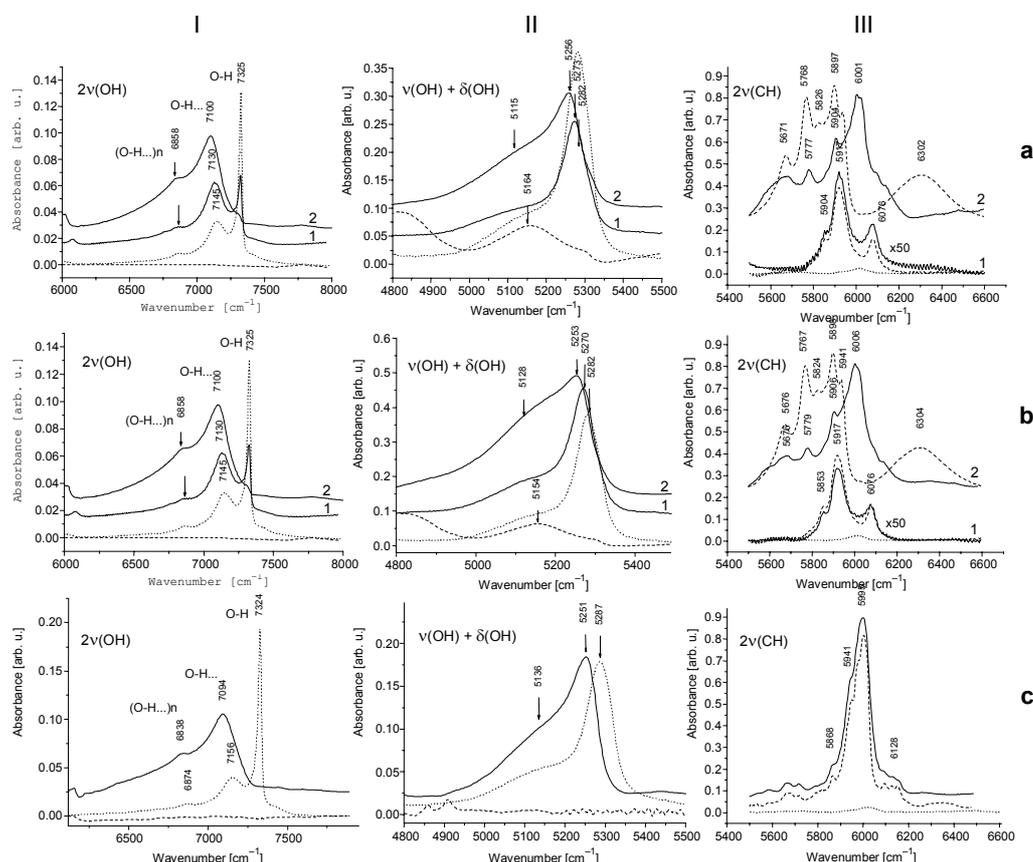


Fig. 4. Fragments of NIR absorption spectra of PG doped with organic luminophore molecules (solid line) in comparison with spectra of separate components (initial porous glass – dashed line, organic luminophore – dotted line) in the region of first overtone of OH stretching vibrations (I), combination of OH stretching and OH bending vibrations (II), and CH stretching vibrations (III): R6G adsorbed on PG(10.0) (a), Alq3 adsorbed on PG(6.6) from DCM (1) and ethanol (2) solutions (b), and benzophenone adsorbed on PG(3.0) from the melt (c).

the fluorescence spectra. If DCM is used as solvent, this interaction is much weaker, which is confirmed by lower intensity of stretching vibrations of surface OH groups at 7327 cm^{-1} . Therefore the interaction of the dye molecules with different surface active sites becomes possible, which results in the red-shift of the fluorescence spectra. The analysis of bands related to R6G adsorption was hampered due to low concentration of the dye in the solutions.

Similar features are observed in the near infrared spectra of porous glasses doped with Alq3 (Fig. 4b). Here again, if Alq3 is adsorbed on PG from ethanol solution, we see disappearance of OH stretching band at 7325 cm^{-1} and appearance of broad red-shifted band at 7100 cm^{-1} together with blue shift of CH stretching vibration band, which indicates the formation of strong hydrogen bonds between the alcohol molecules and surface hydroxyl groups. This is also evidenced by the increased intensity of the combination adsorption band of associated OH groups centered at 5128 cm^{-1} . As can be seen from the CH absorption region of the NIR spectra (region II in Fig. 4), for the PG samples doped with R6G and Alq3 from ethanol solution the CH bands of the adsorbed solvent dominate, however there are also bands related to “free” solvent (the bands centered at 5777 and 5904 cm^{-1} in the spectra of PG doped with R6G, and 5779 and 5906 cm^{-1} in the spectra of PG doped with Alq3). Thus it appears that our samples contain both ethanol bound to the pore surface and a small amount of free ethanol. Therefore, in the porous glass effective solvation of Alq3 molecules by alcohol molecules takes place, and therefore only small part of Alq3 molecules are interacting with the strongest adsorption centers of the matrix resulting in the blue shift of the luminescence maximum. In the case of Alq3 adsorbed on PG from DCM solution, due to weaker interaction of DCM molecules with surface active centers, Alq3 molecules are adsorbed on the adsorption centers of different strength that leads to the possibility of different conformational states of the molecules on the pore surface. This results in inhomogeneous broadening and red-shift of the luminescence spectra. It worth mentioning that the comparison of the intensities of CH stretching bands for ethanol and DCM solutions after their sorption by the porous glass also shows that sorption of DCM is much lower.

In Figure 4c, fragments of NIR spectra of benzophenone adsorbed on porous glass are shown. The changes observed in the spectra (disappearance of OH stretching band of surface hydroxyl groups at 7324 cm^{-1} and appearance of broad absorption band at 7094 cm^{-1}) prove that carbonyl groups of benzophenone molecules form strong hydrogen bonds with surface hydroxyl groups. The bands of CH stretching vibrations of phenyl ring centered at 5868 , 5941 and 5995 cm^{-1} do not change their position after benzophenone adsorption on PG, however, their half-width increases, which may be caused by the existence of distorted conformations of adsorbed benzophenone molecules.

Thus, our results of near infrared spectroscopy fully agree with the luminescence data and confirm that in porous glass strong interaction of alcohol molecules with surface hydroxyl groups takes place, and that the interaction of aprotic DCM solution with these adsorption centers is much weaker. This leads to different mechanisms

of the porous matrix effect on the absorption and luminescence characteristics of the adsorbed luminophore molecules depending on the solvent used for their incorporation into the porous structure.

4. Conclusions

The absorption and emission spectra of luminophore molecules in porous matrices are shifted in relation to solutions, and these shifts are determined by the balance between physical interaction of the organic molecule with the surface groups on the pore walls and solvation effect. The analysis of NIR absorption spectra confirms that the molecules are adsorbed in different ways depending on the solvent used for their incorporation into the porous structure. In protolytic solvents, an adsorption on surface active sites of highest chemical binding takes place, while in aprotic solvents adsorption on less strongly binding physisorption sites occurs. Summarizing, our results have shown that a combination of luminescence and near infrared spectroscopy allows more information to be obtained about the nature of porous matrix effect and about the mechanisms of interface interactions in nanostructured photonic nanocomposites.

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