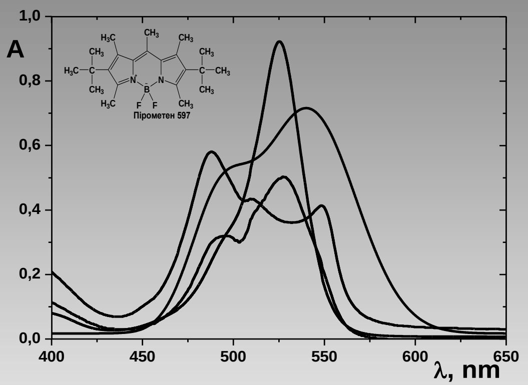
L.V. Pisarzhevsky Institute of Physical Chemistry, NASU
pr. Nauki, 31, Kiev-03028, Ukraine.
E-mail: scorpion5d@rambler.ru



Optical manifold of spatial localization of dyes molecules self-organized in the body of silica thin films

Leonenko E. V.

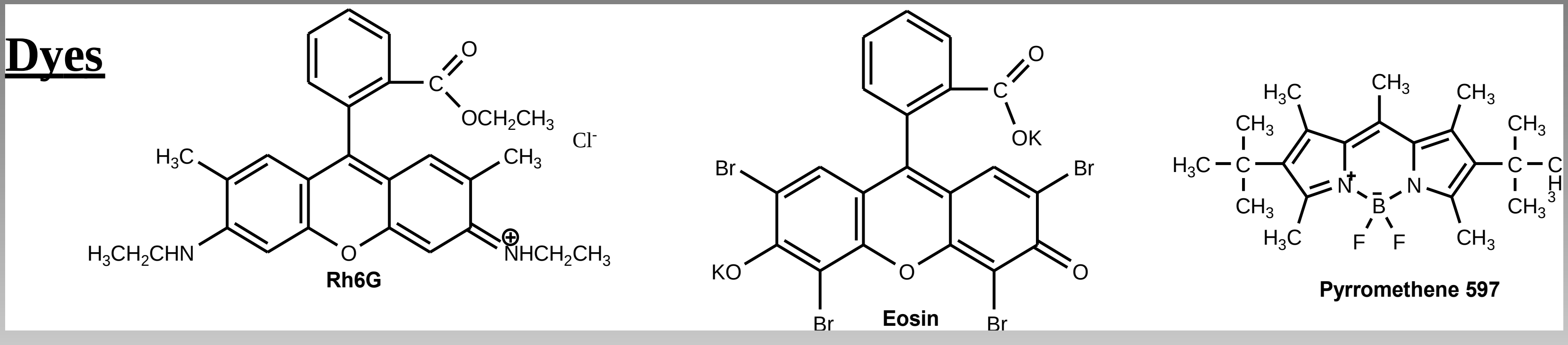
Introduction

The incorporation of dye molecules into solid matrixes is an attractive and widely investigated method to prepare dye-doped solid-state devices. Large quantum yield of organic dye molecules combined with the advantages by the solid host with respect to liquid solutions indicate that these materials are good candidates for solid-state dye laser applications. Solid matrix offers a larger mechanical and thermal stability, reduces the risks of environmental and operator hazards and allows to increase achievement of larger concentrations of the dye, reducing the formation of aggregates responsible for the quenching of the luminescence. Among the investigated possibilities, the embedding of dye molecules into silica materials prepared via sol-gel methods can offer the highest physical and chemical performances.

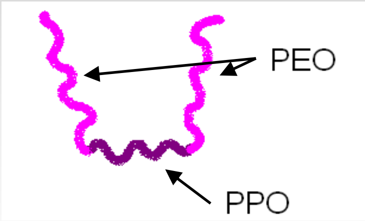
The aim of present work was developing of method of controlled aggregation of dye molecules embedded in the body of mesostructured films, with the view of development of the solid-state luminescence device with increased photostability.

Here we present the analysis and comparison of the optical characteristics of dyes molecules self-organized in the body of mesostructured silica thin films. Samples with different concentration of the dye were prepared by one-step one-pot sol–gel method as homogeneous and transparent films deposited by spin and dip-coating on the various substrate. The physical nature of the optical manifold was connected with the number of dye molecules and their self-organization in the hydrophobic core of the micelles with a hydrophilic shell of the counterion in the micelle, as well as the combined electrostatic-hydrophobic interactions during aging of hybrid sol-gel film.

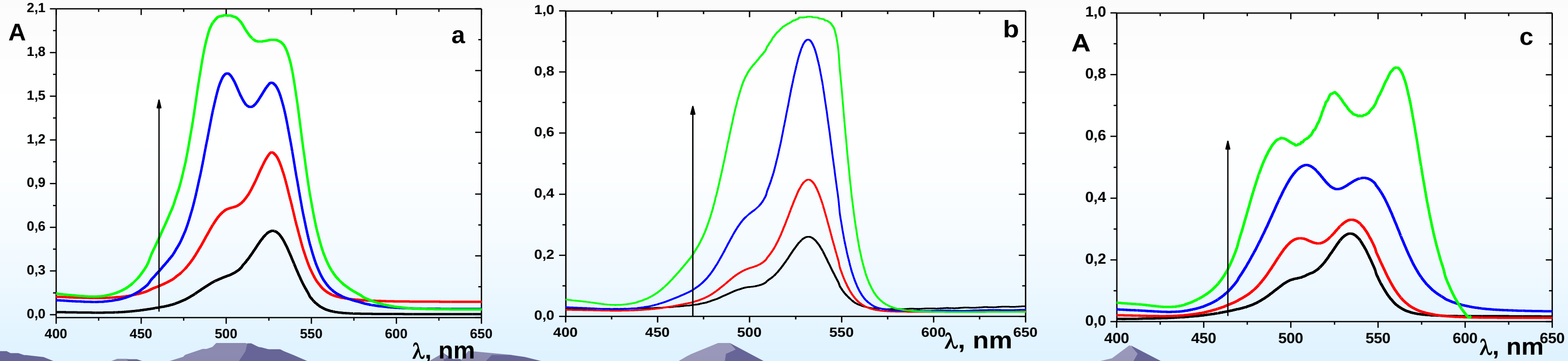
Dye and surfactant



Pluronic 123, triblock copolymers $(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}$

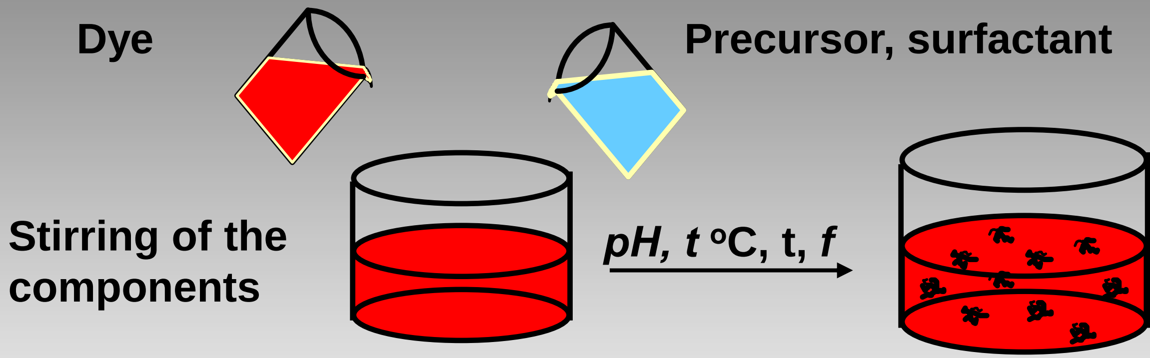


It was established that Pluronic 123 molecules can self-aggregate and forming micelles with a hydrophobic core composed mainly of polyoxypropylene (PPO) segments and a corona composed mainly of the hydrophilic polyoxyethylene (PEO) segments. We experimentally validated that selected dyes can be solubilized in aqueous PEO-PPO-PEO solutions with formation of hybrid micelle.



Changes of absorption spectra of Rh6G in different environment with growth concentration of dye: a) aqueous solution: b) sol: c) mesostructured hybrid sol-gel film.

As we prepared and controlled film-forming substance



Film-forming substance:
1TEOS : 0,01 P123 : 0,5 HCl : 8 C_2H_5OH : 2 H_2O : 0,1 dye

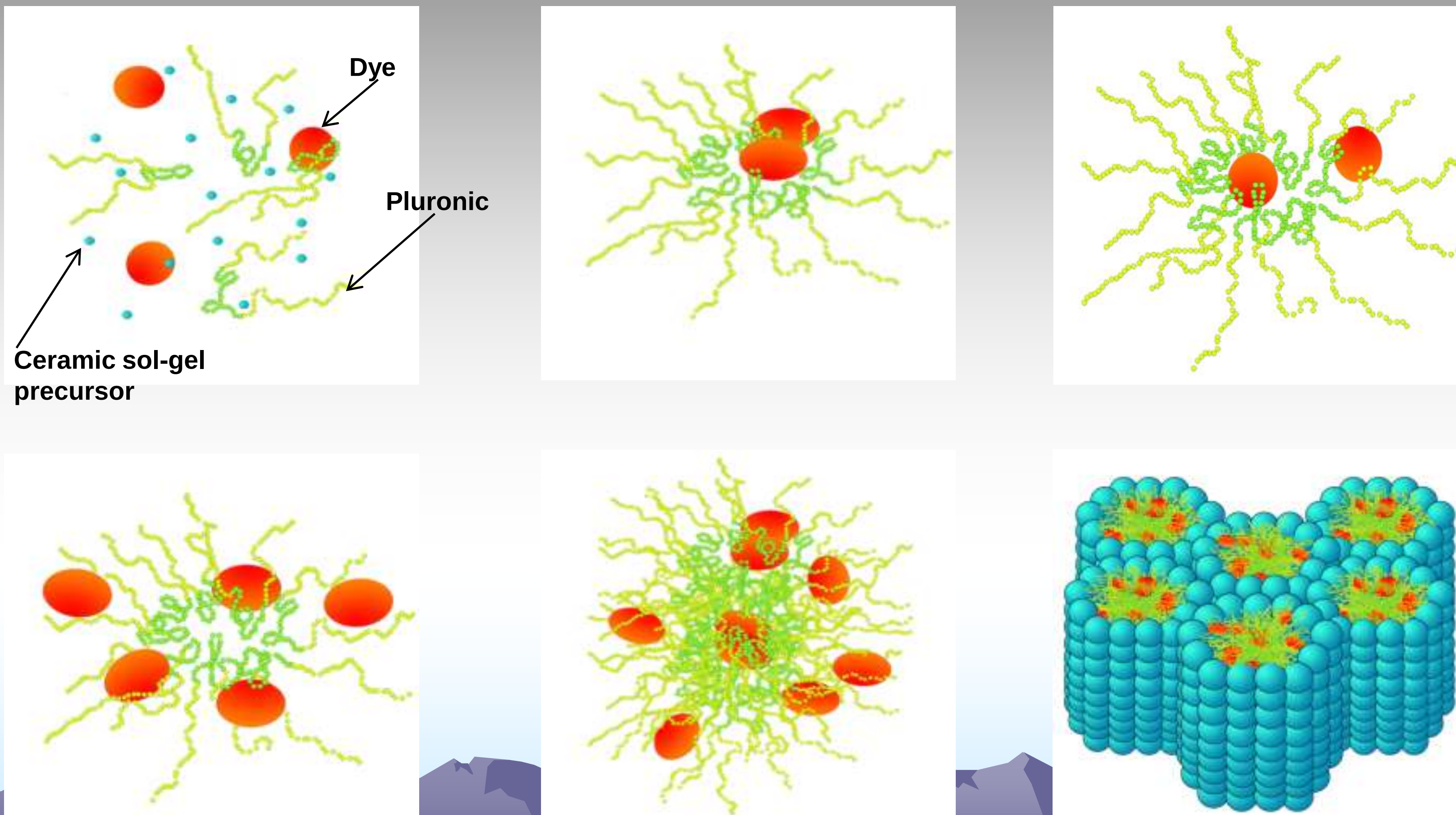
Parameters, that necessary to control

- Proportion of the components;
- pH ~ 1 – 5;
- Aging time of sol (1 – 7 days);
- Temperature (30 – 60 °C);
- Humidity (50 – 75 %);
- Viscosity (1,5 – 5 cP);

Substrate characteristics

- Known refraction index
- Low roughness
- Clean surface

Hypothetical model of spatial organization of dye molecules in the body of mesostructured films

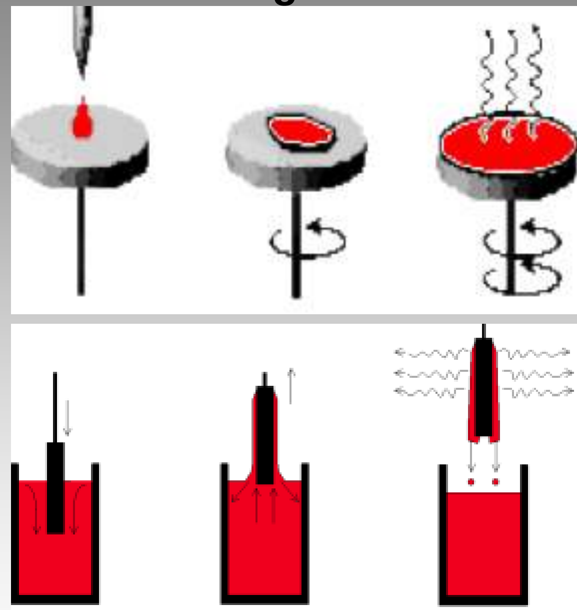


As we deposited hybrid silica films on substrate

Putting sol

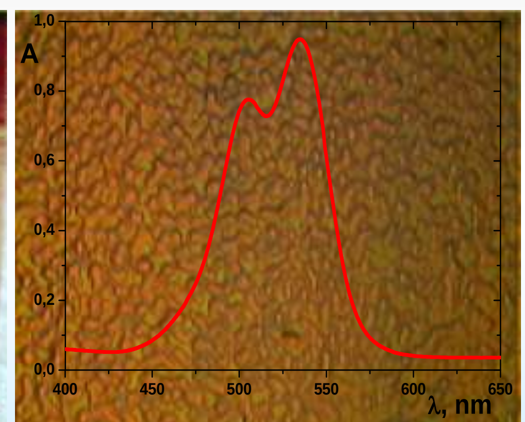
Spin-coating
500 – 2000 rev./min.

Dip-coating
1 – 25 cm/min.



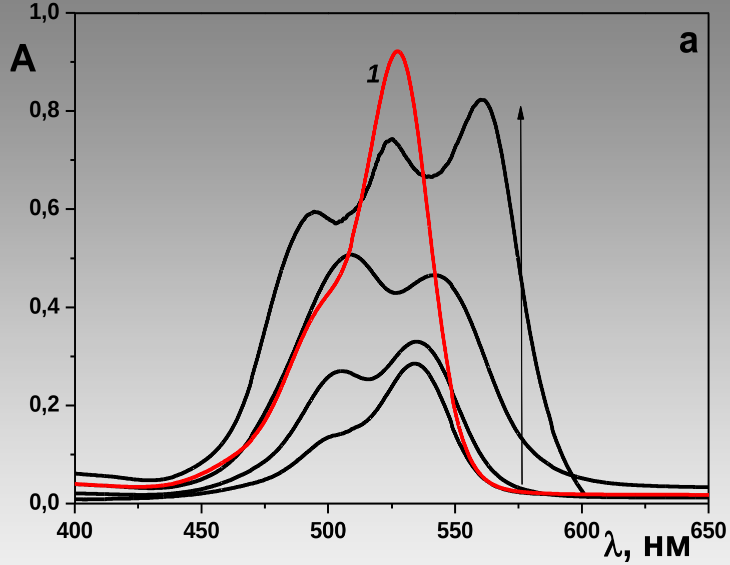
t* °C, t, *f

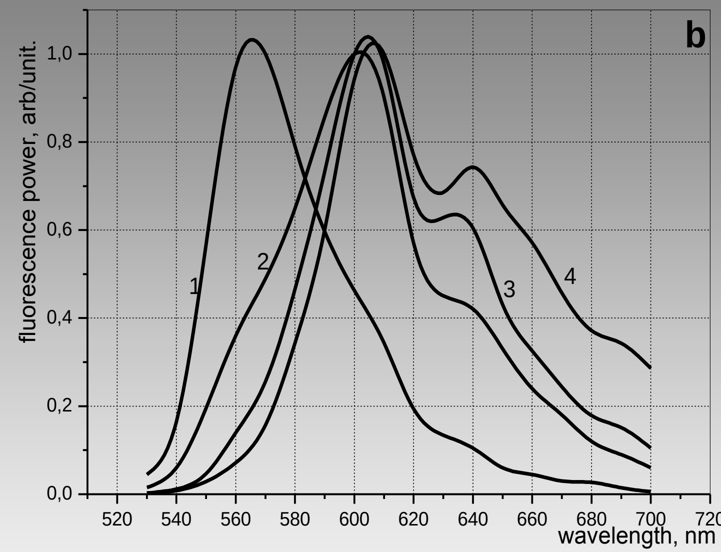
Aging

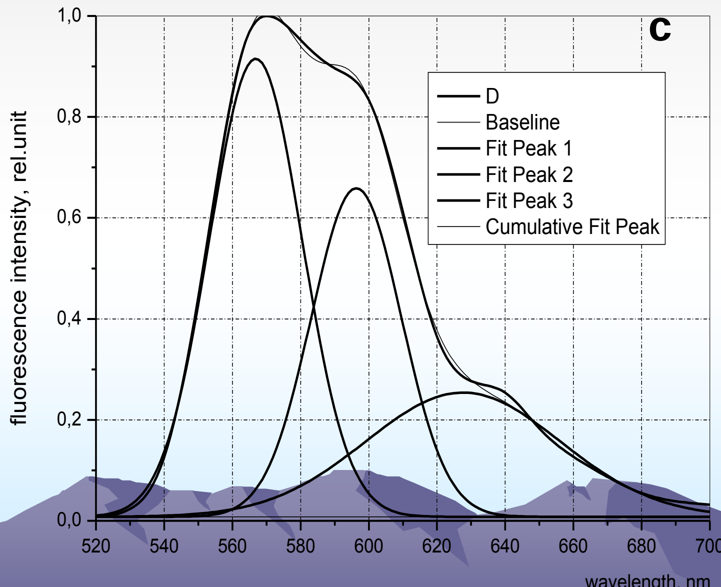


Images of hybrid film SiO_2 / rhodamine 6G

Spectral-luminescent properties of hybrid silica film



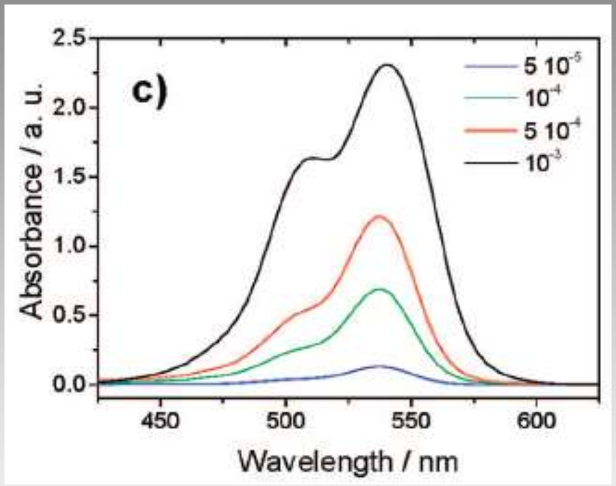


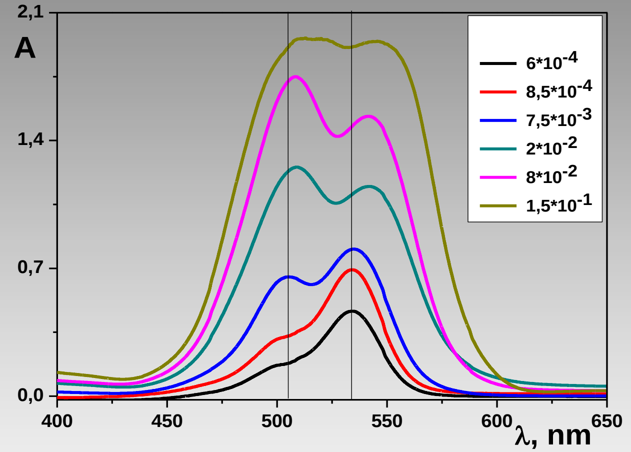


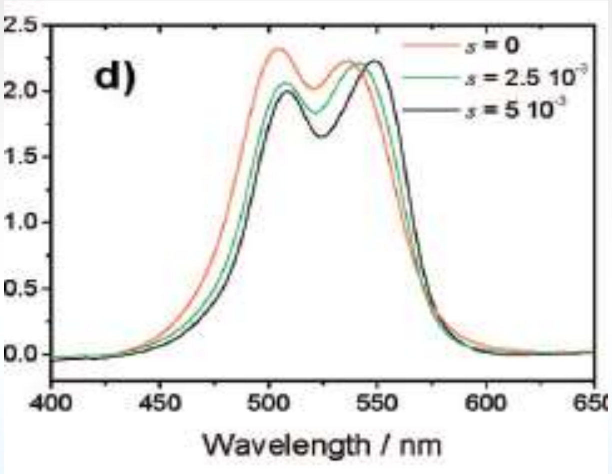
Evolution of absorption (a) and fluorescence (b) spectra Rh6G embedded in mesostructured silica film subject to dye concentration; and deconvolution[1] of integrated spectrum (c) of fluorescence on Gaussian contours.

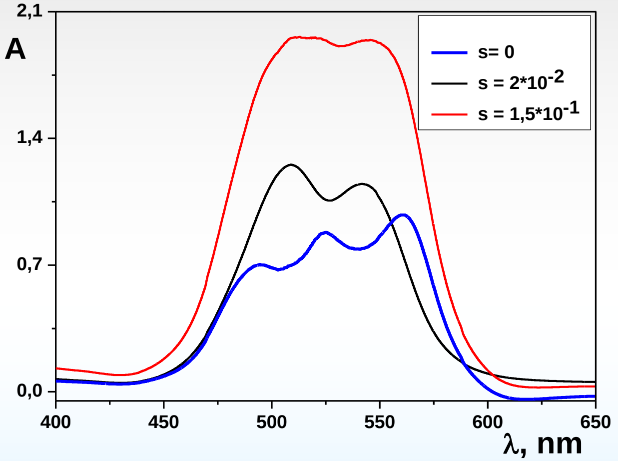
[1]E. A. Tikhonov; G. M. Telbiz // Molecular Crystals and Liquid Crystals, 1563, V. 535, 2011, 82

Optical spectra of hybrid films subject to method of their deposition on substrates





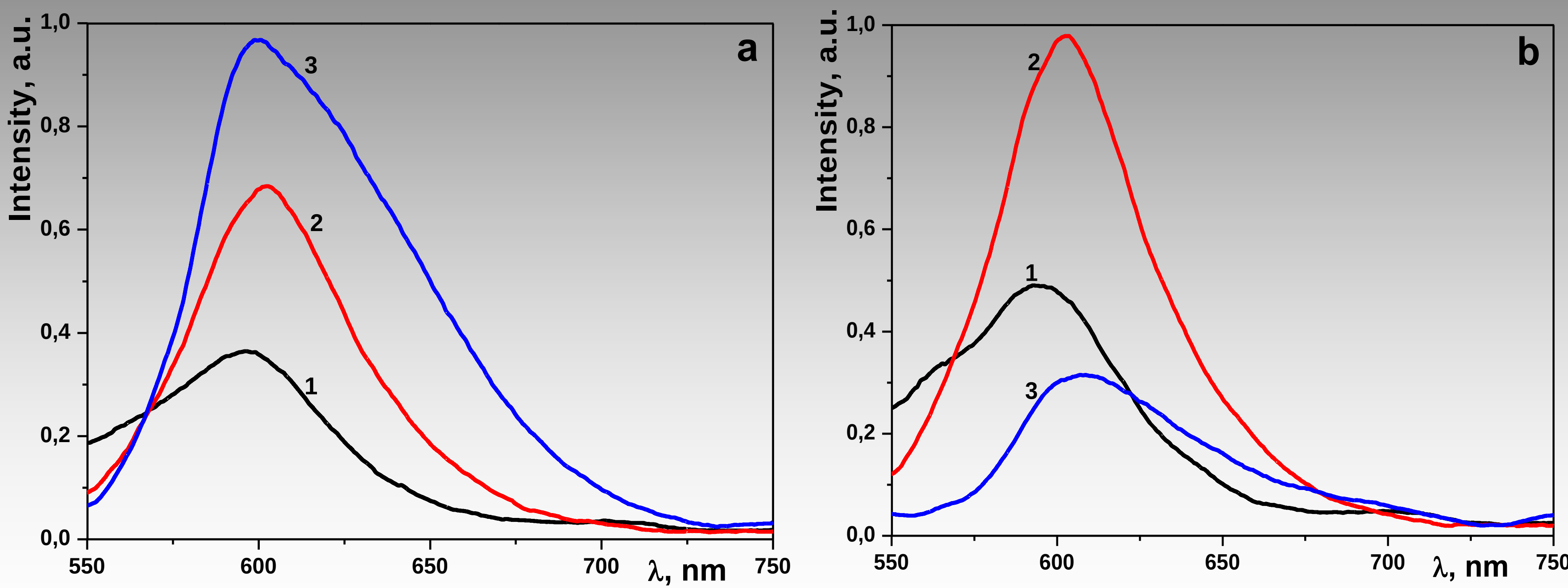




Comparison of absorption spectra of mesostructured silica sol-gel films obtained dip- (left) and spin-coating (right) with growth concentration (in mol/l) of Rh6G and *difference spectra by subtracting the data of the films.*

Dip-coating data from Luca Malfatti et all // J. Phys. Chem. C 2008, 112, 16225.

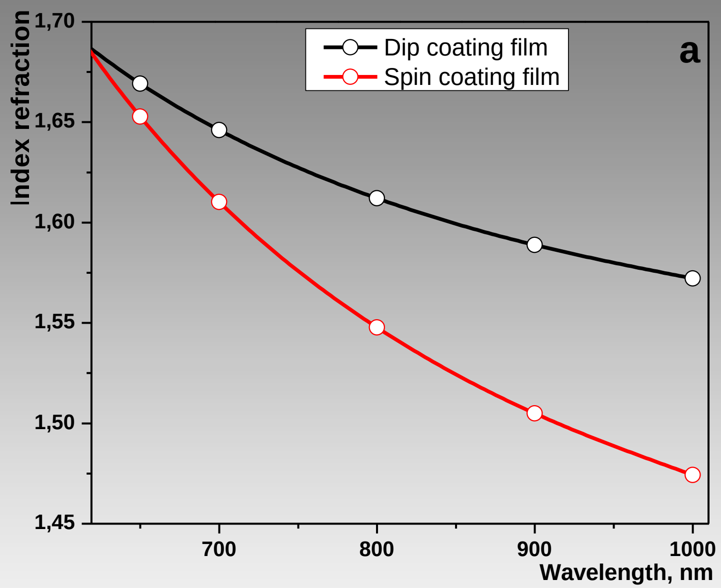
Luminescence spectra of hybrid films of subject to method of deposition on substrates

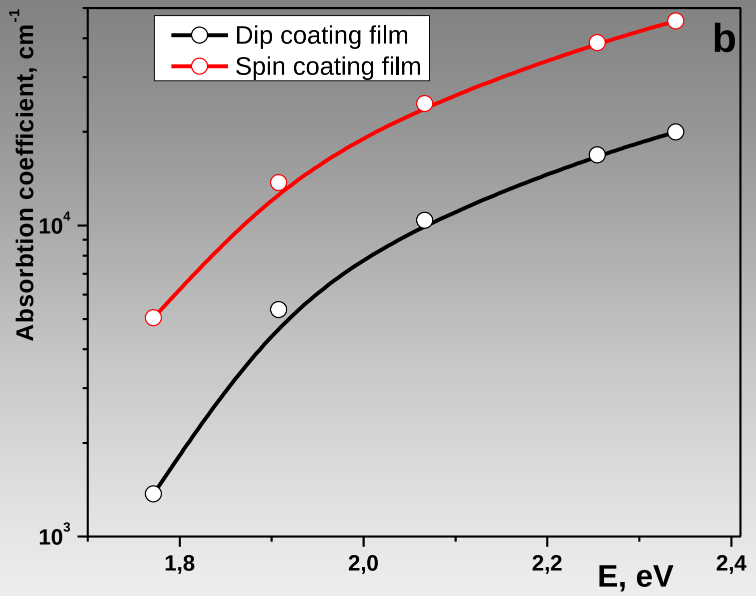


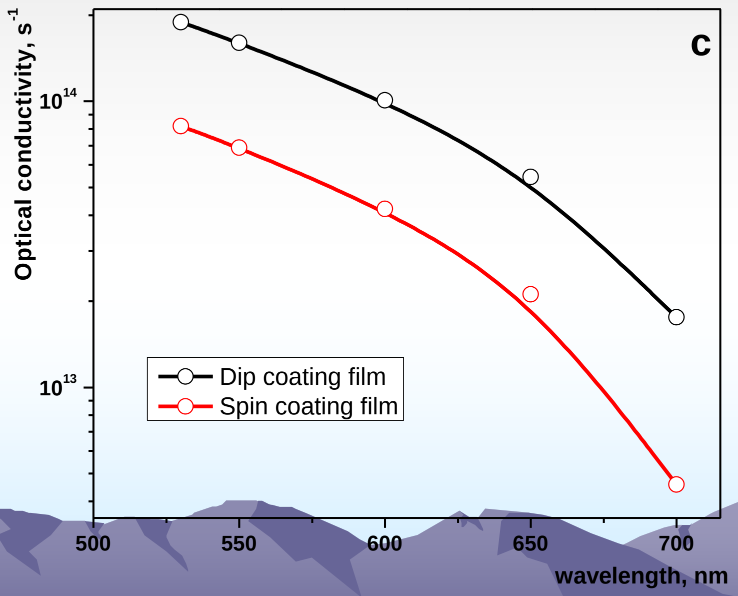
Evolution of fluorescence spectra of hybrid silica sol-gel films with growth concentration of Rh6G of subject to method of deposition on substrates:

a – spin-coating; **b** – dip-coating.

Optical characteristic of hybrid silica film







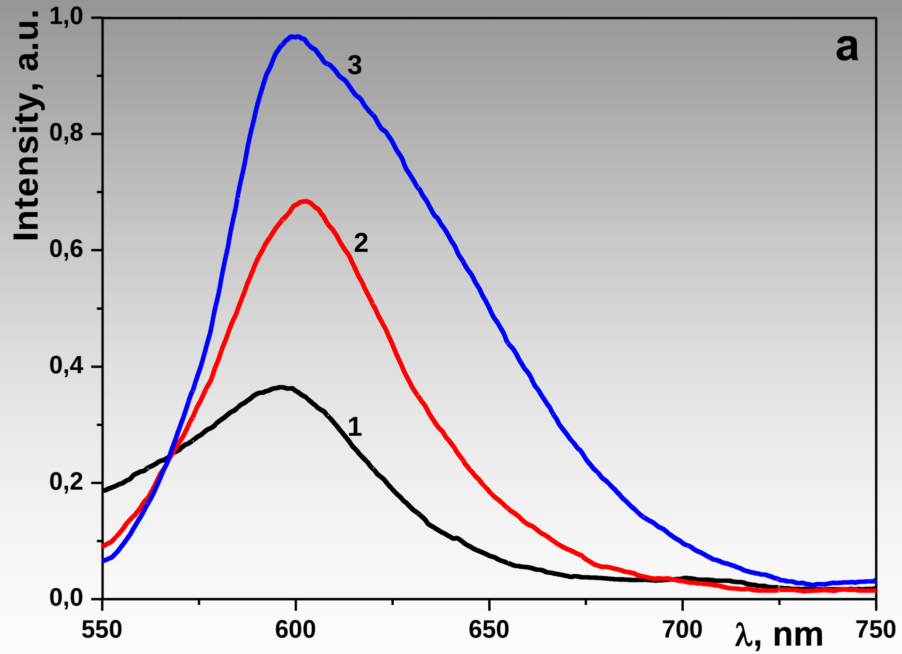
Optical constants of hybrid films subject to method of their deposition on substrates calculated by the envelope method:

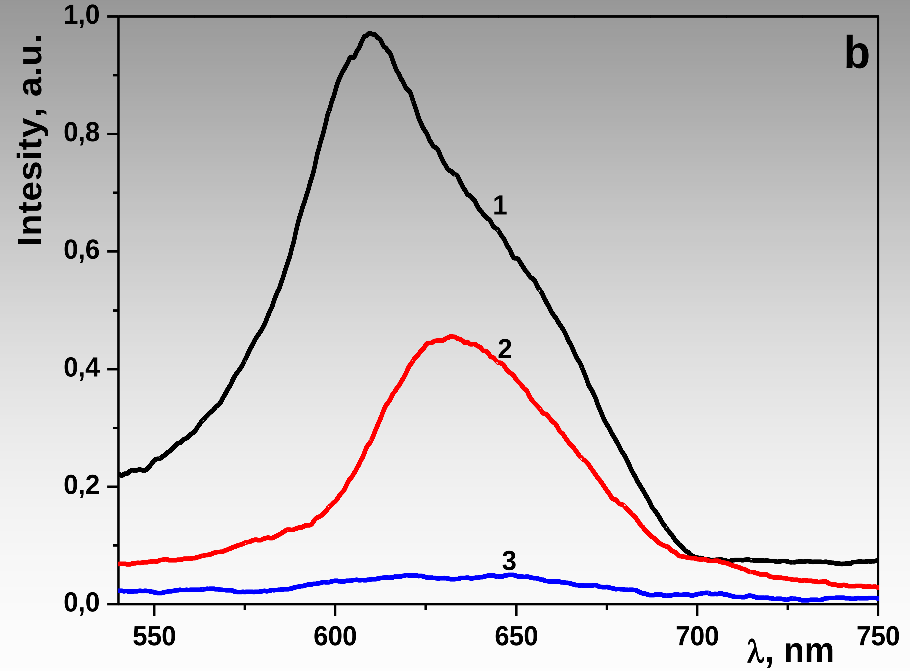
a) index refraction;

b) absorption coefficient;

c) optical conductivity

Influence of type of substrates on luminescence properties hybrid films

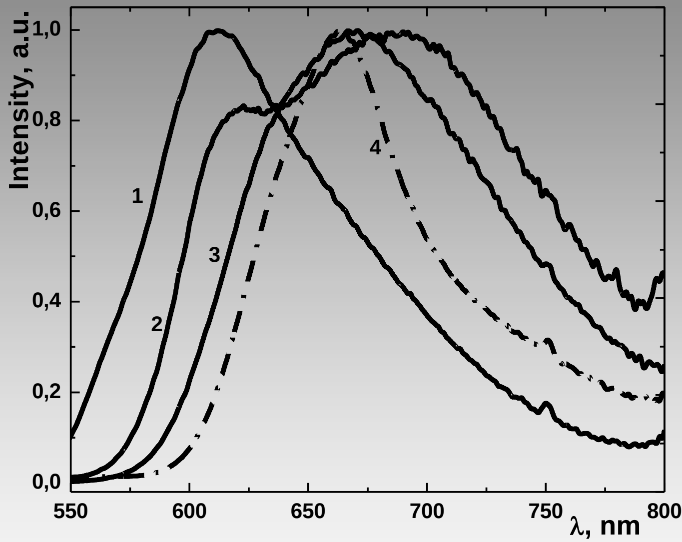




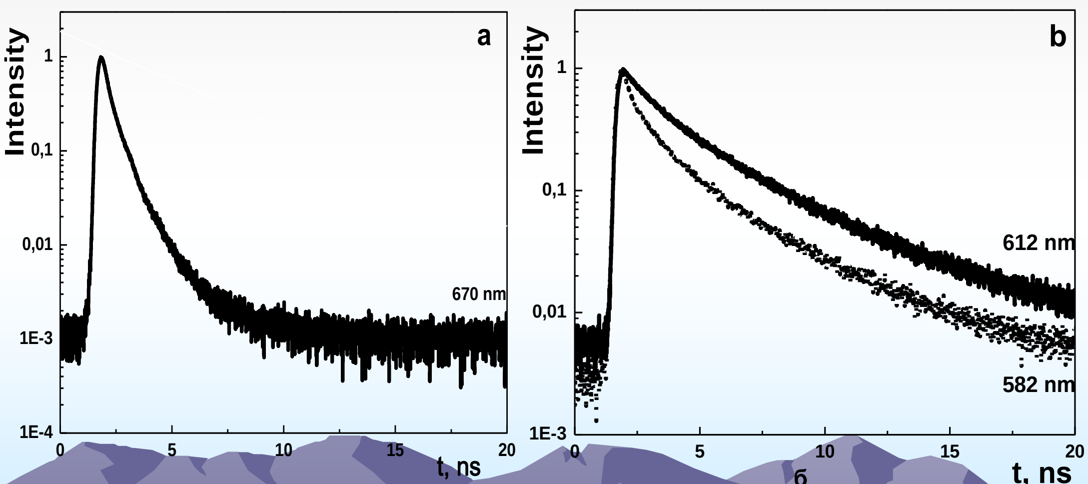
Evolution of fluorescence spectra of hybrid silica sol-gel films with growth concentration of Rh6G and depends on substrates:

a – substrate – glass; **b** – substrate – mica.

Fluorescence characterization rhodamine 6G in silica films

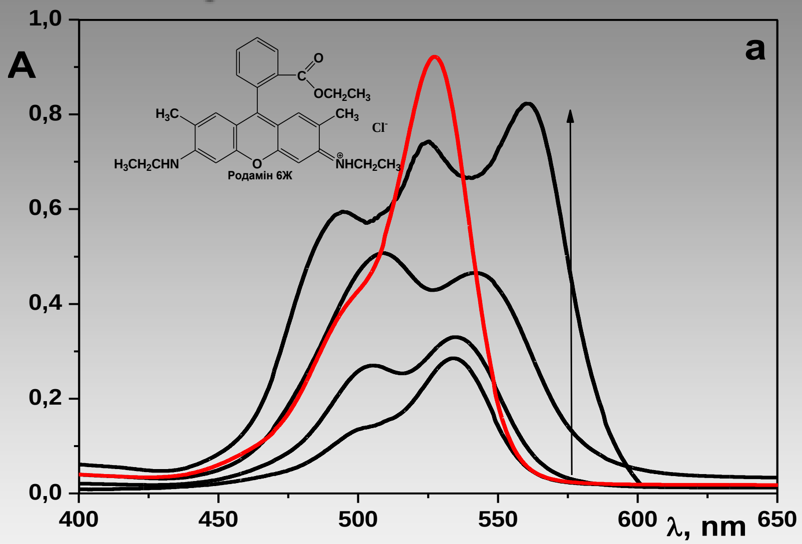


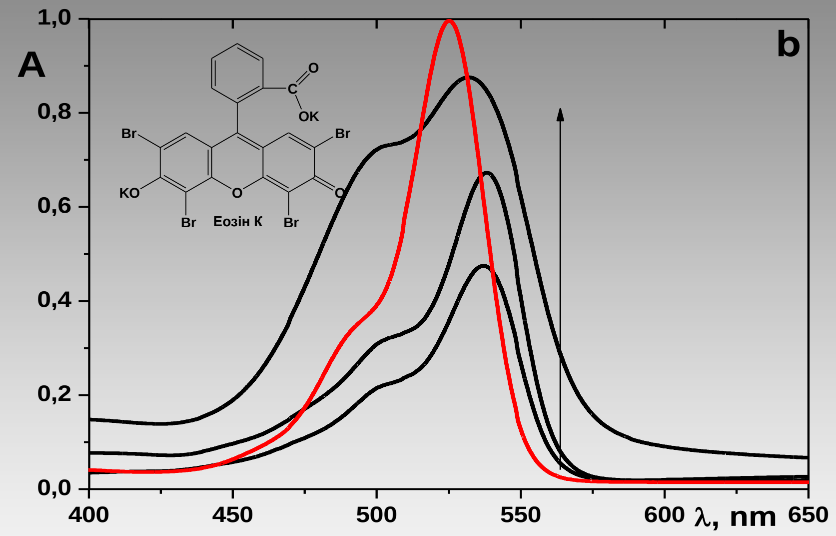
Evolution of fluorescence spectra Rh6G in hybrid film with growth of concentration (1-3); polycrystalline phase (4).

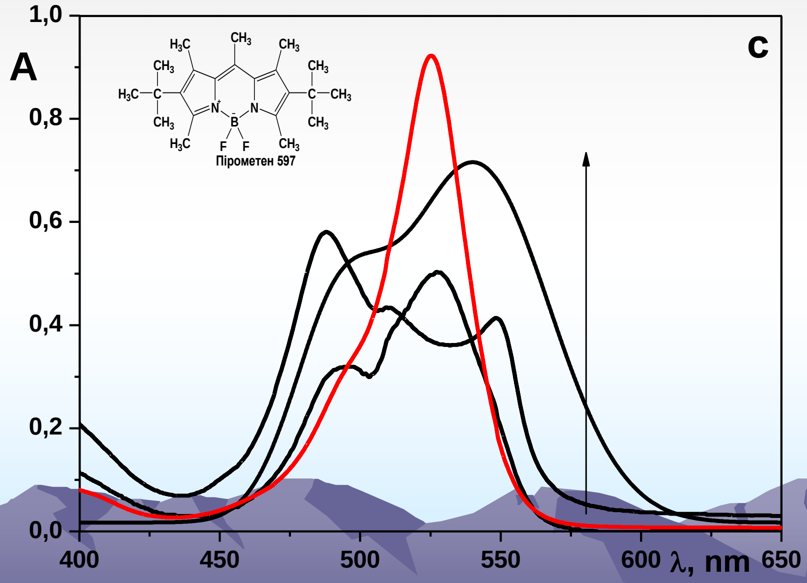


Fluorescence lifetimes of Rh6G bulk (a) and incorporated in body of silica film (b).

Optical properties of various type of dye incorporated within mesostructured silica films







Absorption spectra of hybrid silica sol-gel films with growth concentration of dyes.

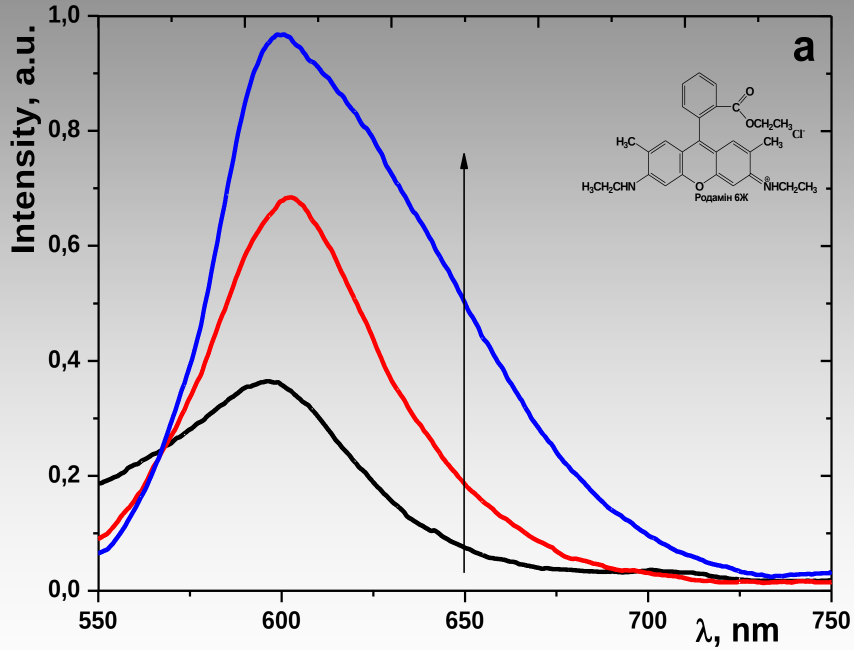
Red - spectra bulk dyes.

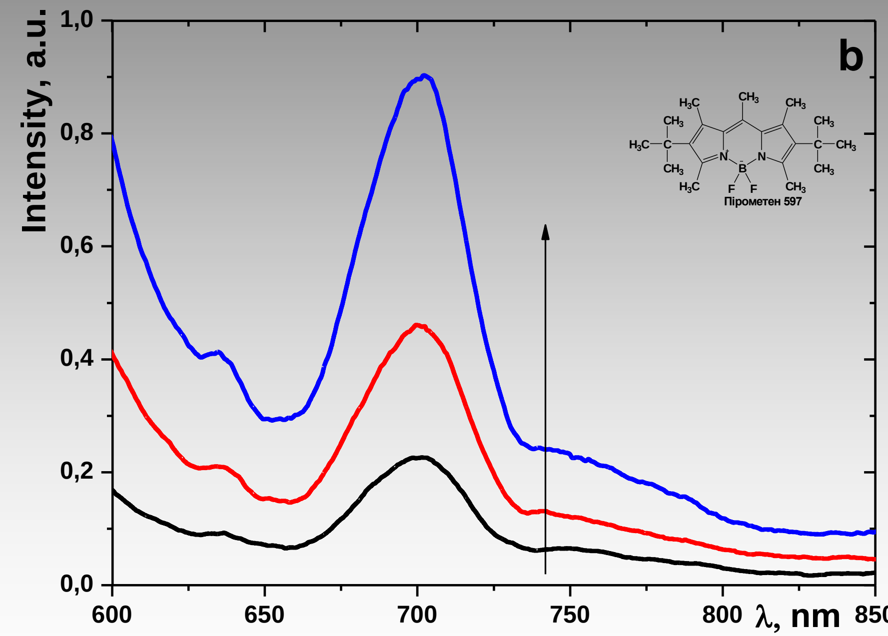
a – rhodamine 6G;

b – eosin K;

c – pyrromethene 597.

Fluorescence spectra of various type of dye incorporated within mesostructured silica films



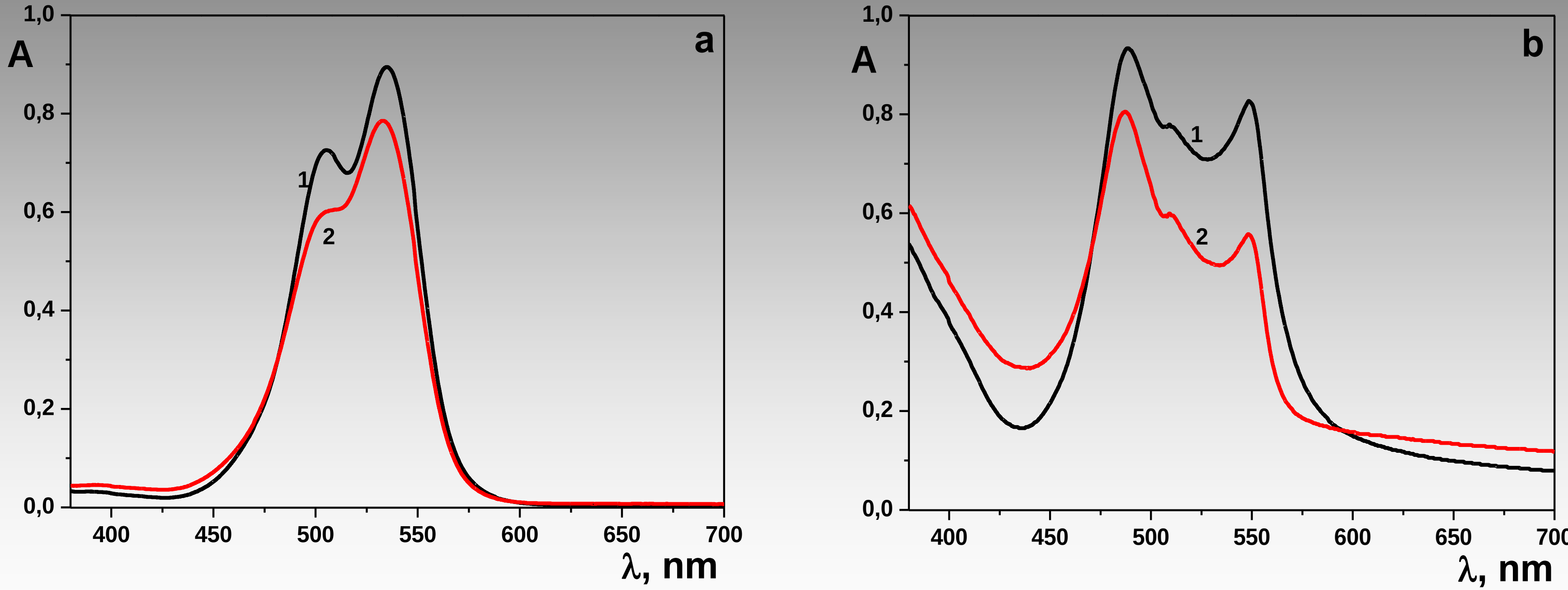


Evolution of fluorescence spectra of hybrid silica sol-gel films with growth concentration of dyes.

a – rhodamine 6G;

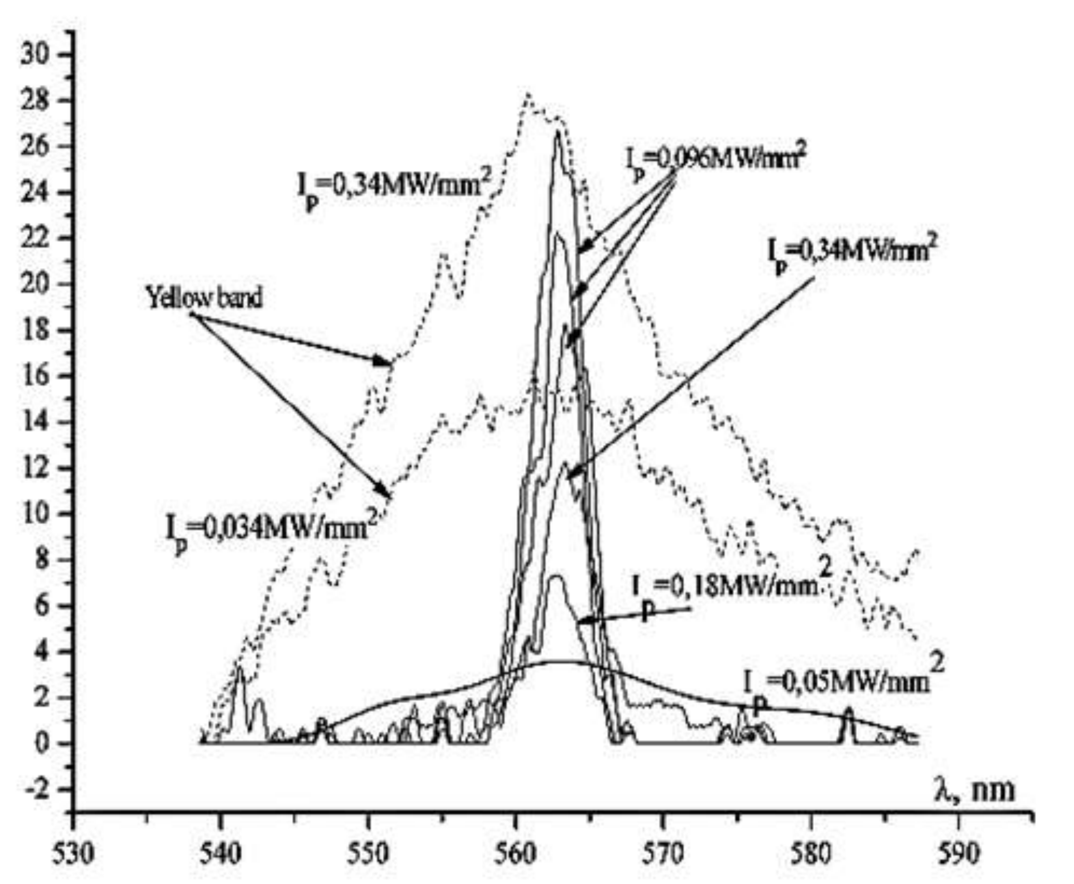
b – pyrromethene 597.

Example of optical stability of hybrid silica films



Normalized optical spectra of mesostructured silica films doped by Rhodamine 6G (a) and Pyrromethene 597 (b) after 1 year standing (2).

Presupposed way for application of hybrid films



Laser emission from surface of doped mesostructured film as planar waveguide.

Conclusion

- The observed manifold of the optical and fluorescence spectra shows the ability of controlled aggregation of dye molecules (such as Rh6G) owing to time-delay of their spontaneous transformation during the process of formation of mesostructured hybrid sol-gel films. Emission in films received by one-step one-pot synthesis observed even at high dye concentrations and characterize of long-term stability.
- The origin of this fluorescence is under investigation now. A distribution of dye molecules is present, corresponding to three extreme configurations, which we attribute to monomers, sandwich H-type dimers and head-to tail J-type aggregates. The formation of fluorescent aggregates can be promoted of the amphiphilic triblock copolymers that favors the formation hybrid micelles with "arrested" monomers and dimers and introduces a constrained environment in which H-type dimers are distorted to give rise to oblique fluorescent aggregates with increasing lifetime.
- Optical constants of hybrid films obtained by spin- and dip- coating methods were calculated based upon the envelope method suggested by Swanepoel. Variation of values of refractive index, absorption coefficient and optical conductivity in this case can be evidence of various spatial organizations of dye molecules within the body of generated films, subject to method of deposition on substrates.
- First attempt of excitation of lasing on hybrid films demonstrated ability waveguide nanolaser with all its featured beam parameters.

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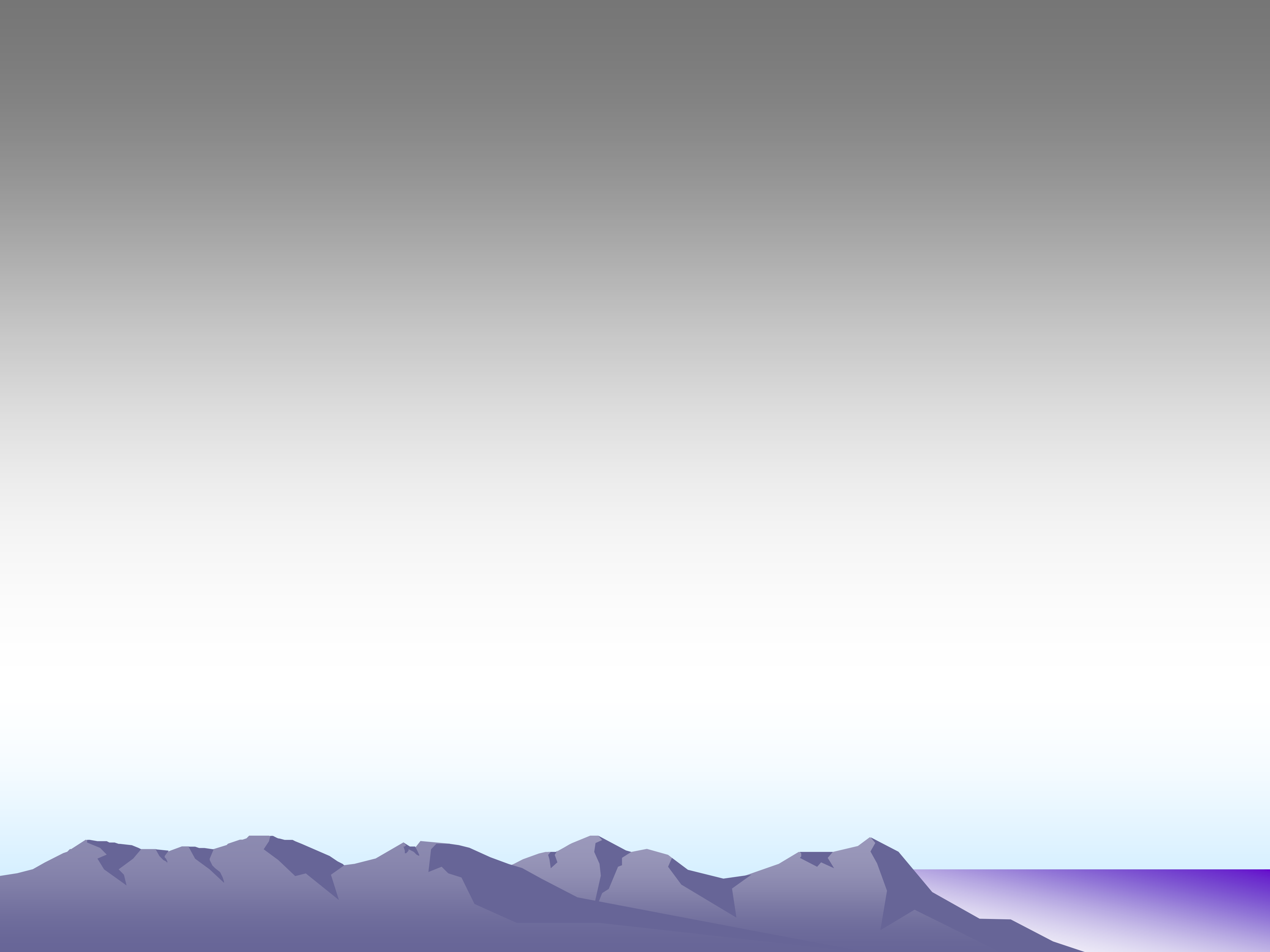
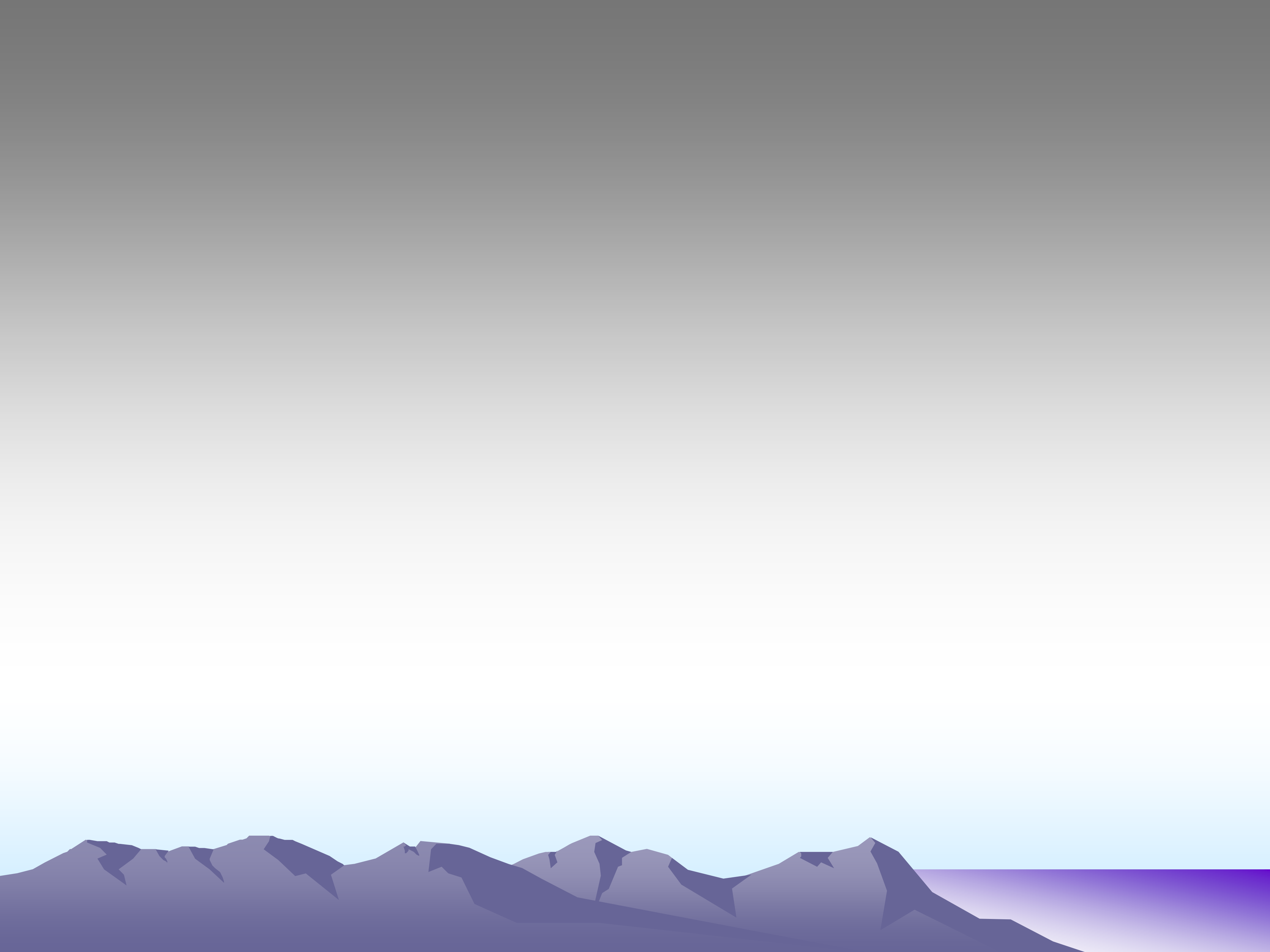
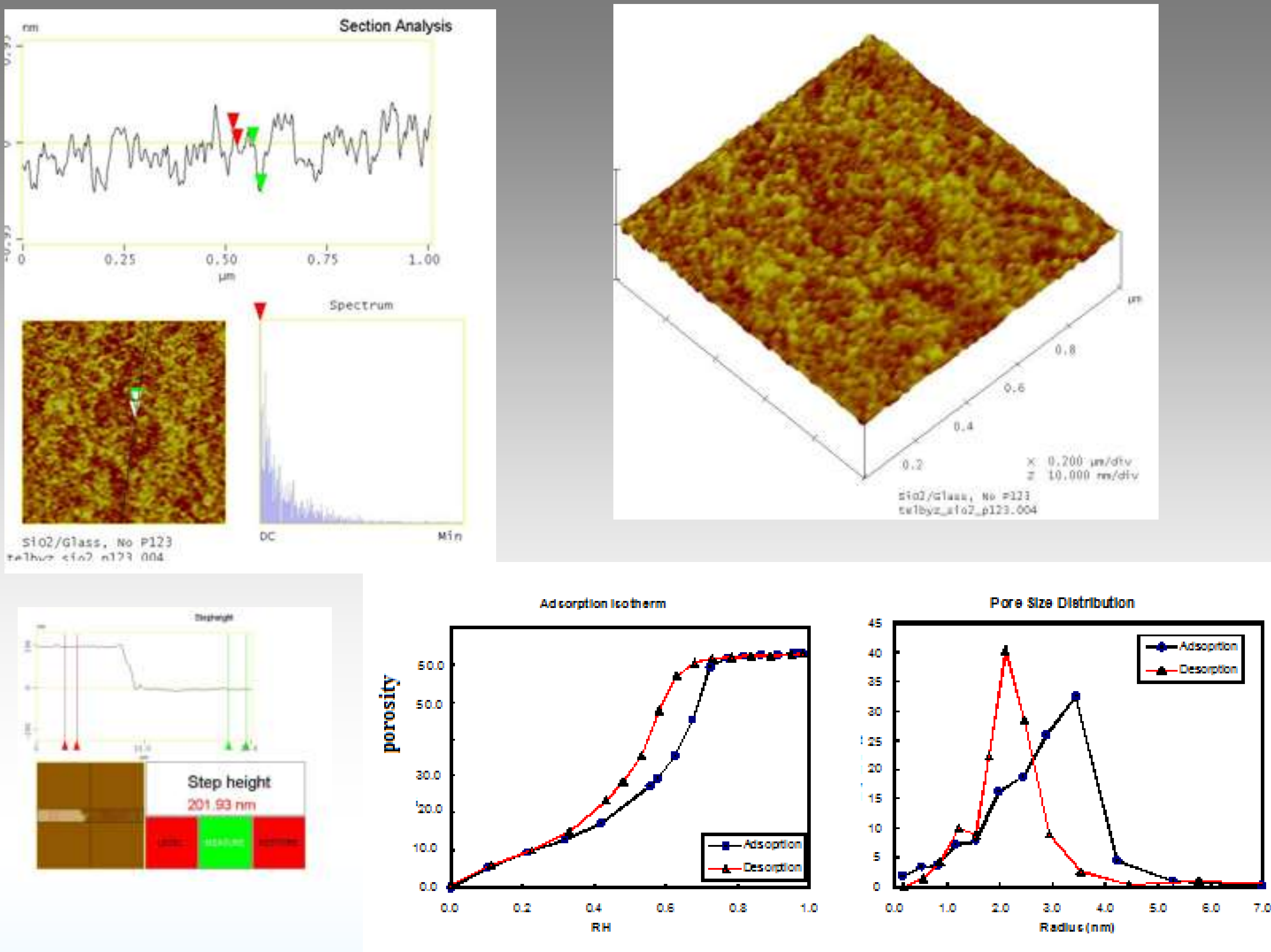
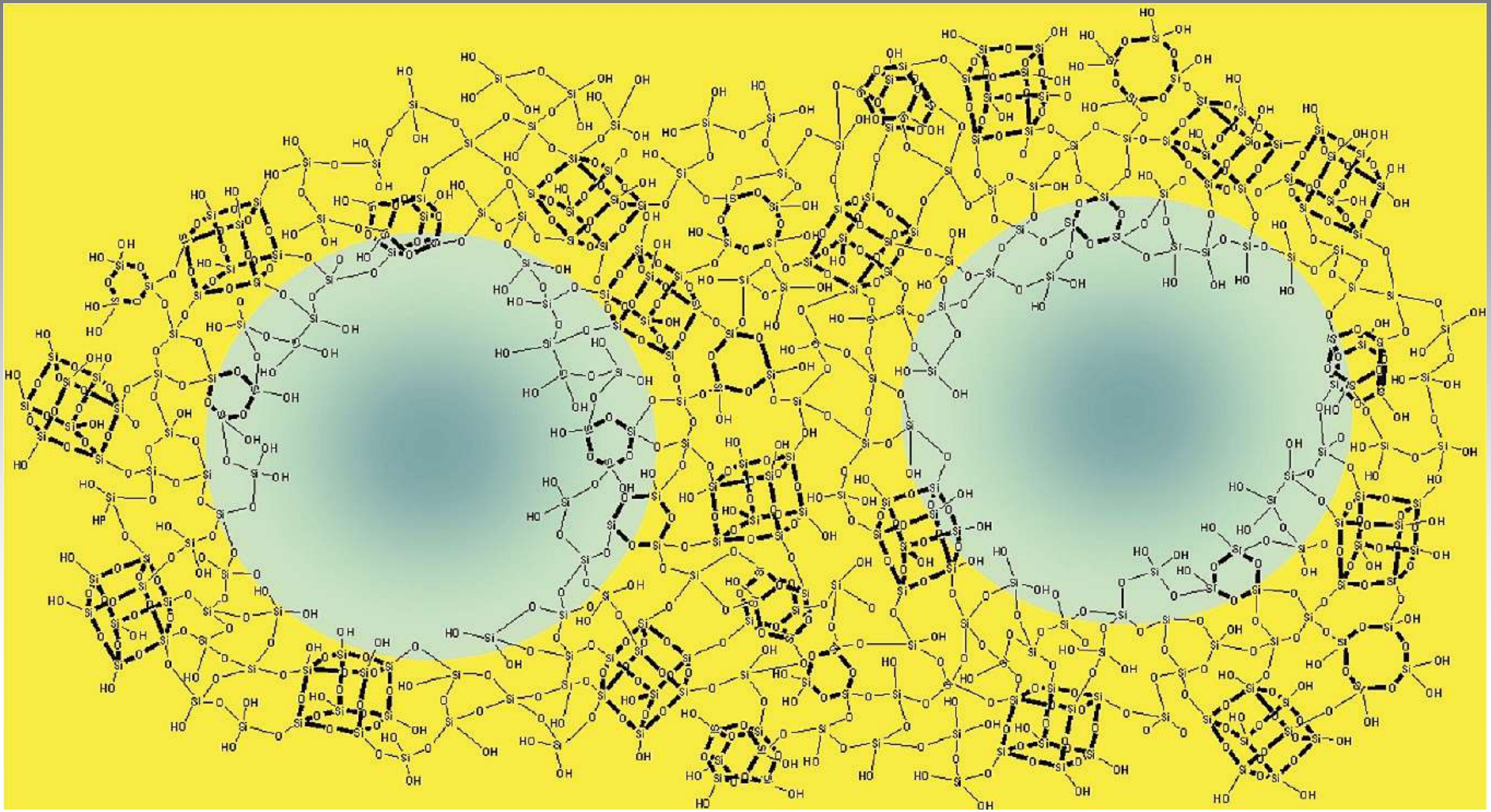
Thanks for attention







Typical AFM and elipsometry-porosimetry data for mesoporous silica film.



Picture of mesoporous walls made with silica cyclic species embedded.

P. Innokenzi et al. Chem. Mater. 2009, 21, 2555–2564