

## fluorescence quenching of dye molecules encapsulated in porous glass matrices

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The spectral dependences of the average excited state lifetime  $\langle\tau\rangle$  of Coumarin 7 (K7) molecules embedded in nanostructured porous glasses (PG) with different pore sizes (with different pore radii  $r$  were studied. It was found that with increasing  $\lambda$ , a monotonic increase in  $\langle\tau\rangle$  was observed in the K7 fluorescence spectrum for all  $r$ . Moreover, the smaller the pore radius, the greater the slope of the  $\langle\tau\rangle(\lambda)$  dependence. The presented dependences of the time characteristics of emission attenuation in different spectral ranges of the emission band indicate a non-uniform broadening of the electronic spectra of the adsorbed molecules. The processes of K7 fluorescence quenching by Rhodamine B (RB) molecules were studied. It was found that both dynamic and static fluorescence quenching were observed in the studied system. The dynamic quenching constant  $k_{\text{din}}$  decreases with increasing pore size  $r$ , while the static quenching constant  $k_{\text{st}}$  increases with increasing  $r$ . In this case,  $\Delta k = k_{\text{st}} - k_{\text{din}}$  depends almost linearly on  $r$ . It is shown that the dynamic quenching of K7 fluorescence is caused by the transfer of electronic excitation energy from K7 to RB, the efficiency of which increases with increasing  $r$ .

**Keywords:** Nanoporous glasses, dye molecules, fluorescence spectra, fluorescence lifetime, fluorescence quenching, electron excitation energy transfer.

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### Introduction

Porous materials, where molecules are encapsulated, are used in various applications, such as biological and environmental probing [1,2], delivery of drugs [3,4], sensors, in particular, of oxygen [5] etc. Understanding of nanoconfinement (nanoscale restriction) in such materials causes great interest, since the restricted molecules may in principle change their chemical and physical properties compared to those that are located in volume conditions [5–9]. Among the porous materials, nanoporous glasses (PG) hold a special place — being the structures with unique properties. They have pores of nanometer sizes, bonded to each other and forming a three-dimensional network, providing for an extremely high ratio of the pore surface area to the pore volume [10]. Since this material has a high potential for use as a platform to fix various molecules. Large free volume in such structures plays a significant role in the processes of translational and rotary diffusion of molecules adsorbed in pores, therefore PGs were used to study the behavior of complex molecules, in particular, having a luminescent ability [11].

In this connection the understanding of the principle of interaction between the molecule and nanopore (guest–host) in the porous systems has a fundamental value [11]. Methods of fluorescent spectroscopy of guest molecules in excited state help to obtain information about molecular dynamics under the condition of nanoconfinement in

porous materials. The phenomena of charge transfer and electron excitation energy transfer (EEET) are the key events of such processes. Besides, PGs are a superb platform for implementation of EEET, since they allow for encapsulation of a wide spectrum of fluorophores, decrease and control of the distance between the donor and the acceptor. EEET processes may be studied by the decrease of the intensity of glow of donor molecules with the growth of concentration of acceptor molecules and by change of time of the donor's excited state in presence of the acceptor molecules [12].

This paper presents the results of the study of the time characteristics of fluorescence for coumarin 7 (C7) and EEET between C7 molecules (donor) and Rodamine B (RB) (acceptor) in the PG by the methods of stationary and time-resolved fluorescence.

### Experiment

The paper studied porous glasses (PGs) with different pore radii made of DV-1 grade glasses, which contained  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ , using the method described in [10]. Fig. 1 presents the image of the nanostructured PG (sample № 4) obtained on a scanning electron microscope (SEM). REM of samples was conducted using a high-resolution electron field-emission column Gemini, included into a workstation NVision 40. From the figure you can see that porous glass has a spongy corpuscular structure.

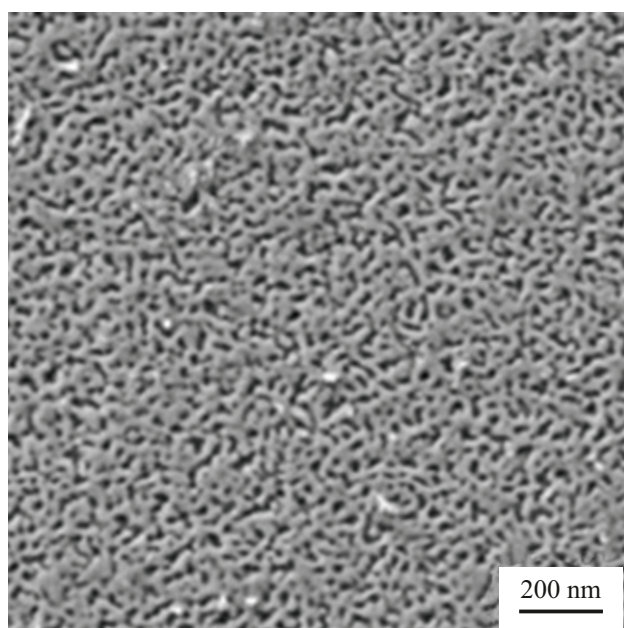


**Figure 1.** SEM-image of nanostructured porous glass.

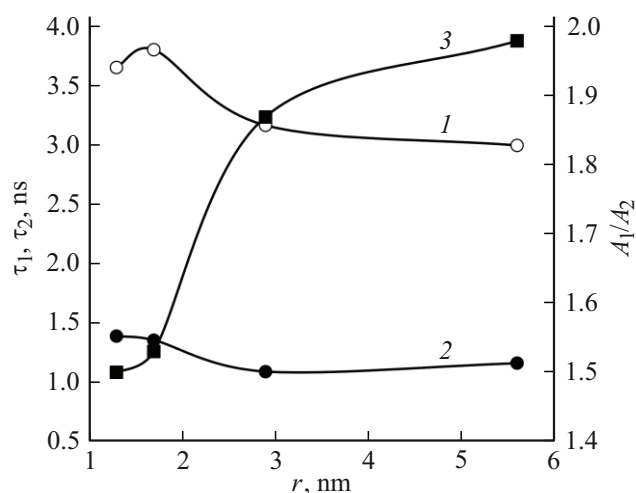


**Figure 3.** Dependences  $\tau_1$  (1),  $\tau_2$  (2) and  $A_1/A_2$  (3) for C7 in PG in pore radius  $r$ .

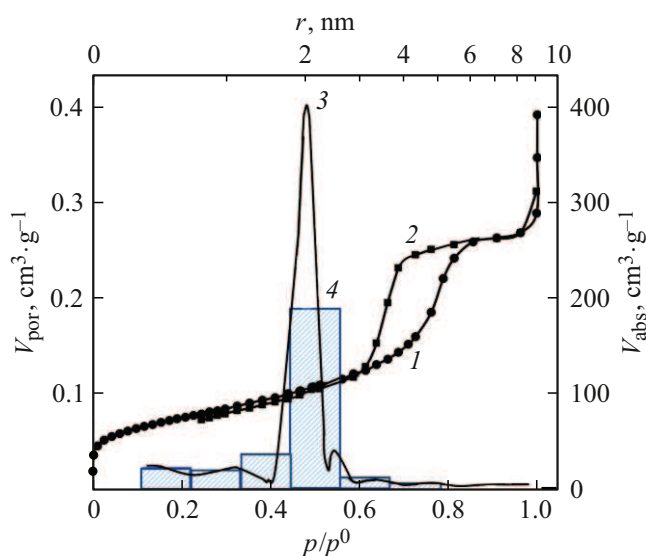


**Figure 2.** Chart of adsorption (1) — desorption (2) of nitrogen in sample № 3, dependence of the pore volume  $V_{\text{por}}$  (3) and pore radius  $r$  (4) on the ratio  $p/p_0$ .

For all samples isotherms of nitrogen adsorption-desorption were measured (Fig. 2, curves 1 and 2) at temperature of 77 K in the interval of relative pressures from  $10^{-4}$  to 1 on equipment Sorptomatic 1990 by Thermo Electron Corporation. The value of the specific surface was determined by BET (Brunauer, Emmet, Teller) method by nitrogen adsorption in the interval of  $0.05-0.4 p/p_0$  ( $p$  — equilibrium pressure,  $p_0$  — pressure of saturated vapors of the adsorptive). The desorption branch of the isotherm (Fig. 2, curve 2) in the range of relative pressures from 0.3 to  $0.95 p/p_0$  was used for BJH (Barrett, Joyner, Halenda)

method to calculate the distribution of mesopores by sizes (Fig. 2, curve 3) and most specific dimensions of pores in the samples (Fig. 2, curve 4). As a result, samples were chosen for the study with the average pore sizes of 1.3, 1.7, 2.9 and 5.6 nm.

To study the kinetic characteristics of fluorescence and EEET, a pair of dyes Coumarin 7 (C7, donor) and Rhodamine B (RB, acceptor) was selected. Dye molecules were adsorbed onto the samples both from ethanol solutions of dyes and from their mixtures. When EEET was studied between C7 and RB, to exclude migration of energy in donors and reverse transfer of energy from the acceptor to the donor, the concentration of C7 in the solutions was selected as  $4 \cdot 10^{-5}$  mol/L, concentration for the RB acceptor varied from  $1 \cdot 10^{-4}$  to  $3 \cdot 10^{-4}$  mol/L (in this area of concentrations the RB dimerization process was absent).

Dye luminescence spectra in PK were measured in the geometry for reflection. Measurements were conducted with the help of an attachment to a spectrofluorometer „SOLAR“ CM2203. The excitation wave of 436 nm was chosen with account of the fact that the acceptor absorption at this wavelength was minimum.

To study the kinetics of fluorescence, a pulse laser BDL-405 (wavelength of 405 nm) was used with the pulse duration of 80 fs. Fluorescence was recorded via a monochromator (SOLAR TII MS2004), with a photodetector PMC-100 installed at the outlet. Luminescence kinetics are recorded with a module of a time-correlated count of single photons (Becker & Hickl GmbH). The measured width at half maximum of the instrument function was 200 ps. The spectral width of monochromator slots was 5 nm.

## Results and discussion

*Time characteristics of C7 fluorescence in PG.* Kinetics of glow  $I(t)$  of C47 molecules in PG were studied. As the

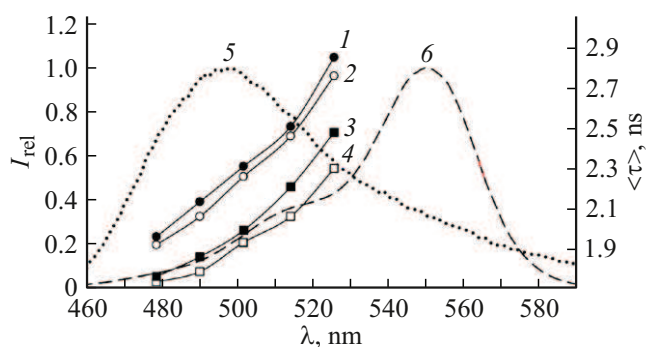


**Figure 4.** Dependences  $\langle \tau \rangle$  on  $\lambda$  for C7 in PG with pore size: 1.3 (1), 1.7 (2), 2.9 (3) and 5.6 (4) nm. Curves 5 and 6 — normalized spectrum of fluorescence of C7 (5) and absorption of RB (6) in PG for samples with pore size 5.6 nm.

results of measurements showed, satisfactory coincidence with the experimental curves  $I(t)$  is provided by approximation of kinetics of C7 fluorescence attenuation in PG by two exponents

$$I(t) = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)}, \quad (1)$$

where  $A_i$  — amplitudes of exponents, attenuation times of exponents,  $t$  — time after excitation of fluorescence.

Fig. 3 presents dependences  $\tau_2$  (curve 1) and  $\tau_1$  (curve 2) on pore radius  $r$ . As you can see from Fig. 3,  $\tau_1 > \tau_2$  for all pore radii of PG. Dependences  $\tau_1(r)$  and  $\tau_2(r)$  have the same appearance — with growth of  $r$   $\tau_1$  and  $\tau_2$  decrease. The same figure presents dependence of ratio  $A_2/A_1$  on  $r$  (curve — 3). You can see that with growth of  $r$  the share of molecules with time  $\tau_1$  increases.

To analyze the kinetics of C7 molecule glow change processes, let us consider the average lifetime of fluorescence

$$\tau = \langle \tau \rangle = \frac{A_1 \tau_1 + A_2 \tau_2}{A_1 + A_2}. \quad (2)$$

Fig. 4 presents dependences of  $\langle \tau \rangle$  for PG on the wavelength of glow for various values of  $r$ . From Fig. 4 you can see that as  $\lambda$  increases, the monotonous growth of  $\langle \tau \rangle$  is observed in the C7 fluorescence spectrum (curve 5 in Fig. 4 the C7 fluorescence spectrum) for all  $r$ . Besides, the smaller the pore radius, the more the inclination is in the dependence of  $\langle \tau \rangle$  on  $\lambda$ . Thus, under linear approximation for dependences of  $\tau$  on  $\lambda$  the inclination coefficients are 0.018 for  $r = 1.3$  nm, 0.017 for  $r = 1.7$  nm, 0.0145 for  $r = 2.9$  nm and 0.011 for  $r = 5.6$  nm.

The presented dependences of time characteristics of emission attenuation in different spectral ranges of the emission band indicate heterogeneous broadening of electron spectra of adsorbed molecules, which has a complex nature and is caused by simultaneous action of several factors.

Individual sections of the PG pore surface may have different adsorption characteristics (heterogeneity of the adsorbent surface due to variability of the local curvature of the pore surface), and molecules adsorbed on the sections of the surface with various characteristics will form subsystems

of molecules with different  $\langle \tau \rangle$ . In PG several subsystems of adsorbed molecules of different orientation may exist relative to the local section of the pore surface and different lifetime of the excited state of C7 ( $\tau_1$  and  $\tau_2$ ).

Besides, the heterogeneous broadening of electron spectra of adsorbates may be caused by induction-resonance interaction of adsorbed molecules under the conditions of heterogeneity of their spatial distribution together with the heterogeneity of the local environment of each molecule.

**C7 fluorescence quenching with RB molecules.** *Transfer of electron excitation energy between C7 and RB molecules.* Interaction between molecules of various types causes quenching of donor fluorescence for all studied concentrations of RB. As the example, Fig. 5 presents the spectra of fluorescence of C7+RB mixture at various concentrations of RB (for  $r = 2.9$  nm). As you can see from Fig. 5, as the concentration of RB grows, the intensity of C7 molecule glow changes (fluorescence is quenched).

The fluorescence quenching processes may be both dynamic and static. Dynamic quenching is a process that prevents emission from the excited state of fluorophore after the excited state has formed [13]. According to this definition, dynamic quenching of fluorescence was caused not only by deactivation of fluorophore in the excited state upon contact or collision with another molecule (quenching agent) in a solution, but by transfer of energy, transfer of electrons etc. At the same time the lifetime of the excited state of fluorophores changes. Static quenching may happen, when fluorophore and quenching agent form non-fluorescent complexes and does not depend on diffusion or collisions of molecules. Under static quenching the lifetime of the excited state of fluorophore will not change.

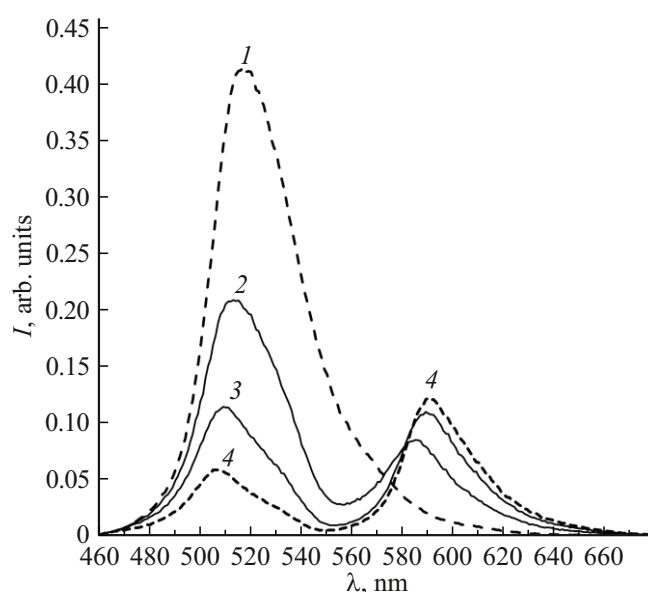


**Figure 5.** Fluorescence spectra of C7+RB mix in PG with  $r = 2.9$  nm for concentrations of RB: 0 (1),  $1.4 \cdot 10^{-4}$  (2),  $2.0 \cdot 10^{-4}$  (3) and  $2.5 \cdot 10^{-4}$  mol/L (4).

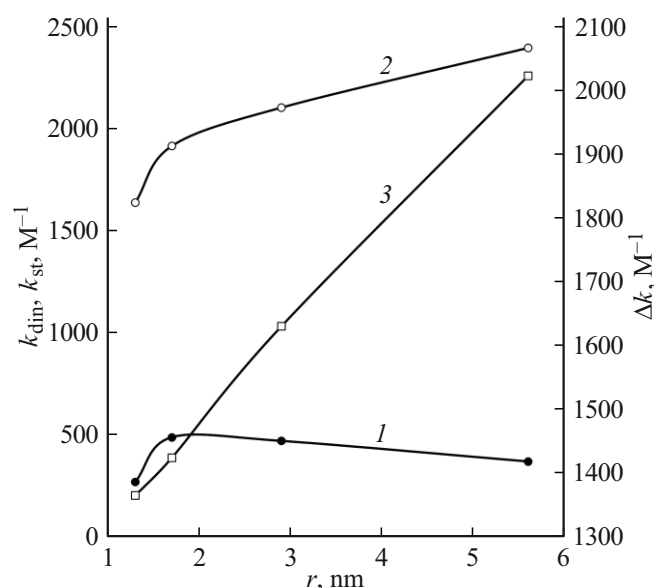


**Figure 6.** Dependences  $k_{\text{din}}$  (1),  $k_{\text{st}}$  (2) and  $\Delta k$  (3) on pore radius  $r$ .

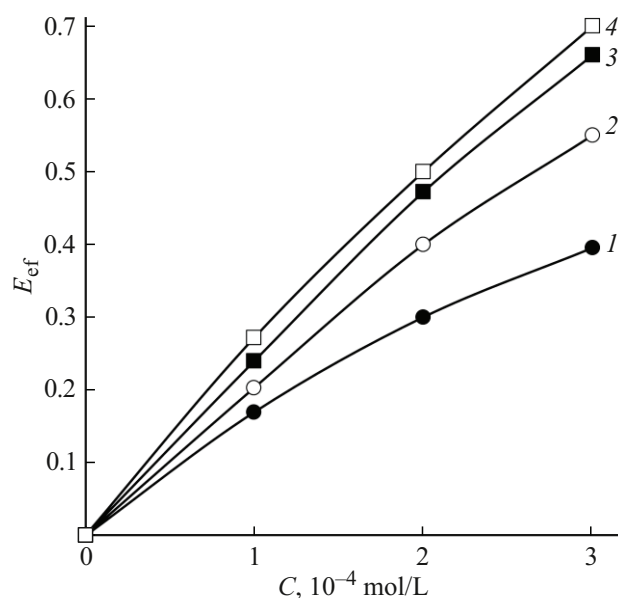


**Figure 7.** Dependences of EEET efficiency  $E_{\text{ef}}$  on concentration of RB in PG with pore radii of 1.3 (1), 1.7 (2), 2.9 (3) and 5.6 (4) nm.

In the general case the intensity of molecule fluorescence may decrease both at the expense of both dynamic and static mechanism of fluorescence quenching. Change in the intensity of fluorescence at various concentrations of a quenching agent may be defined as [14]

$$\frac{I_0}{I} = (1 + k_{\text{din}}[Q])(1 + k_{\text{st}}[Q]), \quad (3)$$

where  $I_0$ ,  $I$  — intensities of C7 fluorescence in PG and in the mixture of C7 and RB, accordingly,  $[Q]$  — concentration

of a quenching agent (RB),  $k_{\text{din}}$  and  $k_{\text{st}}$  — constants of the dynamic and static quenching of fluorescence, accordingly.

For the dynamic quenching it is possible to define the speed constant from the observed decrease in the fluorescence intensity  $k_{\text{din}}$  using the change of the attenuation time

$$\frac{\tau_0}{\tau} = 1 + k_{\text{din}}[Q], \quad (4)$$

where  $\tau_0$  and  $\tau$  — fluorescence attenuation time in absence and presence of quenching agent molecules, accordingly.

Having built the dependence  $\tau_0/\tau$  on the concentration of the quenching agent  $[Q]$  by the least square method,  $k_{\text{din}}$  was determined. Fig. 6 presents the dependence  $k_{\text{din}}$  on  $r$  (curve 1). From Fig. 6 you can see that at small  $r$  there is a minor growth of  $k_{\text{din}}$ . Further increase of  $r$  is accompanied with decrease of  $k_{\text{din}}$ .

To determine  $k_{\text{st}}$ , let us imagine ratio (3) in the following form:

$$B = \frac{I_0/I}{1 + k_{\text{din}}[Q]} - 1 = k_{\text{st}}[Q]. \quad (5)$$

Using the experimental values of  $I_0$  and  $I$ , and also the determined values of  $k_{\text{din}}$ , let us build the dependence of  $B$  on  $[Q]$ , and using the least square method, we will determine  $k_{\text{st}}$ . Fig. 6 presents the dependence  $k_{\text{st}}$  on  $r$  (curve 2). You can see that as  $r$  grows, increase of  $k_{\text{st}}$  is observed, which is provided for by the growth of interaction between C7 and RB molecules. The same figure presents dependence  $\Delta k = k_{\text{st}} - k_{\text{din}}$  on pore radius  $r$  (curve 3). The practically linear dependence  $\Delta k$  on  $r$  is observed.

In the studied system the acceptor (RB) has fluorescent capacity, therefore, to assess the efficiency of energy transfer, a relative index  $E_{\text{ef}}$  was determined, equal to

$$E_{\text{eff}} = \frac{I_A}{I_A + I_D}, \quad (6)$$

where  $I_A$  and  $I_D$  — integral intensities of luminescence of the acceptor (RB) and donor (C7), determined as a result of spectra separation. Fig. 7 shows dependences  $E_{\text{ef}}$  on concentration of the acceptor for the system with different values of  $r$ .

From Fig. 7 you can see that as the pore size grows, the efficiency of excitation energy transfer increases  $E_{\text{ef}}$ . Besides, as the concentration of acceptor (RB) molecules grows,  $E_{\text{ef}}$  increases considerably at  $r = 5.6$  nm and slightly for  $r = 1.3$  nm.

## Conclusion

Therefore, as a result of the study of spectral dependences of average lifetime of the excited state of C7 molecules  $\langle \tau \rangle$  introduced into the nanostructured PGs, it was established that monotonous growth  $\langle \tau \rangle$  is observed in the spectrum of fluorescence of C7 for all  $r$ , which decreases with the growth of pore size. The presented dependences of time characteristics of emission attenuation in various spectral ranges of the emission band indicate heterogeneous

broadening of electron spectra of adsorbed molecules, this is related to the fact that individual sections of PG pore surface may have different adsorption characteristics (heterogeneity of adsorbent surface due to variability of the local curvature of the pore surface), and molecules adsorbed in the sections of the surface with different characteristics form molecule subsystems with different  $\langle\tau\rangle$ . In PG several subsystems of adsorbed molecules of different orientation may exist relative to the local section of the pore surface and different lifetime of the excited state of C7 ( $\tau_1$  and  $\tau_2$ ). The studied system shows both dynamic and static quenching of C7 fluorescence with RB molecules. The constant of dynamic quenching  $k_{\text{din}}$  decreases with the growth of pore size  $r$ , whereas the constant of static quenching  $k_{\text{st}}$  increases with the growth of  $r$ . And  $\Delta k = k_{\text{st}} - k_{\text{din}}$  practically linearly depends on  $r$ . It is shown that dynamic quenching of C7 fluorescence is due to the electron excitation energy transfer from C7 to RB, the efficiency of which increases with growth of  $r$ .

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## Conflict of interest

The authors declare no conflict of interest.

## References

- [1] P. Samanta, A.V. Desai, S. Let, S.K. Ghosh. ACS Sustainable Chem. Eng., **7**, 7456 (2019). DOI: 10.1021/acssuschemeng.9b00155
- [2] S. Rapti, D. Sarma, S.A. Diamantis, E. Skliri, G.S. Armatas, A.C. Tsipis, Y.S. Hassan, M. Alkordi, C.D. Malliakas, M.G. Kanatzidis, T. Lazarides, J.C. Plakatouras, M.J. Manos. J. Mater. Chem. A, **5**, 14707 (2017). DOI: 10.1039/C7TA04496H
- [3] Q. Fang, J. Wang, S. Gu, R.B. Kaspar, Z. Zhuang, J. Zheng, H. Guo, S. Qiu, Y. Yan. J. Am. Chem. Soc., **137**, 8352 (2015). DOI: 10.1021/jacs.5b04147
- [4] T. Lebold, J. Michaelis, C. Brauchle. Phys. Chem. Chem. Phys., **13**, 5017 (2011). DOI: 10.1039/C0CP02210A
- [5] I. Dalfen, S.M. Borisov. Analytical and Bioanalytical Chemistry, **414**, 4311 (2022). DOI: 10.1007/s00216-022-04014-6
- [6] A.B. Grommet, M. Feller, R. Klajn. Nat. Nanotechnol., **15**, 256 (2020). DOI: 10.1038/s41565-020-0652-2
- [7] B. Mitschke, M. Turberg, B. List. Chem., **6**, 2515 (2020). DOI: 10.1016/j.chempr.2020.09.007
- [8] M. Zeeshan, T. Javed, C. Kumari, A. Thumma, M. Wasim, M.B. Taj, I. Sharma, M.N. Haider, M. Batool. Sustainable Chemistry for the Environment, **9**, 100217 (2025). DOI: 10.1016/j.scenv.2025.100217
- [9] X. Xiao, Q. Hong, X. Yan, R. Liu, Y. Wu, C.B. Gu, G. He, H. Chen. Aggregate, **6**(8), e70093 (2025). DOI: 10.1002/agt2.70093
- [10] V.N. Pak, Yu.Yu. Gavronskaya, T.M. Burkat. *Poristye stekla i nanostrukturirovannye materialy na ikh osnove* (Izd-vo RGPU im. A.I. Gertsena, SPb., 2013) (in Russian).
- [11] D.A. Afanasyev, N.Kh. Ibrayev, A.M. Saletsky. J. Luminescence, **136**, 358 (2013). DOI: 10.1016/j.jlumin.2012.11.013
- [12] L.V. Levshin, A.M. Saletsky. *Lyuminesstsiya i ee izmereniya. Molekulyarnaya lyuminesstsiya* (Izd.-vo MGU, M., 1989), s. 143–155 (in Russian).
- [13] S.E. Braslavsky. Pure Appl. Chem., **79**(3), 293 (2007). DOI: 10.1351/pac200779030293
- [14] Dzh. Lakovich. *Osnovy fluorestsentnoy spektroskopii* (Mir, M., 1986), s. 262–305 (in Russian).

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