

Comparative analysis of functional properties of the bimodal fluoride nanophosphors $\text{MGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ ($\text{M} = \text{Na}, \text{K}$) and $\text{RbGd}_{2.1}\text{Eu}_{0.9}\text{F}_{10}$

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Synthesis of compounds

All used reagents are obtained from commercial sources and used without prior purification. Synthesis of $\text{MGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ ($\text{M} = \text{Na}, \text{K}$) and $\text{RbGd}_{2.1}\text{Eu}_{0.9}\text{F}_{10}$ was performed using a modified hydrothermal protocol. As a source of Gd^{3+} and Eu^{3+} ions, aqueous solutions of gadolinium(III) and europium(III) chlorides with a concentration of 0.25 M were used, which were preliminarily standardized by the method of reverse titration of excess trilon B with nickel(II) chloride in the presence of an ammonia buffer ($\text{pH} = 9$) and murexide.

For the preparation of reaction mixtures for hydrothermal synthesis, solutions of gadolinium and europium salts were mixed in the required ratio, taking into account the appropriate stoichiometry of the synthesized compounds. Then, 1.8 mmol of citric acid was added to the resulting mixtures and the volume was adjusted to 5 ml. The total content of rare earth element chlorides in the obtained mixtures was 1 mmol. 2 ml 5 M ammonia (10 mmol) was added dropwise to the resulting solutions with intensive stirring and the stirring was maintained on a magnetic stirrer for another 15 minutes. Then, 12.5 ml of 0.8 M MF, where M - Na, K, Rb (10 mmol) was added drop by drop and left to mix for another 15 minutes. Further, the reaction mixture was placed in a sealed steel autoclave with a teflon liner and kept for 17 hours at 180 ° C. The suspension obtained after synthesis in an autoclave was transferred to test tubes, and the obtained solid solutions were centrifuged and separated from the liquid phase on a centrifuge for 5 minutes at a rotor speed of 4000 rpm. The white precipitate was separated by decanting. Then, 3 ml of ethanol was added for washing, and the precipitate was dispersed in ethanol using an ultrasonic bath or manually, and then separated again on a centrifuge. After that, the resulting precipitate was washed 3 times with water and dried in an air for 24 hours at a temperature of 60 °C.

Methods of studying

The composition of the obtained microcrystalline compounds was confirmed by energy dispersion spectroscopy (EDX). The morphology of microparticles was studied using scanning electron microscopy (a Zeiss Merlin electron microscope (Zeiss) equipped with energy dispersion spectroscopy (Oxford Instruments Inc.-act). X-ray images were recorded using a D2 Phaser (Bruker) X-ray diffractometer using radiation from Cu Ka, $\lambda = 1.54056 \text{ \AA}$. The luminescence spectra were measured using a FluoroMax-4 spectrofluorimeter (Horiba Jobin Yvon) under the same conditions. To measure the luminescence spectra, the samples were compressed into tablets containing 20 mg of synthesized compounds and 300 mg of pre-calcined at 120 °C potassium bromide. Lifetime measurements were performed with the Fluorolog 3 fluorescence spectrometer (Horiba Jobin Yvon, Japan) using a pulsed Xe lamp (pulse duration: 3 μs). The absolute values of the photoluminescence quantum yields were recorded using a Fluorolog 3 Quanta-phi device. All measurements were performed at 25 °C.

Luminescence part

Values τ_1 and τ_2 were obtained by approximating decay curves using biexponential function:

$$I(t) = A_1 e^{\frac{t}{\tau_1}} + A_2 e^{\frac{t}{\tau_2}}$$

A_1, A_2 – pre-exponential constants, τ_1, τ_2 – fitting lifetimes.

Average lifetime can be approximately calculated using equation

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

Total decay rate constant (A_{tot}) can be calculated as τ^{-1} . Radiative decay rate constant (A_{rad}) can be calculated as a sum of decay rate constants of radiative transitions. Decay rate constant of $^5\text{D}_0 - ^7\text{F}_1$ transition can be calculated using formula:

$$A_{0-1} = 14.65 n_0^3$$

n_0 – refractive index = 1.49.

Decay rate constants of other transitions can be calculated using formula:

$$A_{0-j} = A_{0-1} \frac{\nu_{0-1} I_{0-j}}{\nu_{0-j} I_{0-1}},$$

I_{0-j} and I_{0-1} – integral intensities of $^5\text{D}_0 - ^7\text{F}_j$ and $^5\text{D}_0 - ^7\text{F}_1$ transitions, ν_{0-j} and ν_{0-1} – frequencies of $^5\text{D}_0 - ^7\text{F}_j$ and $^5\text{D}_0 - ^7\text{F}_1$ transitions.

PLQY values were obtained empirically using integration sphere method.

R_{21} can be calculated as a ratio of $^5\text{D}_0 - ^7\text{F}_2$ and $^5\text{D}_0 - ^7\text{F}_1$ integral intensities. [I. E. Kolesnikov, A. A. Vidyakina, M. S. Vasileva, V. G. Nosov, N. A. Bogachev, V. B. Sosnovsky, M. Y. Skripkin, I. I. Tumkin, E. Lähderanta and A. S. Mereshchenko *New J. Chem.*, 2021, **45**, 10599; <https://doi.org/10.1039/D1NJ02193A>.]

Cytotoxicity

The data on cytotoxicity of nanoparticles $\text{NaGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ were taken from our previous work [T. S. Bulatova, N. A. Bogachev, A. A. Betina, A. N. Smirnov, E. V. Solovieva, M. Yu. Skripkin and A. S. Mereshchenko, *Russ. J. Gen. Chem.*, 2022, **92**, 2845; <https://doi.org/10.1134/S1070363222120362>]. To determine the cytotoxicity of compounds with potassium and rubidium in this work, the following protocol was used.

The cytotoxicity of the synthesized nanoparticles was evaluated using HEK-293 (human embryonic kidney) and HeLa (human cervical carcinoma) cell lines. Cells were cultured with nanoparticle suspensions (12.5-100 μM) for 24 hours in complete DMEM medium (supplemented with 10% fetal bovine serum, 2 mM L-glutamine, 1 g/L glucose, and 10 $\mu\text{g/mL}$ gentamicin) at 37°C under 5% CO_2 atmosphere. Viability was assessed via MTT assay, measuring the reduction of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide to formazan by mitochondrial dehydrogenases in viable cells. Formazan absorbance was quantified at 590 nm after dissolution in DMSO. Experiments were performed in triplicate for each concentration.

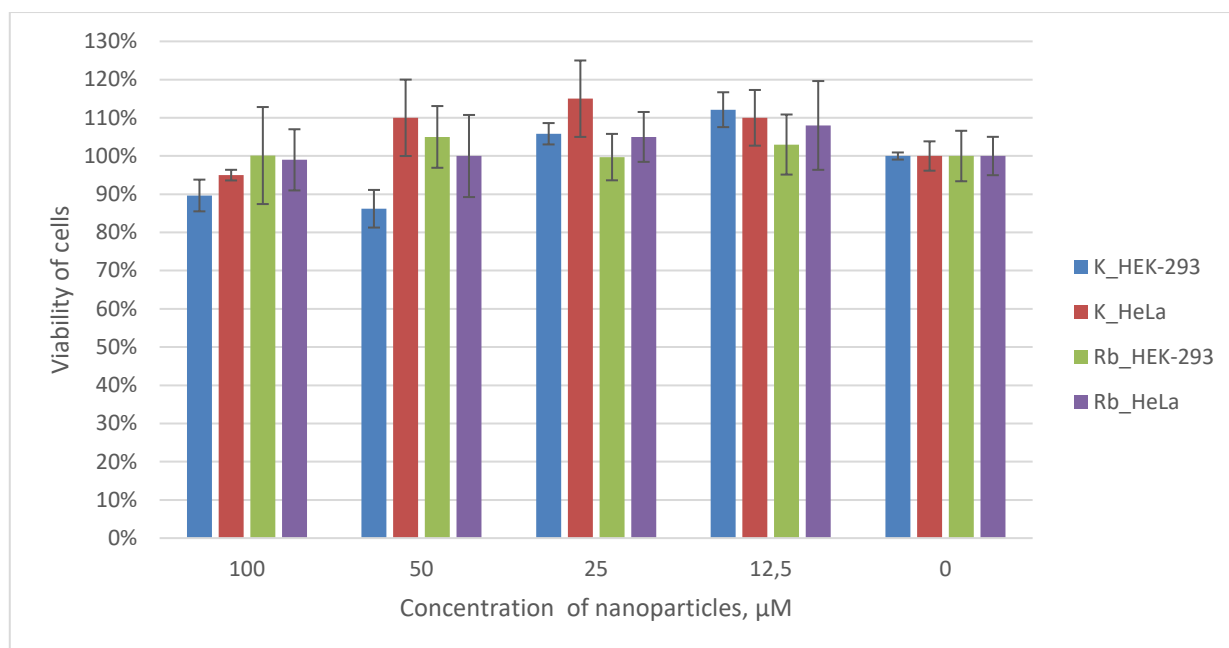


Figure S1. The results of cytotoxicity testing for $\text{KGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ (K_HEK-293, K_HeLa) and $\text{RbGd}_{2.1}\text{Eu}_{0.9}\text{F}_{10}$ (Rb_HEK-293, Rb_HeLa) samples.