Luminescent Heterometallic Europium(III)-Lutetium(III) Metal-Organic Frameworks

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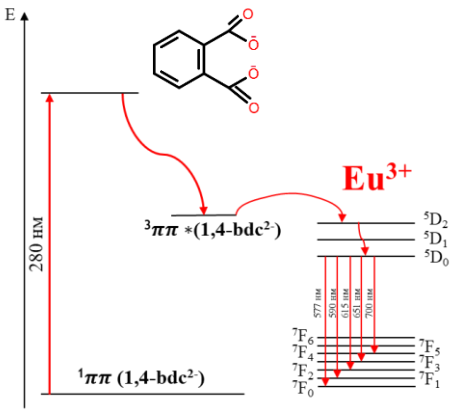
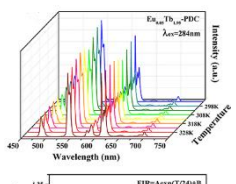
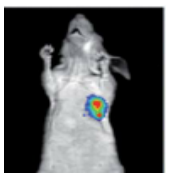
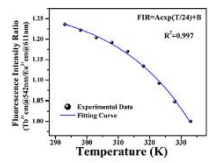
1,2-bdc^{2-}

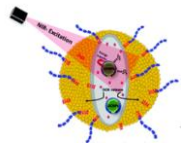


Application of REE MOFs



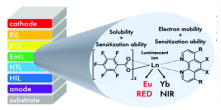


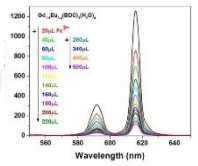




Luminescent thermometers

Bioimaging





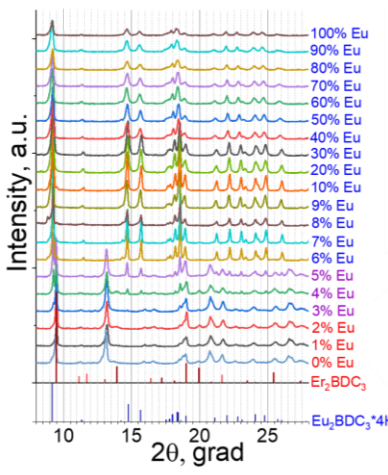
LEDs

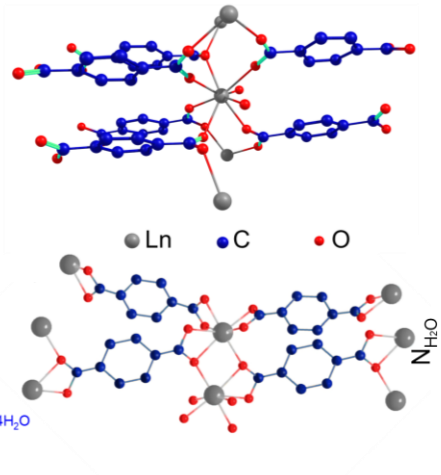
Luminescent sensors

Synthesis

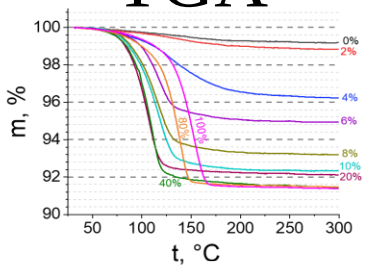
$$(2x)EuCl_3+(2-2x)LuCl_3+3Na_2(1,4\text{-bdc})=(Eu_xLu_{1-x})_2(1,4\text{-bdc})_3\downarrow+6NaCl$$

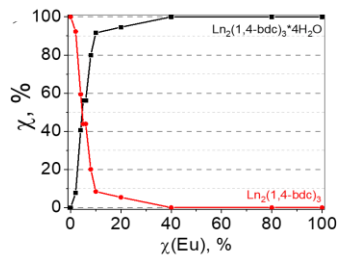
XRD





TGA

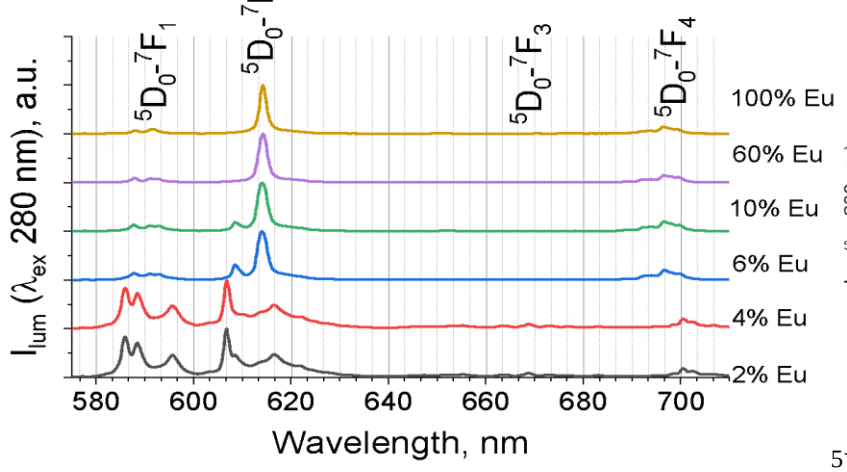


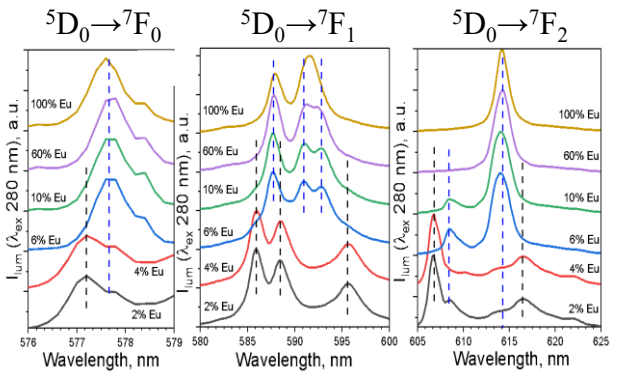


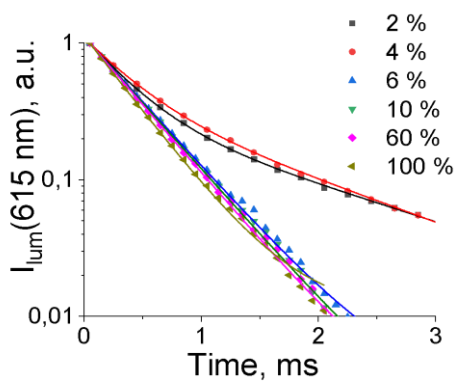
100-180 ^{0}C: de-hydration

$$Eu_xLu_{1-x}(1,4-bdc)_3*nH_2O\rightarrow Eu_xLu_{1-x}(1,4-bdc)_3+nH_2O\uparrow$$

Luminescent properties λ_{ex}= 280 nm







$^5D_0$ excited state lifetimes and luminescence quantum yields

x_{Eu} (%)	τ_1, ms	τ_2, ms	Φ, %
100	0.390		10±1
60	0.435		11±1
10	0.449		12±1
6	0.459		16±1
4	0.392	1.602	22±1
2	0.367	1.878	22±1

Acknowledgements

The measurements were performed at the Research Park of Saint-Petersburg State University (''Magnetic Resonance Research Centre'', ''SPbU Computing Centre'', ''Cryogenic Department'', ''Interdisciplinary Resource Centre for Nanotechnology'', ''Centre for X-ray Diffraction Studies'', ''Chemical Analysis and Materials Research Centre'', and ''Centre for Optical and Laser Materials Research'').

Conclusions

1. At Eu^{3+} concentration 1-20 at. %, heterometallic europium(III)-lutetium(III) terephthalates are formed as a mixture of $(Eu_xLu_{1-x})_2bdc_3$ and $(Eu_xLu_{1-x})_2bdc_3{\cdot}4H_2O$ crystalline phases. At higher Eu concentrations, a single crystalline phase is formed, $(Eu_xLu_{1-x})_2bdc_3{\cdot}4H_2O$.
2. All the synthesized samples containing Eu^{3+} demonstrate bright red emission corresponding to $^5D_0\rightarrow^7F_J$ (J = 0-4) transitions of Eu^{3+} ion ($\lambda_{ex.}$=280 nm).
3. Eu^{3+} ion unevenly distributed between Ln_2bdc_3 and $Ln_2bdc_3{\cdot}4H_2O$ phases: $Ln_2bdc_3{\cdot}4H_2O$ crystalline phase is enriched by Eu^{3+} ions.
4. In $Eu_2bdc_3{\cdot}4H_2O$, the local symmetry of Eu^{3+} ion is pseudo-C_4. In $(Eu_xLu_{1-x})_2bdc_3{\cdot}4H_2O$, the increase of Lu^{3+} ions ratio leads to the Eu^{3+} local symmetry distortion to C_2 or lower point group (symmetry). The local symmetry of Eu^{3+} is proposed to be C_1 in anhydrous $(Eu_xLu_{1-x})_2bdc_3$.
5. $^5D_0$ excited state lifetimes are 4 - 4.8 times larger for Eu^{3+} in Ln_2bdc_3 crystalline phase than in $Ln_2bdc_3{\cdot}4H_2O$ due to the absence of luminescence quenching of Eu^{3+} by coordinated water molecules.
6. The luminescence quantum yields of terephthalate ions decrease with the increase of europium concentration from 2 to 100 at. % Eu^{3+} upon excitation into S_1 ($^1\pi\pi$*) singlet electronic excited state.