Single excited dual band luminescent hybrid carbon dots – terbium chelate nanothermometer

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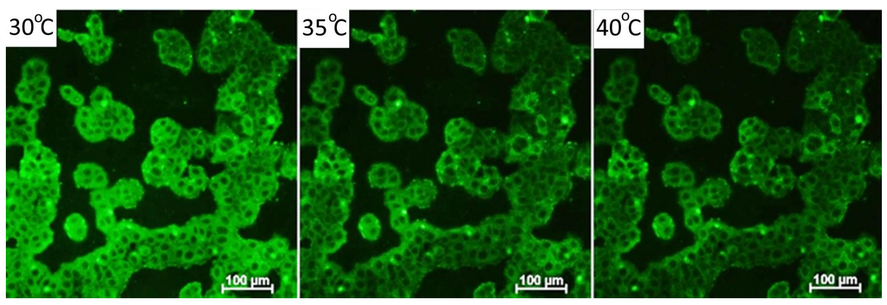
❑*Relevance*

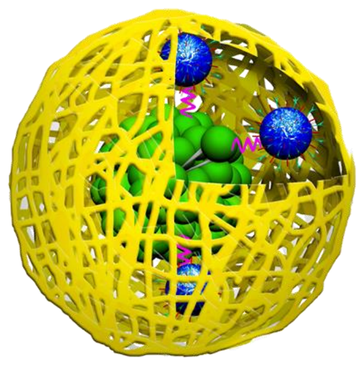
Many intracellular processes (cell division, metabolism, etc.) proceed with a change in cell temperature. One of the most convenient methods for its determination is fluorescence microscopy. The creation of sensitive, biocompatible contrast agents is an urgent task for modern researchers.

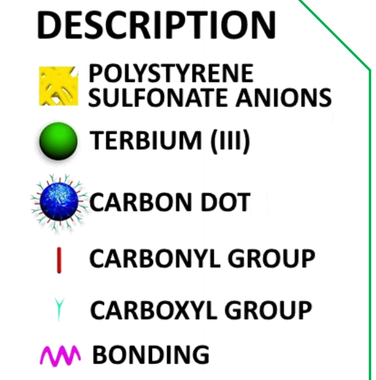


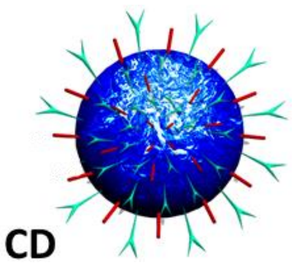
Zairov R.R., Dovzhenko A.P. et al. Scientific reports, 2020, 10, № 1, 20541.

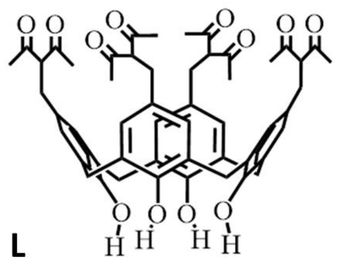
❑*Research objectives*

– Development of stable hybrid poly-electrolyte (PSS) nanoparticles based on carbon quantum dots (CD) and terbium complexes (TbL) with luminescence in two regions of the visible spectrum





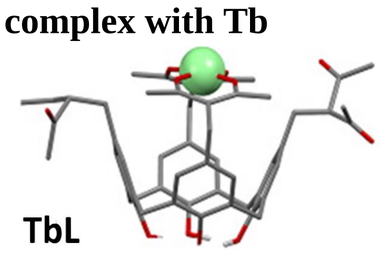


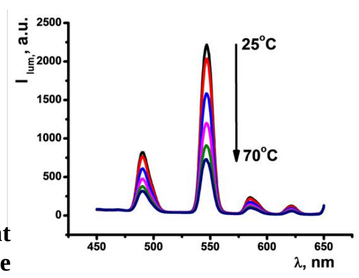


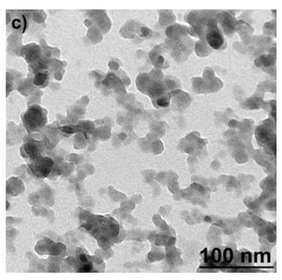
– examination of the obtained hybrid nanoparticles for the possibility of using them as a rationometric determination of the temperature inside the cell.

❑*PSS-{[TbL} properties*

– The $[TbL]^+$ complex derives from efficient bis-chelating of Tb^{3+} via two diketonate groups of the tetra-1,3-diketone calix[4]arene.
– The synthesis of hydrophilic colloids from TbL and hybrid complexes is based on their efficient self-assembly in the synthetic conditions of the solvent-exchange technique
– Ligand (L) was choused because of pronounced and reversible temperature-induced changes of the luminescence of it`s complex with Tb

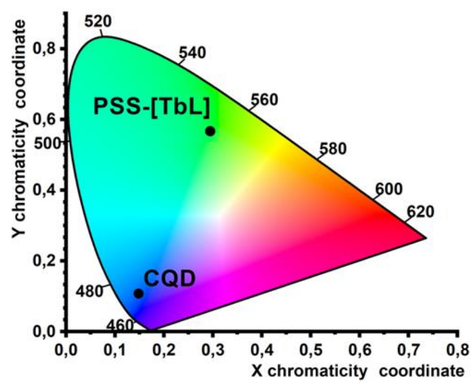






TbL -structure, -thermoluminescent dependence, -TEM image

❑*Common*

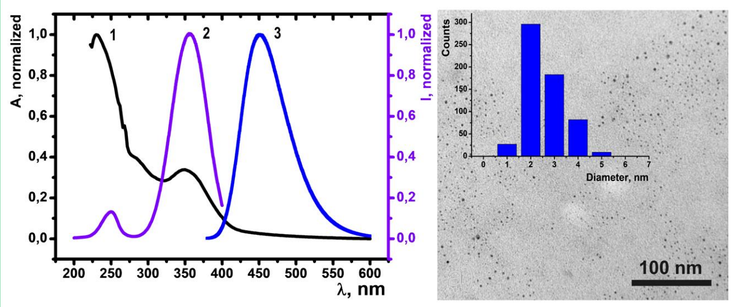


Diameter (d), polydispersity index (PDI), zeta potential (Zp) obtained by DLS method, thermal sensitivity (S_I)

	d, nm	PDI	Zp, mV	S_I,%K^{-1}
PSS-{TbL}	193.3	0.171	-26.2	3,55
CDs	-	0.951	-39.9	1,25

Diameter of CDs is too small to be determined by DLS method

❑CD *properties*

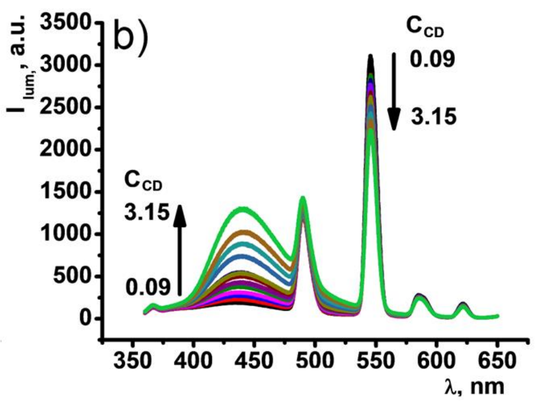


Absorbance (1), excitation (2), luminescence (3), TEM image

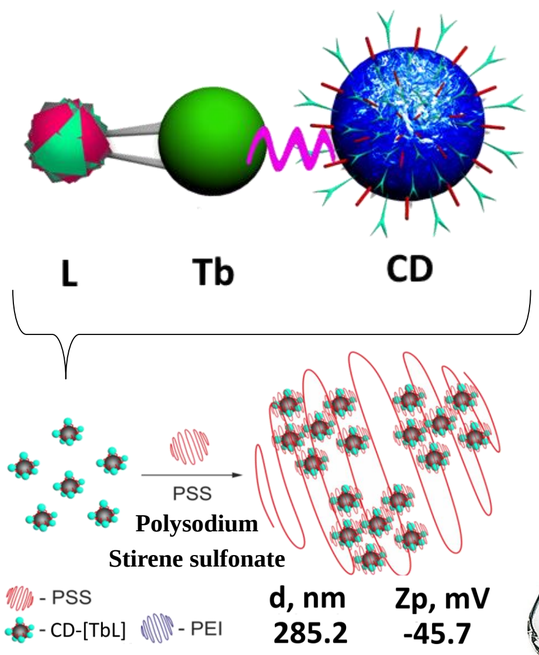
– CDs were obtained by facile microwave-assisted synthesis from citric acid and urea.
– The size of CD lies in the vicinity of 3nm (TEM image). Their thermal sensitivity is quite low (presented in *supplementary)*

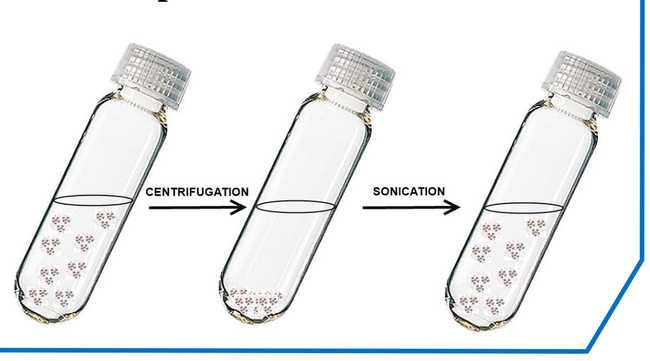
❑*Synthesis of hybrid nanoparticles*

The spectra (represented on the right) demonstrates gradual decrease of Tb-centered luminescence intensity upon addition of CDs to $[TbL]^+$ complexes, which amplifies their interaction.



The coordinative binding $[TbL]^+$ complex with active groups on the surface of CDs is used as a tool for their combination within the PSS-nanoplatform.

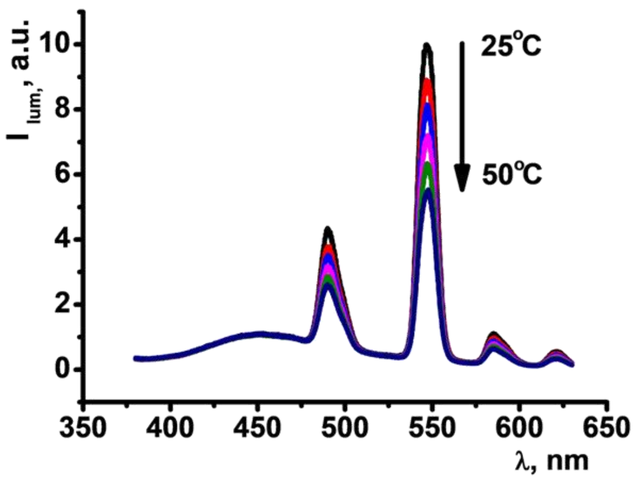


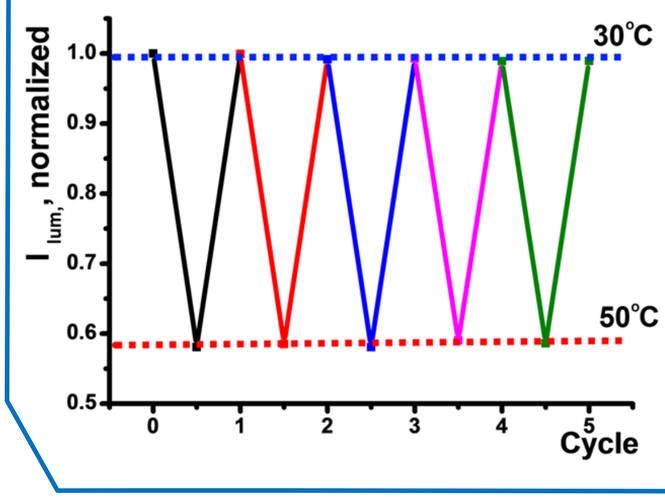


❑ *Luminescent thermometers*

By choosing the optimal ratio of CD and $[TbL]^+$ in hybrid system, their interactions as well as the temperature sensitivity of SD were suppressed, which made it possible to create a sensitive ratiometric temperature sensor PSS-{CDs-[TbL]}

The green 547 nm band of [TbL] colloid remains highly sensitive to the changes of temperature in the range of 25-50 °C, while the fluorescence of the CDs exhibit the insignificant changes.

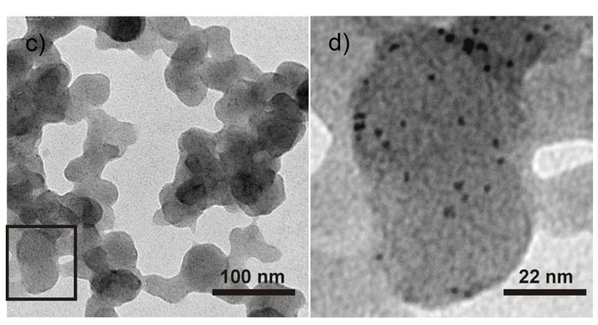




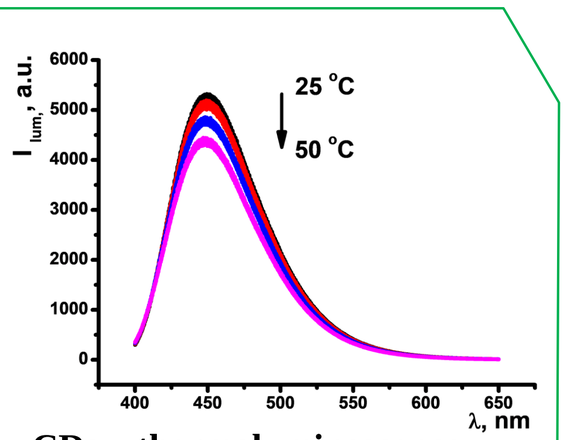
The resulting hybrids have complete reversibility of luminescence in the temperature range 25 - 50 °C, at least in five cycles. The maximum temperature sensitivity was 2.89% K^{-1}.

These hybrids were also studied in the BSA environment, as the simplest model of the environment, where they showed insignificant deviations from the presented results.

❑ *Supplementary*



TEM images of hybrid system



CDs – thermoluminescence

❑ *Conclusions:*

– By replacing the solvent, were synthesized hybrid polyelectrolyte nanoparticles containing blocks of different nature, CD and $[TbL]^+$. The coordinative binding between Tb^{3+} centers and the surface groups of CDs out to be the main driving force of their joint incorporation into the PSS-based nanobeads.
– Has been proven that the novel hybrid carbon dots-terbium chelate based platform can be used as single excited dual band emission ratiometric temperature sensor with temperature sensitivity up to 2.89 % K^{-1}

The authors gratefully acknowledge the Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS.