Supporting information

Core-shell metal fluoride nanoparticles via fluorolytic sol-gel synthesis – a fast and efficient construction kit

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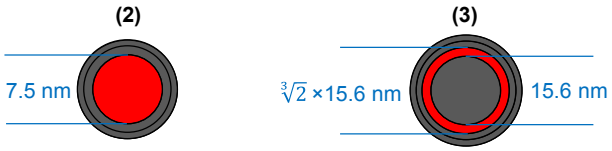
Method to calculate the relative shielding efficiency

The radiation-free relaxation of Eu^{3+} in two different spatial directions in a shell causes a reduction of luminescence intensity and lifetime as compared to Eu^{3+} incorporated in the core (Figure 6). This can be described quantitatively by the decay constants k_1 and k_2 of the particles **(2)** and **(3)** which can be described as follows:

$$k_1 = \frac{1}{\tau_1} = k_{in} + f_1 k_{nr} \quad \text{and} \quad k_2 = \frac{1}{\tau_2} = k_{in} + f_2 k_{nr}$$

Here k_{in} is the "intrinsic" decay constant of SrF_2:Eu10, f_1 and f_2 are the area-to-volume-ratio of SrF_2:Eu10 part, and k_{nr} is the rate constant of the non-radiative relaxation from SrF_2:Eu10 into the adjacent material SrF_2. The values τ_1 (*5.79 ms*) and τ_2 (*5.19* ms) are measured, f_1 (*0.800*) and f_2 (*0.9952*) *are* calculated from DLS data.



Thus it follows that $k_{in} = 90.86\ s^{-1}$ and $\tau_{in} = \frac{1}{k_{in}} = 11.01\ ms^{-1}$. In theory, this "intrinsic lifetime" τ_{in} would be the lifetime of a bulk material SrF_2:Eu10 with a negligible surface area. In practice, not all non-radiative relaxation contributions were considered in this simple model, and hence, the values should not be over-interpreted.

Using this value for k_{in}, the luminescence decay of the particles **(1)**, **(2)** and **(4)** is simply modelled as

$$\frac{1}{\tau_i} = k_i = k_{in} + k_{i,shell}$$

where τ_i is the measured lifetime of the decay of Eu^{3+} and $k_{i,shell}$ is the non-radiative relaxation into the shell material. Since all cores have the same size, no surface-to-volume correction coefficient is necessary. Thus, the non-radiative relaxation rate $k_{i,shell}$ can be calculated for the naked core **(1)** and the shell materials CaF_2 **(4)** and SrF_2 **(2)**. The lower $k_{i,shell}$ is, the more effective the shell is shielding the core from the solvent.

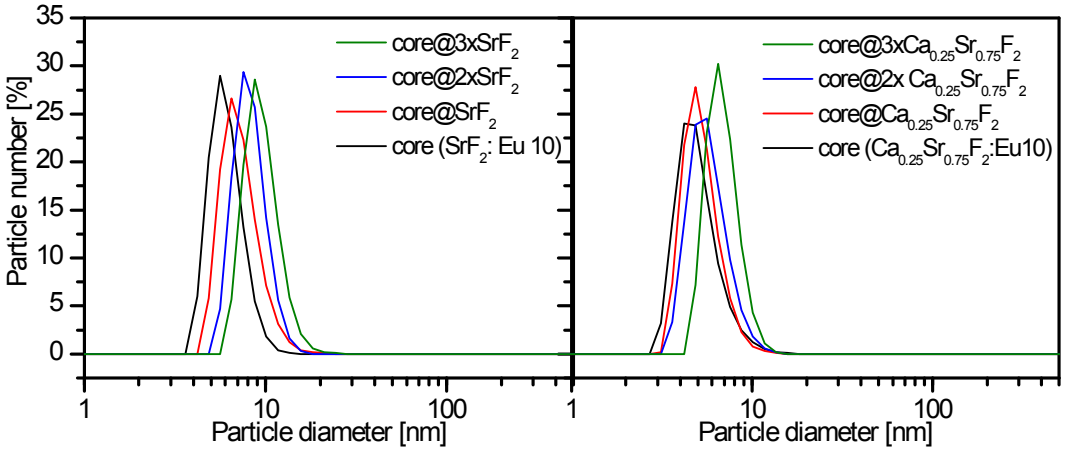


Figure S1. DLS data of (left) SrF_2:Eu10@n×SrF_2 and (right) $Ca_{0.25}Sr_{0.75}F_2$:Eu10@n×$Ca_{0.25}Sr_{0.75}F_2$ (n = 0…3).

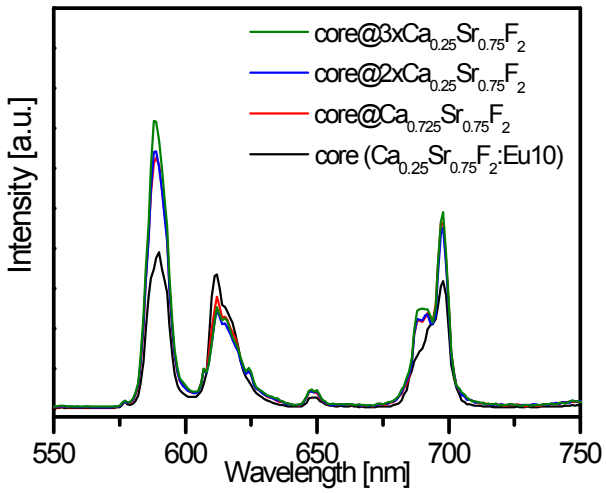


Figure S2. PL emission spectra (λ_{ex} = 393 nm) of $Ca_{0.25}Sr_{0.75}F_2$:Eu10@n×$Ca_{0.25}Sr_{0.75}F_2$ (n = 0…3).

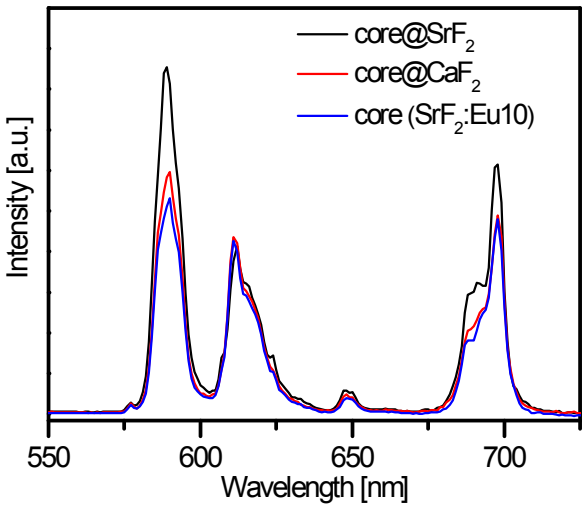


Figure S3. PL emission spectra (λ_{ex} = 393 nm) of SrF_2:Eu10 (core), SrF_2:Eu10@CaF_2 and SrF_2:Eu10@SrF_2.

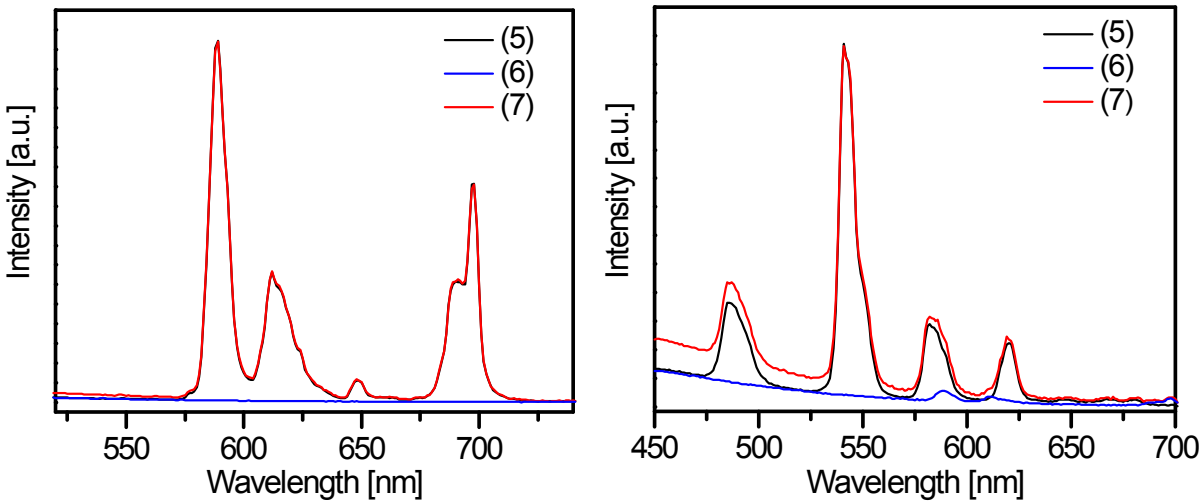


Figure S4. PL emission spectra of SrF_2:Eu10@2×SrF_2 (5) and SrF_2:Tb10@2×SrF_2 (6) and the 50:50 mixture (7) excited at 393 nm (left) and 350 nm (right). All spectra are normalized to the rare earth content.

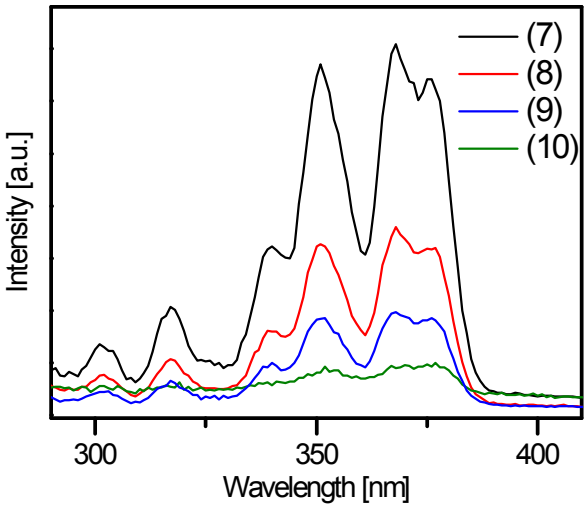


Figure S5. PL excitation spectra (λ_{em} = 542 nm, emission of Tb^{3+}) (7)…(10). All spectra are normalized to the rare earth content.

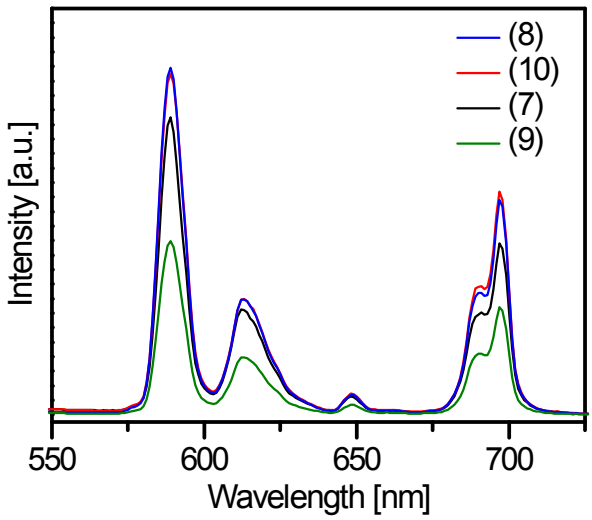


Figure S6. PL emission spectra (λ_{ex} = 393 nm, excitation of Eu^{3+}) of (7)…(10). All spectra are normalized to the rare earth content.

Table S1. Calculated and measured DLS and TEM diameters of SrF_2:Eu10@n×SrF_2 (n = 0…3). * The measured core diameter is used as starting value for the calculation of the expected diameter of the core-shell particles.

sample	calculated diam. [nm] *	DLS diam.[nm]	calculated TEM diam.[nm] *	TEM diam.[nm]
core		7.8		9.1
1st shell	9.9	10.3		
2nd shell	11.3	11.4		
3rd shell	12.4	13.8	14.5	13.7

Table S2. Luminescence lifetimes for SrF_2:Eu10@n×CaF_2, SrF_2:Eu10@n×SrF_2 and $Ca_{0.25}Sr_{0.75}F_2$:Eu10@n×$Ca_{0.25}Sr_{0.75}F_2$ (n = 0…3) (t_1= lifetime and q_1 = asymmetry parameter).

Samples	Lum. lifetimes	Samples	Lum. lifetimes
SrF_2:Eu10	t_1 2.4 ms q_1 1.123	$Ca_{0.25}Sr_{0.75}F_2$:Eu10	t_1 2.2 ms q_1 1.182
SrF_2:Eu10@SrF_2	t_1 5.2 ms q_1 1.135	$Ca_{0.25}Sr_{0.75}F_2$:Eu10@$Ca_{0.25}Sr_{0.75}F_2$	t_1 4.3 ms q_1 1.194
SrF_2:Eu10@2×SrF_2	t_1 6.2 ms q_1 1.115	$Ca_{0.25}Sr_{0.75}F_2$:Eu10@2×$Ca_{0.25}Sr_{0.75}F_2$	t_1 5.3 ms q_1 1.167
SrF_2:Eu10@3×SrF_2	t_1 6.6 ms q_1 1.097	$Ca_{0.25}Sr_{0.75}F_2$:Eu10@3×$Ca_{0.25}Sr_{0.75}F_2$	t_1 6.0 ms q_1 1.137
SrF_2:Eu10@CaF_2	t_1 2.6 ms q_1 1.180		
SrF_2:Eu10@2×CaF_2	t_1 2.9 ms q_1 1.212		

Table S3. Luminescence lifetimes of co-doped core-shell particles for different excitation and emission wavelengths.

Sample	Tb^{3+}→Tb^{3+} ex 350 nm em 542 nm	Eu^{3+}→Eu^{3+} ex 393 nm em 698 nm
(5)	-	4.34
(6)	5.24	-
(7)	5.17	4.31
(8)	3.11	5.22
(9)	2.92	3.31
(10)	2.17	4.91