Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Novel and Easy Access to Highly Luminescent Eu and Tb Doped Ultra-small CaF_2, SrF_2 and BaF_2 Nanoparticles – Structure and Luminescence

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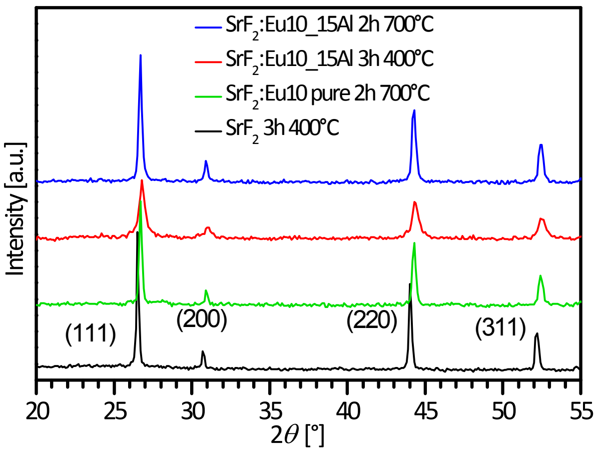

Figure S1. Powder diffractograms of SrF_2 and SrF_2:Eu10 xerogels with and without Al(O^{i}Pr)$_3$ annealed at 400°C and 700°C.

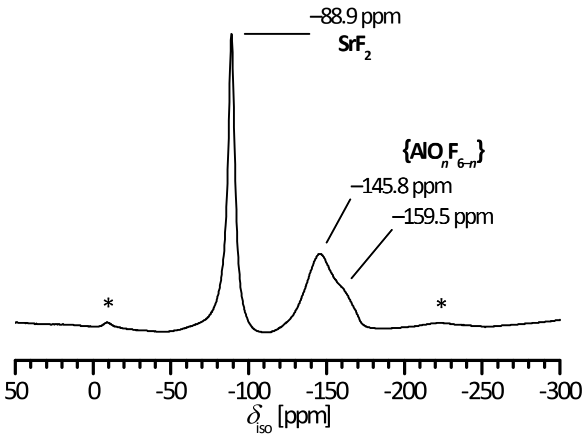

Figure S2. ^{19}F MAS NMR spectrum (ν_{rot} = 30 kHz) of the SrF_2 xerogel with 15 mol% Al(O^{i}Pr)$_3$. * ~spinning side bands.

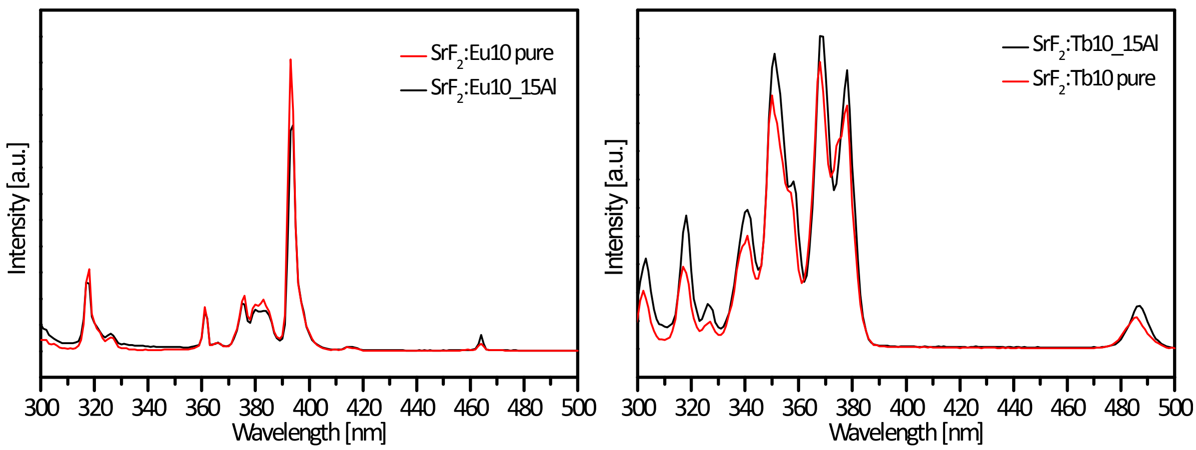

Figure S3. Luminescence excitation spectra. left: SrF_2:Eu10 (λ_{em} = 590 nm), right: SrF_2:Tb10 (λ_{em} = 542 nm). Both pure and with 15 mol% Al(O^{i}Pr)$_3$ added.

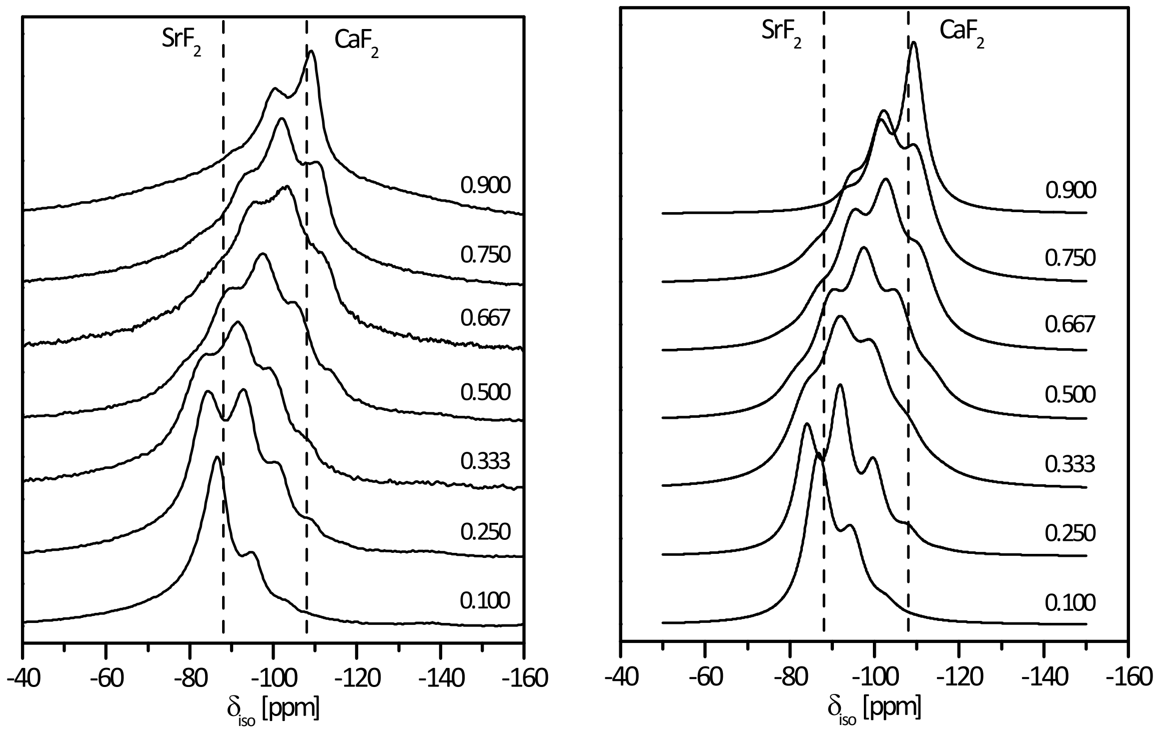

Figure S4. Comparison of measured (left) and simulated (right) ^{19}F NMR spectra of *nano*-$Ca_{1-x}Sr_xF_2$ sols in ethylene glycol with $0.10 \leq \chi_c \leq 0.90$ (dashed lines show the chemical shifts for pure CaF_2 and SrF_2).

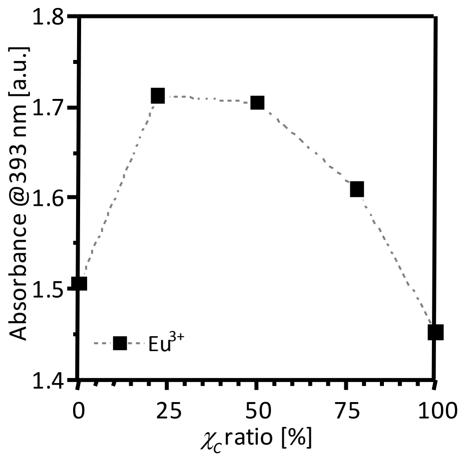

Figure S5. Absorbance of $Ca_xSr_{1-x}F_2$:Eu10 at 393 nm (0.2 M sol, 1 cm sample thickness).

Table S1. Labelling of the samples $Ca_xSr_{1-x}F_2$:*RE*10.

Shortcut *RE* = Eu, Tb	**Sum formula** *RE* = Eu, Tb	χ_C
SrF_2:*RE*10	$Sr_{0.9}RE_{0.1}F_{2.1}$	0.000
$Ca_{0.1}Sr_{0.9}F_2$:*RE*10	$Ca_{0.05}Sr_{0.85}RE_{0.1}F_{2.1}$	0.056
$Ca_{0.25}Sr_{0.75}F_2$:*RE*10	$Ca_{0.20}Sr_{0.70}RE_{0.1}F_{2.1}$	0.222
$Ca_{0.33}Sr_{0.67}F_2$:*RE*10	$Ca_{0.28}Sr_{0.62}RE_{0.1}F_{2.1}$	0.311
$Ca_{0.5}Sr_{0.5}F_2$:*RE*10	$Ca_{0.45}Sr_{0.45}RE_{0.1}F_{2.1}$	0.500
$Ca_{0.67}Sr_{0.33}F_2$:*RE*10	$Ca_{0.62}Sr_{0.28}RE_{0.1}F_{2.1}$	0.689
$Ca_{0.75}Sr_{0.25}F_2$:*RE*10	$Ca_{0.70}Sr_{0.20}RE_{0.1}F_{2.1}$	0.778
$Ca_{0.9}Sr_{0.1}F_2$:*RE*10	$Ca_{0.85}Sr_{0.05}RE_{0.1}F_{2.1}$	0.944
CaF_2:*RE*10	$Ca_{0.9}RE_{0.1}F_{2.1}$	1.000

Table S2. Particle diameter of 0.2 M sols of SrF_2:Eu*X* and SrF_2:Tb*X* (*X* = 1-15 mol%) by DLS (number).

***X* [mol%]**	**DLS diam. (nm) SrF_2:Eu*X***	**DLS diam. (nm) SrF_2:Tb*X***	**Solvent and additive**
1	3	3	synthesis 2 in methanol, +15 mol% $Al(O^iPr)_3$
2	3	3	
4	11	14	
10	24	5	
15	24	24	
10	5	5	synthesis 1 in ethylene glycol, no additive

Table S3. Lifetime changes of the SrF_2:Eu10 sols in ethylene glycol with 15 mol% of different additives. Note the large asymmetry parameter in the case of $Al(O^iPr)_3$. **T1**: $^5D_0 \rightarrow ^7F_1$, **T2**: $^5D_0 \rightarrow ^7F_2$.

Additive	**Luminescence lifetime**	**T1 : T2 intensity**
none	t_1 3.1 ms q_1 1.121	63 : 37
Citric acid	t_1 3.1 ms q_1 1.137	62 : 38
Benzoic acid	t_1 3.1 ms q_1 1.148	63 : 37
Phenylphosphonic acid	t_1 3.3 ms q_1 1.141	51 : 49
Tetramethyl orthosilicate	t_1 3.5 ms q_1 1.144	56 : 44
Aluminium isopropoxide	t_1 2.2 ms q_1 1.259	44 : 56
Titanium isopropoxide	t_1 3.0 ms q_1 1.183	50 : 50

Table S4. DLS particle diameters and luminescence lifetimes for SrF_2:Eu*X* and SrF_2:Tb*X* in ethylene glycol with X = 0…40. (λ_{ex}(Eu) = 393 nm, λ_{ex}(Tb) = 350 nm, t_1= lifetime and q_1 = asymmetry parameter).

Abbreviation (*RE* = Eu, Tb)	**Sum formula (*RE* = Eu, Tb)**	**DLS particle diameter (nm)**		**Luminescence lifetime**	
		RE = Eu	*RE* = Tb	*RE* = Eu	*RE* = Tb
SrF_2	SrF_2	13.5		–	
SrF_2:*RE*0.1	$Sr_{0.999}RE_{0.001}F_{2.001}$	24.4		t_1 1.2 ms q_1 1.300	
SrF_2:*RE*0.2	$Sr_{0.998}RE_{0.002}F_{2.002}$	18.2		t_1 1.5 ms q_1 1.300	
SrF_2:*RE*1	$Sr_{0.99}RE_{0.01}F_{2.01}$	6.5	4.2	t_1 2.3 ms q_1 1.300	t_1 2.59 ms q_1 1.300
SrF_2:*RE*2	$Sr_{0.98}RE_{0.02}F_{2.02}$		5.6		t_1 3.23 ms q_1 1.160
SrF_2:*RE*4	$Sr_{0.96}RE_{0.04}F_{2.04}$		8.7		t_1 3.05 ms q_1 1.166
SrF_2:*RE*5	$Sr_{0.95}RE_{0.05}F_{2.05}$	5.6		t_1 2.2 ms q_1 1.296	
SrF_2:*RE*10	$Sr_{0.9}RE_{0.1}F_{2.1}$	5.0	8.5	t_1 2.7 ms q_1 1.174	t_1 3.81 ms q_1 1.013
SrF_2:*RE*20	$Sr_{0.8}RE_{0.2}F_{2.2}$	4.2	10.0	t_1 2.2 ms q_1 1.101	t_1 3.03 ms q_1 1.069
SrF_2:*RE*30	$Sr_{0.7}RE_{0.3}F_{2.3}$	4.2	10.1	t_1 2.2 ms q_1 1.061	t_1 3.43 ms q_1 1.041
SrF_2:*RE*40	$Sr_{0.6}RE_{0.4}F_{2.4}$	3.6	11.7	t_1 2.0 ms q_1 1.026	t_1 2.41 ms q_1 1.092

Table S5. Properties 0.2 M *AE*F_2:Eu10 sols (*AE* = Ca, Sr, Ba) in ethylene glycol (t_1= lifetime, q_1 = asymmetry parameter).

Shortcut	**Sum formula**	**DLS particle diameter (nm)**	**Luminescence lifetime**	**Relative quantum yield**
BaF_2:Eu10_15Al	$Ba_{0.9}Eu_{0.1}F_{2.1}$ +15 mol% Al(O^{i}Pr)$_3$	28.2 nm	t_1 2.87 ms q_1 1.230	
SrF_2:Eu10_15Al	$Sr_{0.9}Eu_{0.1}F_{2.1}$ +15 mol% Al(O^{i}Pr)$_3$	6.5 nm	t_1 2.38 ms q_1 1.289	
CaF_2:Eu10_15Al	$Ca_{0.9}Eu_{0.1}F_{2.1}$ +15 mol% Al(O^{i}Pr)$_3$	4.6 nm	t_1 1.95 ms $q_1$1.300	
BaF_2:Eu10_5BA	$Ba_{0.9}Eu_{0.1}F_{2.1}$ +5 mol% BA	15.7 nm	t_1 3.28 ms q_1 1.021	34.6%
SrF_2:Eu10_5BA	$Sr_{0.9}Eu_{0.1}F_{2.1}$ +5 mol% BA	4.8 nm	t_1 2.80 ms q_1 1.150	29.8%
CaF_2:Eu10_5BA	$Ca_{0.9}Eu_{0.1}F_{2.1}$ +5 mol% BA	3.6 nm	t_1 2.12 ms q_1 1.300	29.4%

Table S6. Properties of 0.2 M $Ca_{1-x}Sr_xF_2$:Eu10 and $Ca_{1-x}Sr_xF_2$:Tb10 sols in ethylene glycol ($0 \leq x \leq 1$). (λ_{ex}(Eu) = 393 nm, λ_{ex}(Tb) = 350 nm, t_1= lifetime and q_1 = asymmetry parameter).

Shortcut RE = Eu, Tb	**Sum formula** RE = Eu, Tb	χ_C	**DLS particle diameter (nm)**		**Luminescence lifetime t_1 (ms)**		**Relative quantum yield**	
			RE = Eu	RE = Tb	RE = Eu	RE = Tb	RE = Eu	RE = Tb
SrF_2:$RE$10	$Sr_{0.9}RE_{0.1}F_{2.1}$	0.000	7.5	6.5	t_1 2.24 q_1 1.157	t_1 3.66 q_1 1.059	27.3%	79.2%
$Ca_{0.1}Sr_{0.9}F_2$:$RE$10	$Ca_{0.05}Sr_{0.85}RE_{0.1}F_{2.1}$	0.056	7.5	6.5	t_1 2.21 q_1 1.160	t_1 3.64 q_1 1.064		
$Ca_{0.25}Sr_{0.75}F_2$:$RE$10	$Ca_{0.20}Sr_{0.70}RE_{0.1}F_{2.1}$	0.222	7.5	4.8	t_1 2.18 q_1 1.178	t_1 3.59 q_1 1.065	26.9%	
$Ca_{0.33}Sr_{0.67}F_2$:$RE$10	$Ca_{0.28}Sr_{0.62}RE_{0.1}F_{2.1}$	0.311	5.6	4.1	t_1 2.12 q_1 1.189	t_1 3.57 q_1 1.061		
$Ca_{0.5}Sr_{0.5}F_2$:$RE$10	$Ca_{0.45}Sr_{0.45}RE_{0.1}F_{2.1}$	0.500	5.6	3.6	t_1 2.08 q_1 1.191	t_1 3.54 q_1 1.069		
$Ca_{0.67}Sr_{0.33}F_2$:$RE$10	$Ca_{0.62}Sr_{0.28}RE_{0.1}F_{2.1}$	0.689	4.2	3.1	t_1 2.01 q_1 1.206	t_1 3.48 q_1 1.073		
$Ca_{0.75}Sr_{0.25}F_2$:$RE$10	$Ca_{0.70}Sr_{0.20}RE_{0.1}F_{2.1}$	0.778	3.6	2.6	t_1 1.92 q_1 1.218	t_1 3.45 q_1 1.078		
$Ca_{0.9}Sr_{0.1}F_2$:$RE$10	$Ca_{0.85}Sr_{0.05}RE_{0.1}F_{2.1}$	0.944	2.4	2.6	t_1 1.70 q_1 1.189	t_1 3.29 q_1 1.083		
CaF_2:$RE$10	$Ca_{0.9}RE_{0.1}F_{2.1}$	1.000	2.4	2.6	t_1 1.64 q_1 1.261	t_1 3.20 q_1 1.086	24.7%	76.5%