

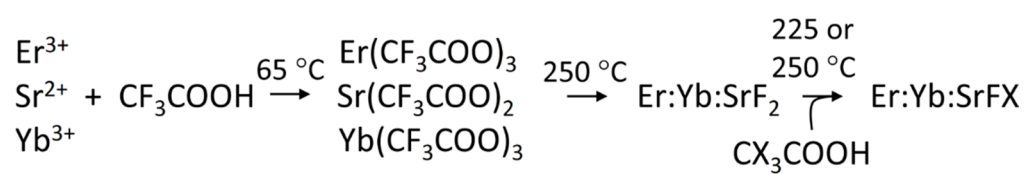
Supporting Information

Multicolor Emission in Chemically and Structurally Tunable

Er:Yb:SrFX (X = Cl, Br) Upconverting Nanocrystals

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Scheme S1. Two-step approach to the synthesis of colloidal Er:Yb:SrFX (X = Cl, Br) nanocrystals.

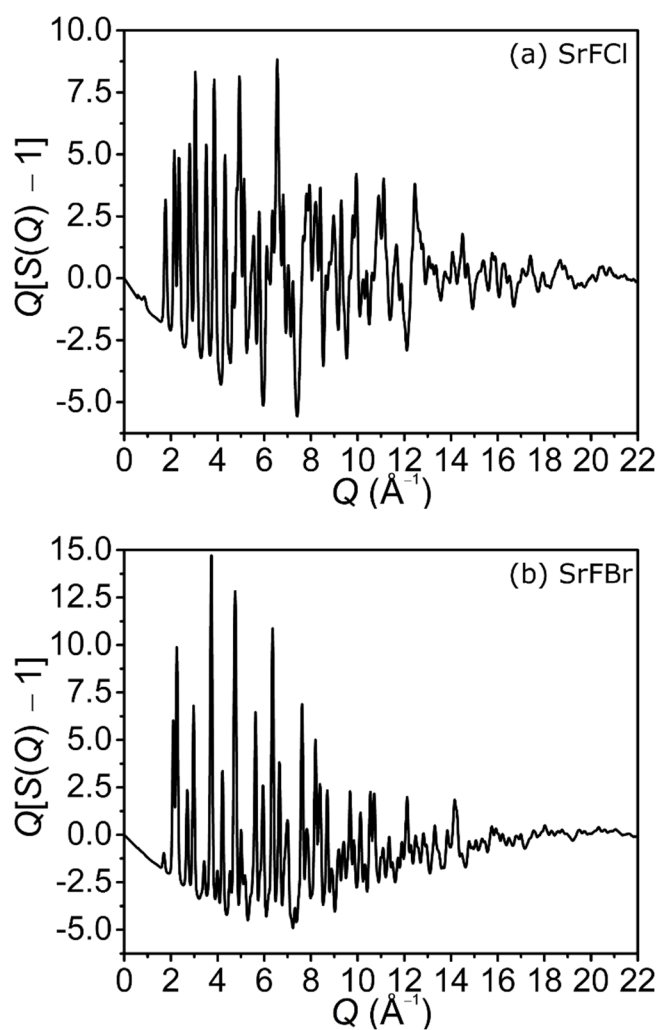


Figure S1. Structure functions $S(Q)$ of Er:Yb:SrFCl (nominal total rare-earth concentration: 6.67 mol. %) and Er:Yb:SrFBr nanocrystals (nominal total rare-earth concentration: 16.7 mol. %) synthesized at 250 °C.

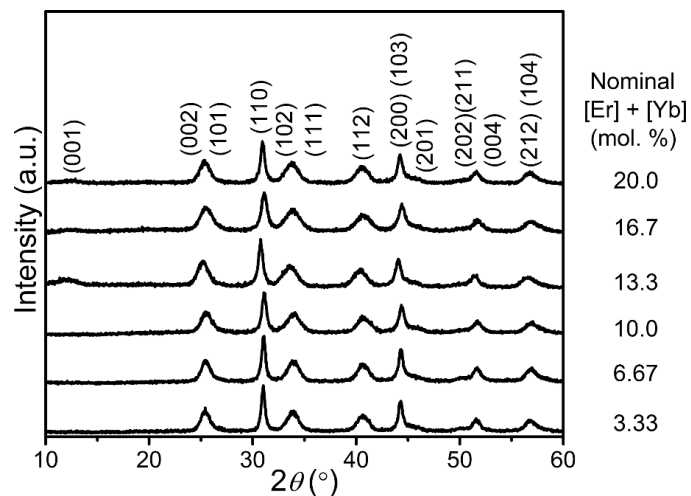


Figure S2. PXRD patterns of Er:Yb:SrFCl nanocrystals synthesized at 225 °C. Nominal total rare-earth concentrations are indicated.

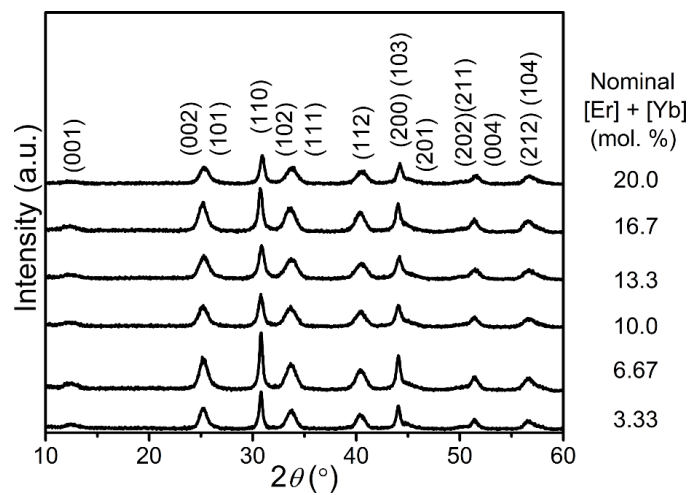


Figure S3. PXRD patterns of Er:Yb:SrFCl nanocrystals synthesized at 250 °C. Nominal total rare-earth concentrations are indicated.

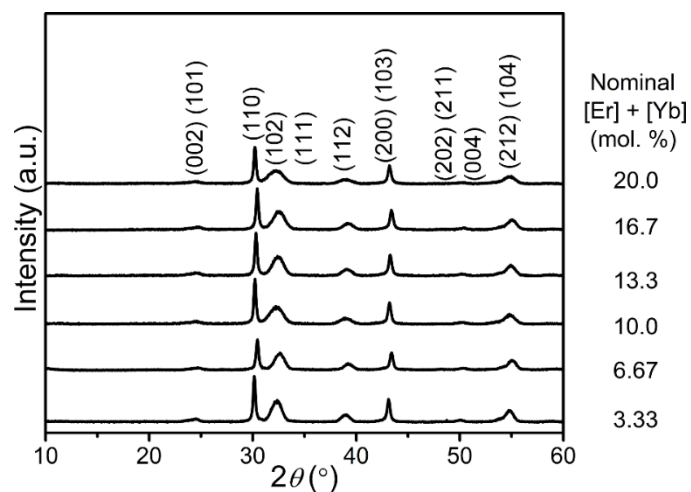


Figure S4. PXRD patterns of Er:Yb:SrFBr nanocrystals synthesized at 225 °C. Nominal total rare-earth concentrations are indicated.

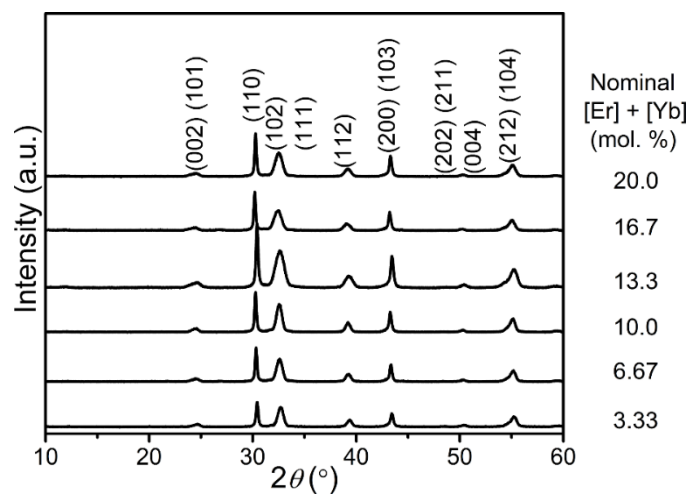


Figure S5. PXRD patterns of Er:Yb:SrFBr nanocrystals synthesized at 250 °C. Nominal total rare-earth concentrations are indicated.

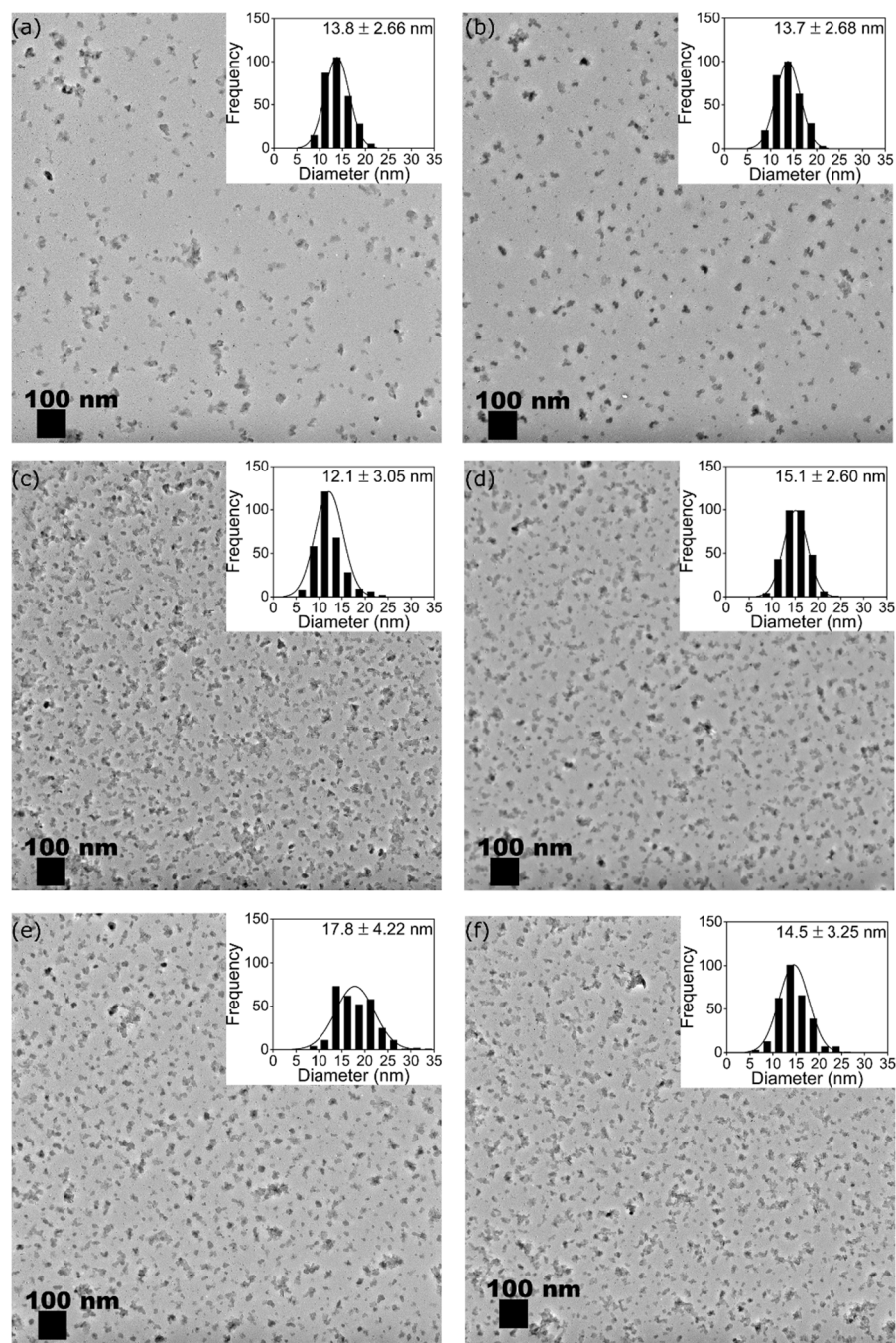


Figure S6. TEM images of Er:Yb:SrFCl nanocrystals synthesized at 225 °C with nominal total rare-earth concentrations 3.33 (a), 6.67 (b), 10.0 (c), 13.3 (d), 16.7 (e), and 20.0 mol. % (f).

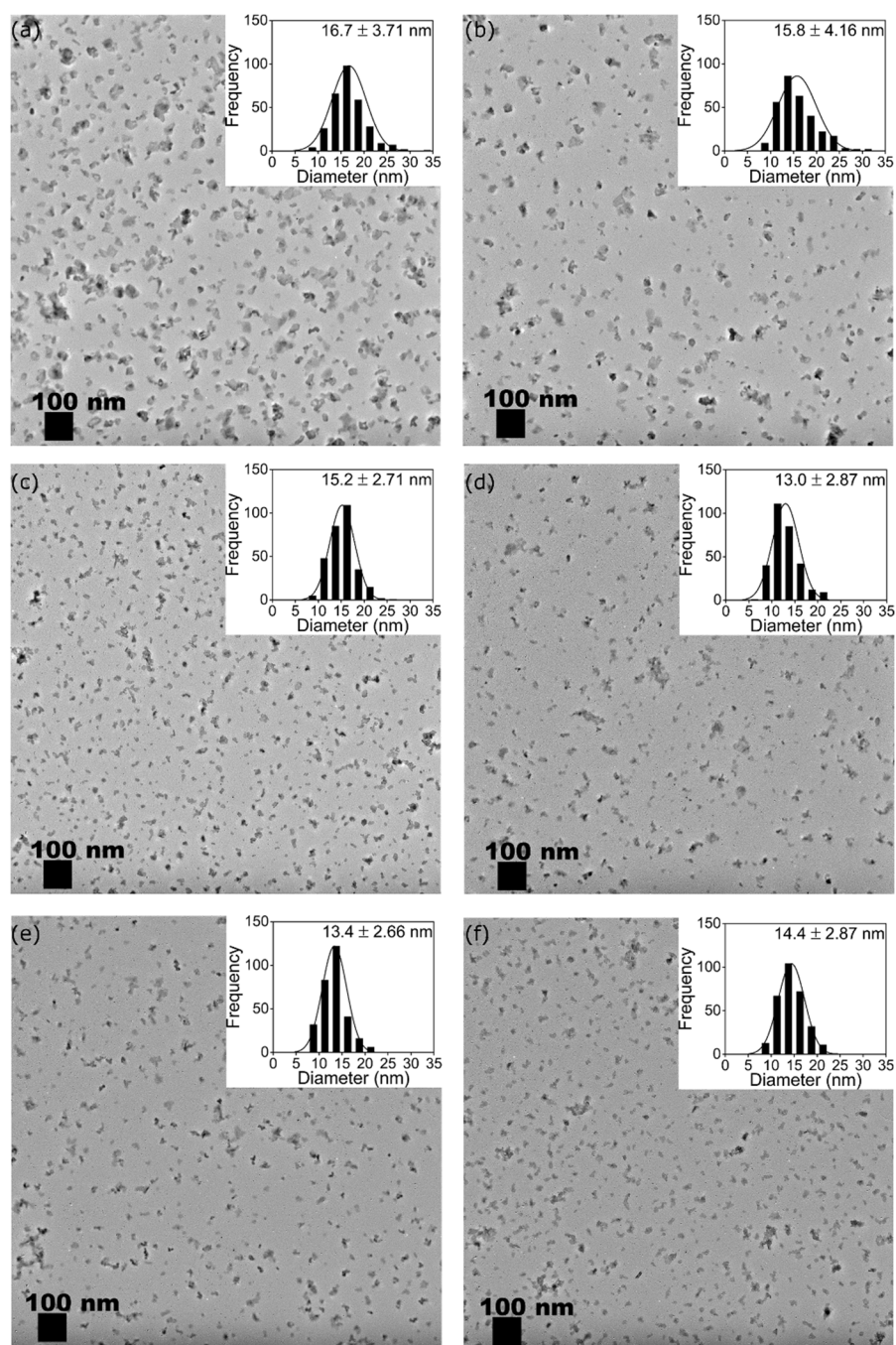


Figure S7. TEM images of Er:Yb:SrFCl nanocrystals synthesized at 250 °C with nominal total rare-earth concentrations 3.33 (a), 6.67 (b), 10.0 (c), 13.3 (d), 16.7 (e), and 20.0 mol. % (f).

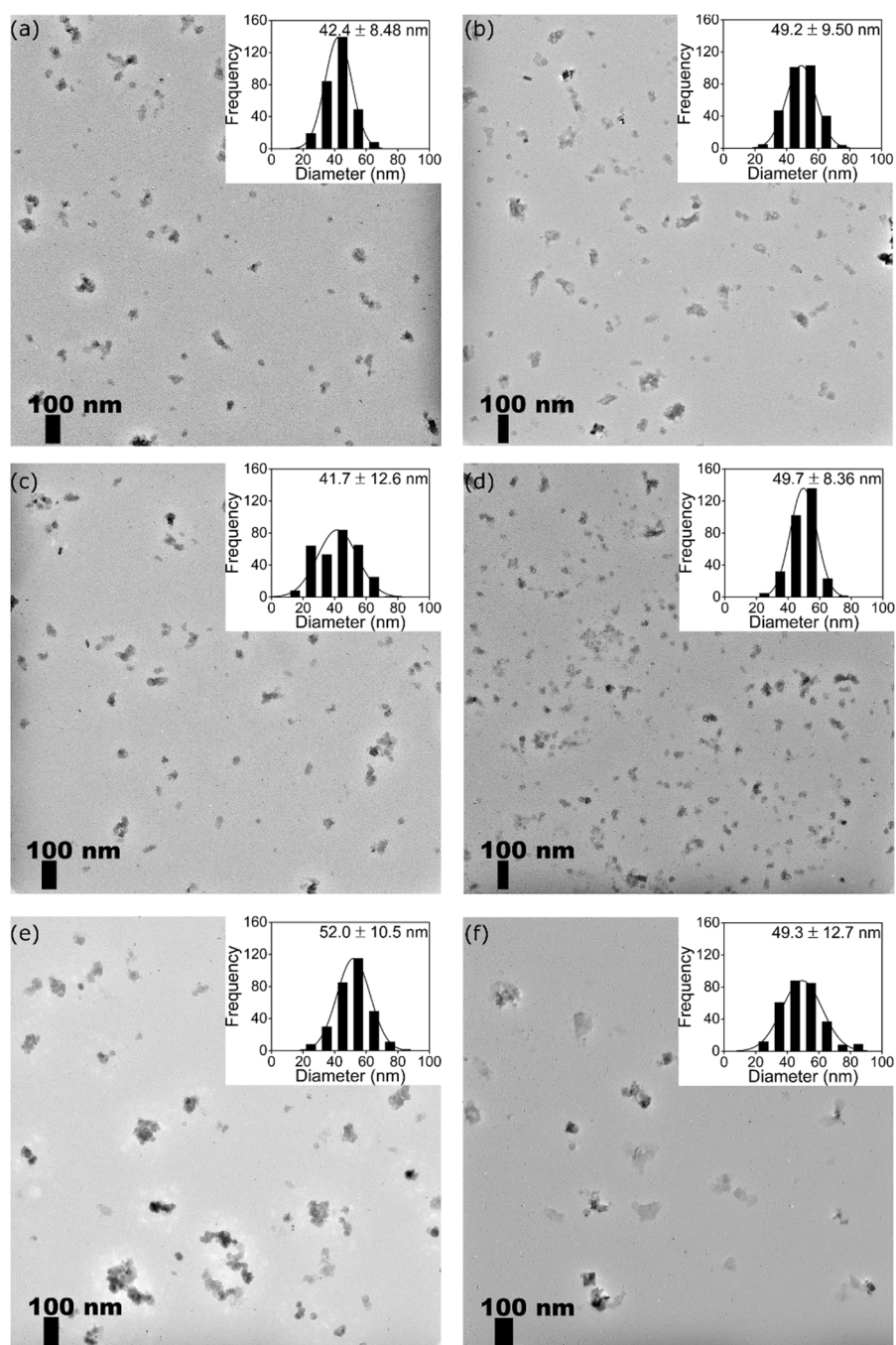


Figure S8. TEM images of Er:Yb:SrFBr nanocrystals synthesized at 225 °C with nominal total rare-earth concentrations 3.33 (a), 6.67 (b), 10.0 (c), 13.3 (d), 16.7 (e), and 20.0 mol. % (f).

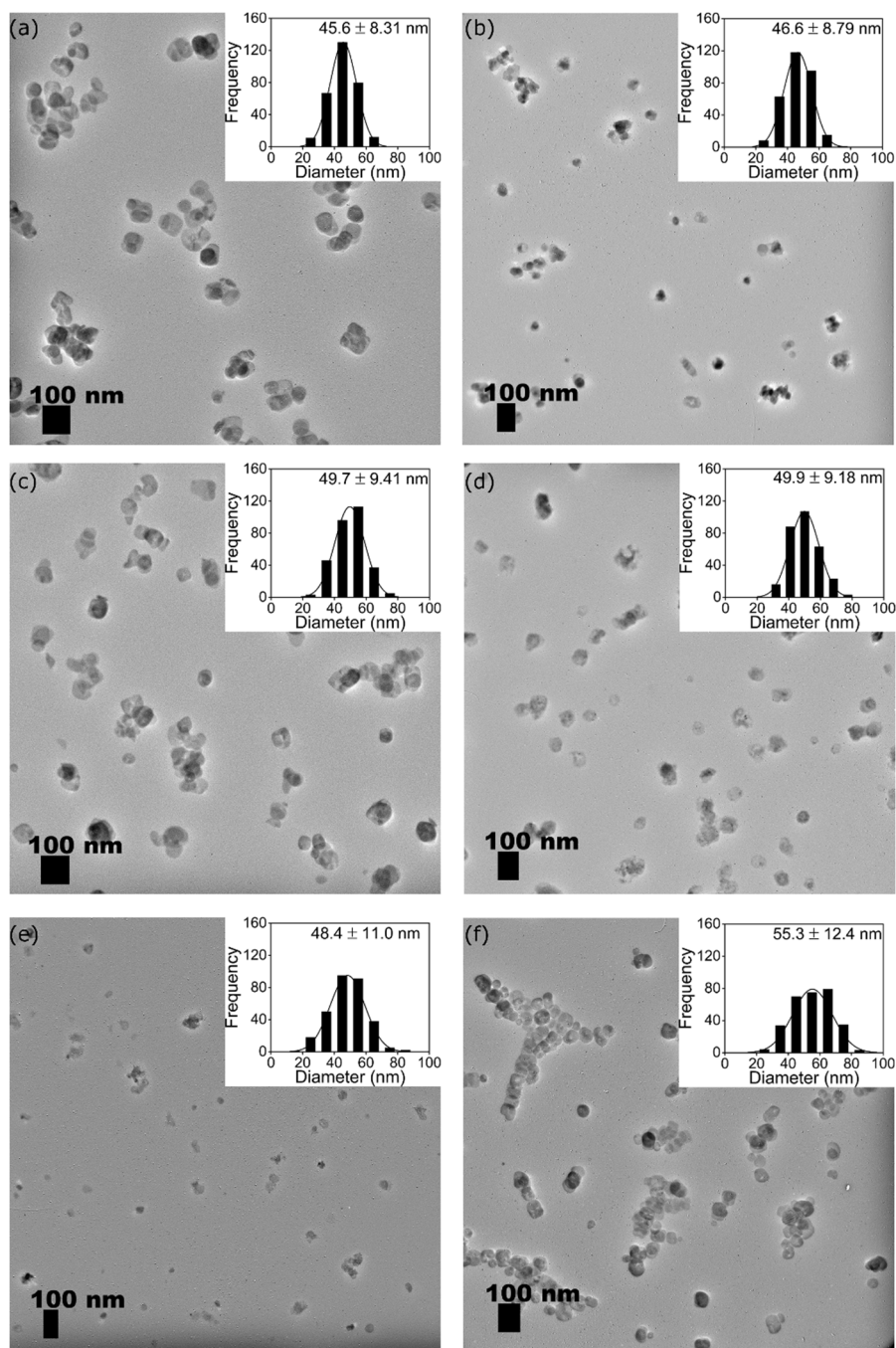


Figure S9. TEM images of Er:Yb:SrFBr nanocrystals synthesized at 250 °C with nominal total rare-earth concentrations 3.33 (a), 6.67 (b), 10.0 (c), 13.3 (d), 16.7 (e), and 20.0 mol. % (f).

Table S1. Size Distributions of Er:Yb:SrFX Nanocrystals

Er:Yb:SrFCl				
Nominal [Er] + [Yb] (mol. %)	225 °C		250 °C	
	Mean Size (nm)	Polydispersity (%)	Mean Size (nm)	Polydispersity (%)
3.33	13.8 ± 2.66	19	16.7 ± 3.71	22
6.67	13.7 ± 2.68	20	15.8 ± 4.16	26
10.0	12.1 ± 3.05	25	15.2 ± 2.71	18
13.3	15.1 ± 2.60	17	13.0 ± 2.87	22
16.7	17.8 ± 4.22	24	13.4 ± 2.66	20
20.0	14.5 ± 3.25	22	14.4 ± 2.87	20

Er:Yb:SrFBr				
Nominal [Er] + [Yb] (mol. %)	225 °C		250 °C	
	Mean Size (nm)	Polydispersity (%)	Mean Size (nm)	Polydispersity (%)
3.33	42.4 ± 8.48	20	45.6 ± 8.31	18
6.67	49.2 ± 9.50	19	46.6 ± 8.79	19
10.0	41.7 ± 12.6	30	49.7 ± 9.41	19
13.3	49.7 ± 8.36	17	49.9 ± 9.18	18
16.7	52.0 ± 10.5	20	48.4 ± 11.0	23
20.0	49.3 ± 12.7	26	55.3 ± 12.4	22

Table S2. ICP–MS Elemental Analyses of Er:Yb:SrFX Nanocrystals

Er:Yb:SrFCl							
Nominal		Experimental					
		225 °C			250 °C		
[Er] + [Yb] (mol. %)	[Yb] / [Er]	[Er] + [Yb] (mol. %)	[Yb] / [Er]	[Er] / ([Er] + [Yb])	[Er] + [Yb] (mol. %)	[Yb] / [Er]	[Er] / ([Er] + [Yb])
3.33	9.0	2.74	8.4	0.11	2.30	8.8	0.10
6.67	9.0	3.14	8.6	0.10	3.67	8.5	0.11
10.0	9.0	4.57	7.8	0.11	4.25	8.6	0.10
13.3	9.0	5.01	7.5	0.12	4.88	8.3	0.11
16.7	9.0	5.05	8.0	0.11	4.85	8.0	0.11
20.0	9.0	5.05	8.2	0.11	5.02	8.6	0.10

Er:Yb:SrFBr							
Nominal		Experimental					
		225 °C			250 °C		
[Er] + [Yb] (mol. %)	[Yb] / [Er]	[Er] + [Yb] (mol. %)	[Yb] / [Er]	[Er] / ([Er] + [Yb])	[Er] + [Yb] (mol. %)	[Yb] / [Er]	[Er] / ([Er] + [Yb])
3.33	9.0	0.161	3.4	0.23	0.135	2.7	0.27
6.67	9.0	0.252	3.9	0.20	0.200	3.0	0.25
10.0	9.0	0.352	3.3	0.23	0.277	4.2	0.19
13.3	9.0	0.372	3.0	0.25	0.323	3.1	0.24
16.7	9.0	0.456	3.0	0.25	0.345	3.7	0.21
20.0	9.0	0.455	2.7	0.27	0.358	3.5	0.22

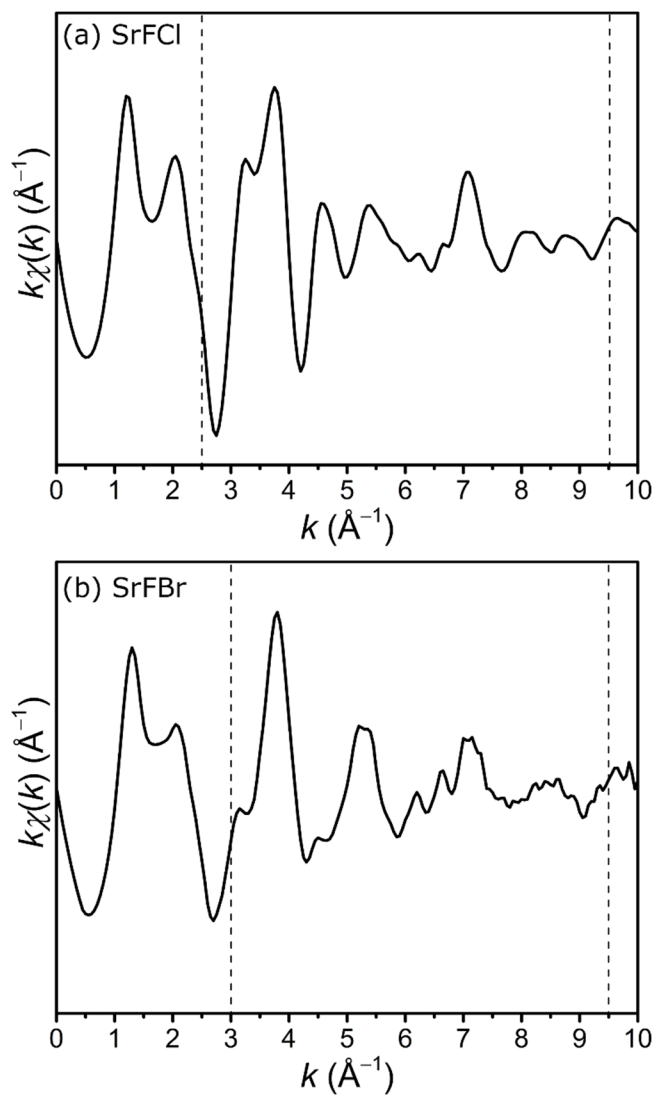


Figure S10. k^1 -weighted $\chi(k)$ functions of Er:Yb:SrFCl (nominal total rare-earth concentration: 6.67 mol. %) and Er:Yb:SrFBr nanocrystals (nominal total rare-earth concentration: 16.7 mol. %) synthesized at 250 °C. k ranges for the Fourier transform are indicated with vertical dashed lines.

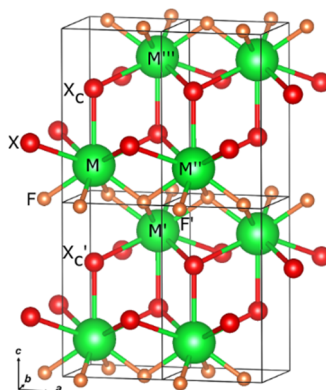


Figure S11. Crystal structure of alkaline-earth fluorohalides MFX (M = Ca, Sr, Ba; X = Cl, Br, I) as a function of their chemical composition. M (green), F (orange), X (red), and X_c atoms defining the MF₄X₅ polyhedron are labeled, as well as other atoms considered in EXAFS analyses.

Table S3. Structural Parameters from EXAFS Analyses

	Er:Yb:SrFCl		Er:Yb:SrFBr	
S_0^2		1.2(2)		1.27(13)
ΔE_0 (eV)		1(1)		1.1(4)
zSr		0.204(5)		0.184(1)
zX		0.639(13)		0.648(5)
$\sigma_{\text{Sr}'}^2$ (Å ²) ^a	$N^b = 4$	0.014	$N = 4$	0.005
$\sigma_{\text{Sr}''}^2$ (Å ²)	$N = 4$	0.010(4)	$N = 4$	0.003(2)
σ_{F}^2 (Å ²)	$N = 4$	0.014(5)	$N = 4$	0.012(2)
$\sigma_{\text{F}'}^2$ (Å ²)	$N = 8$	0.007(6)	$N = 8$	0.009(4)
σ_{X}^2 (Å ²)	$N = 4$		$N = 4$	
σ_{Xc}^2 (Å ²)	$N = 1$	0.018(5)	$N = 1$	0.016(3)
$\sigma_{\text{Xc}'}^2$ (Å ²)	$N = 1$		$N = 1$	
Sr–F (Å)		2.506(19)		2.507(4)
Sr–X (Å)		3.12(3)		3.226(14)
Sr–X _c (Å)		3.05(9)		3.43(4)
Sr–X _{c'} (Å)		3.95(9)		3.96(4)
Sr–Sr' (Å)		4.08(5)		4.034(10)
Sr–Sr'' (Å)		4.122		4.212
Sr–F' (Å)		4.824(10)		4.902(2)
Residual (%)		$R = 4.9$		$R = 1.8$

^a $\sigma_{\text{Sr}'}^2 = 1.5 \times \sigma_{\text{Sr}''}^2$

^b N : number of backscatterers.

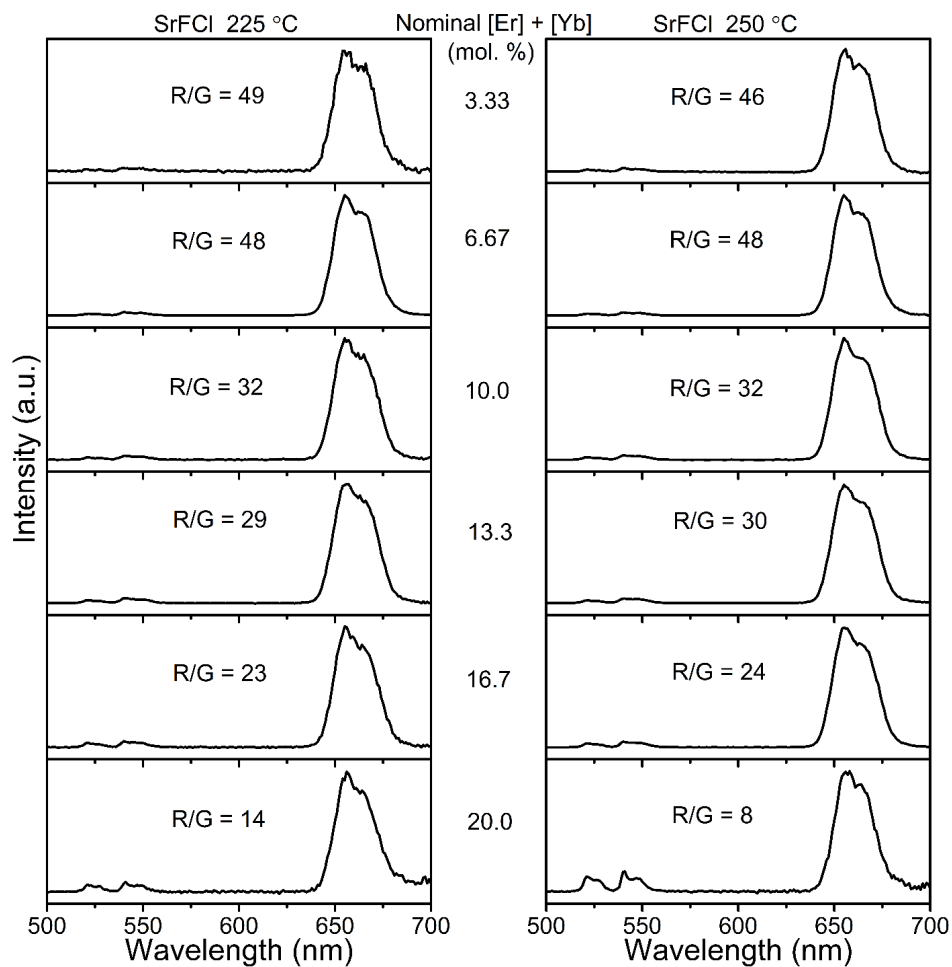


Figure S12. Emission spectra of Er:Yb:SrFCl nanocrystals. Nominal total rare-earth concentrations and red-to-green ratios (R/G) are indicated.

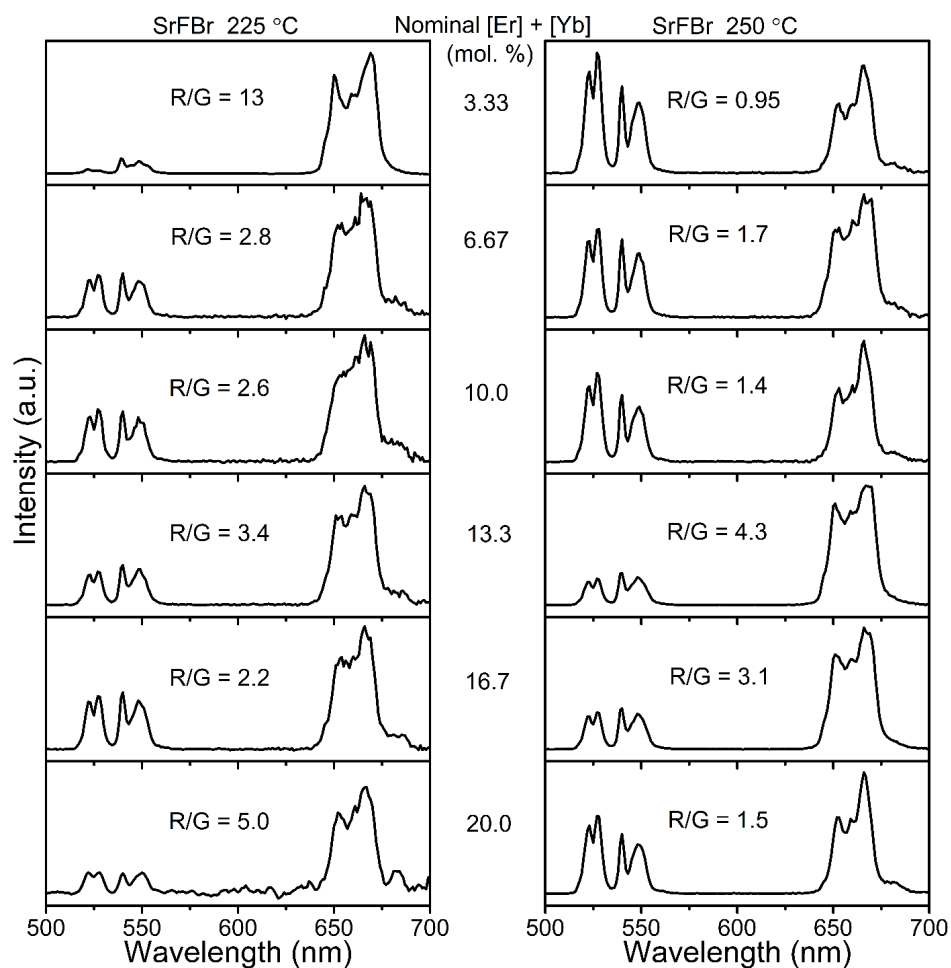


Figure S13. Emission spectra of Er:Yb:SrFBr nanocrystals. Nominal total rare-earth concentrations and red-to-green ratios (R/G) are indicated.

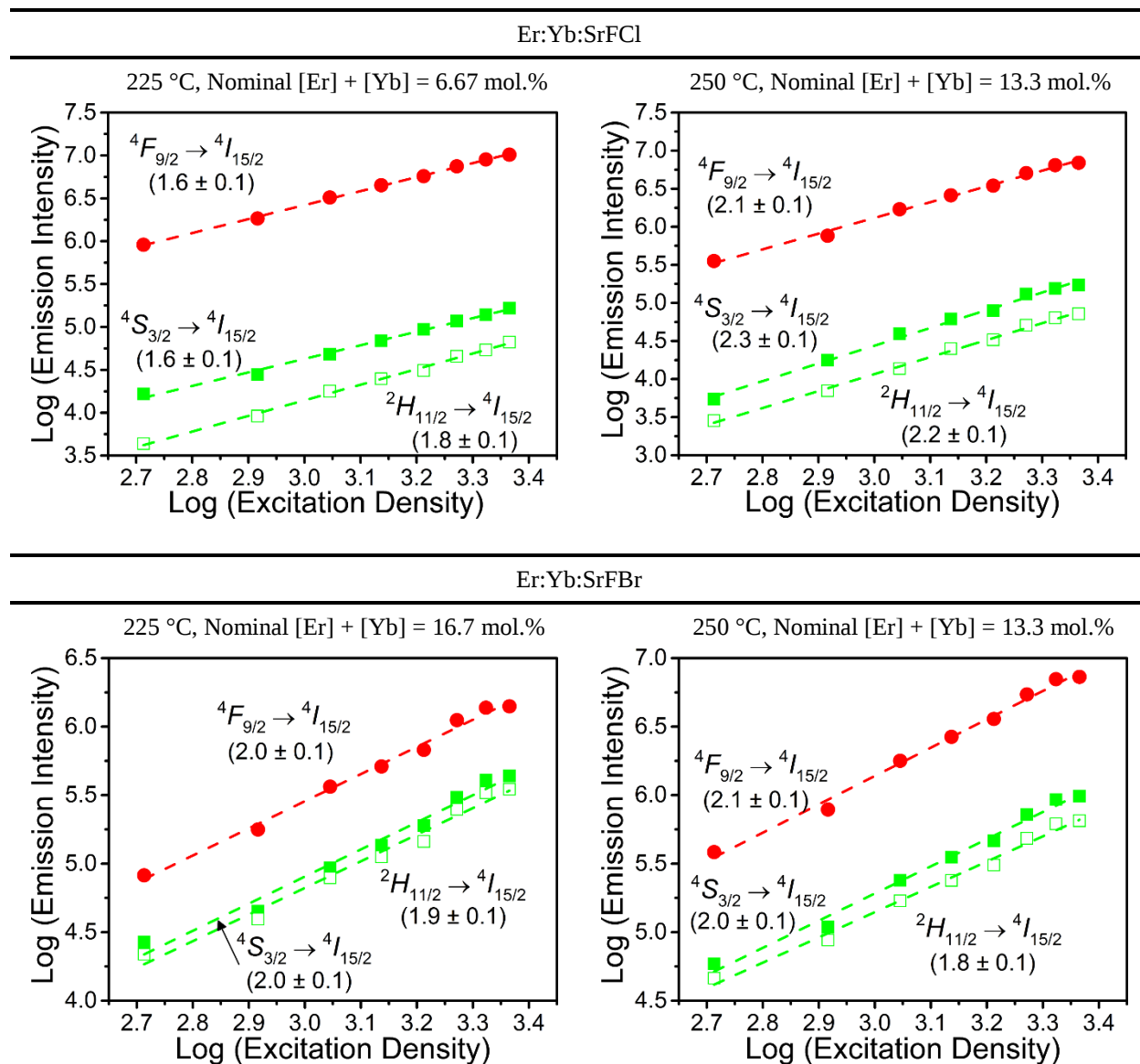


Figure S14. Double logarithmic plots of the integrated emission intensities at 525 ($^2H_{11/2} \rightarrow ^4I_{15/2}$, $\square$), 545 ($^4S_{3/2} \rightarrow ^4I_{15/2}$, $\blacksquare$), and 660 nm ($^4F_{9/2} \rightarrow ^4I_{15/2}$, $\bullet$) as a function of the excitation density for selected Er:Yb:SrFX nanocrystals. Nominal total rare-earth concentrations and reaction temperatures are indicated for each composition. Linear fits are depicted as dashed lines and the corresponding slopes are given.

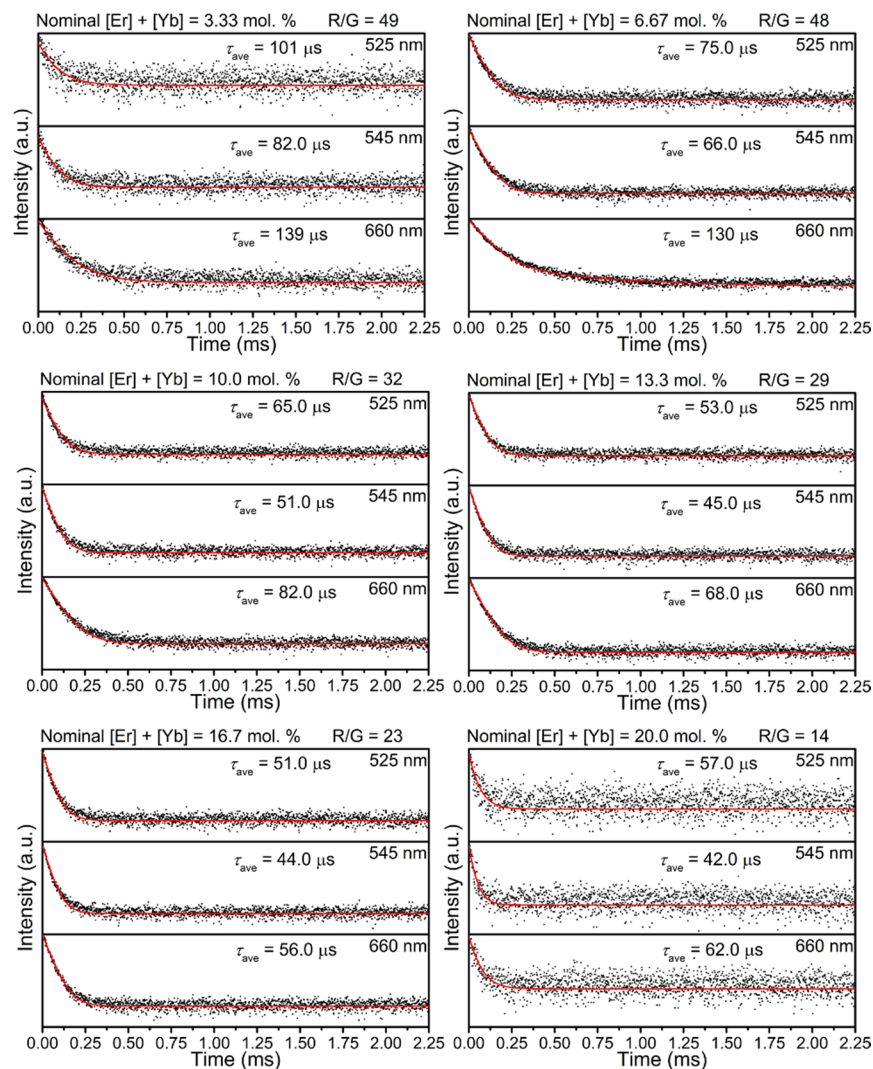


Figure S15. Decay curves of the $^2H_{11/2}$ (525 nm), $^4S_{3/2}$ (545 nm), and $^4I_{15/2}$ (660 nm) excited states of Er^{3+} in Er:Yb:SrFCl nanocrystals synthesized at 225 °C. Nominal total rare-earth concentrations, red-to-green ratios (R/G), and average lifetimes (τ_{ave}) are indicated. Exponential fits are depicted as solid red lines. Plots are shown in logarithmic scale.

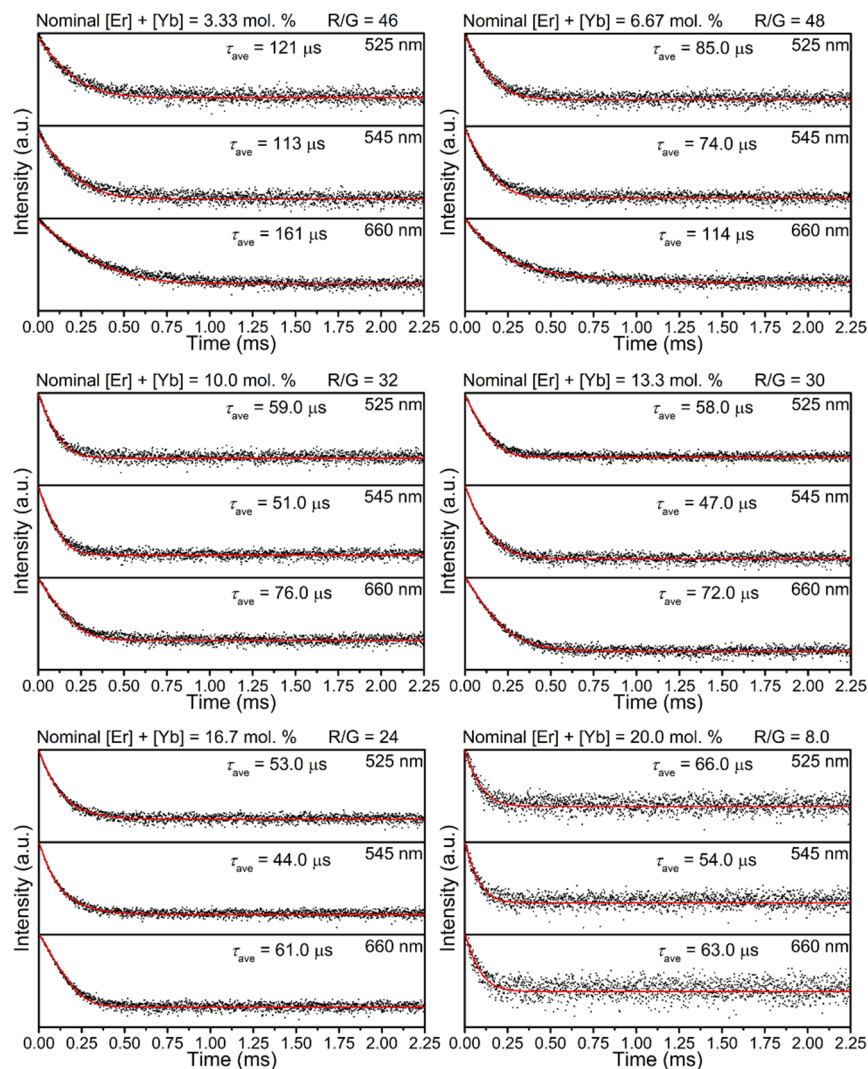


Figure S16. Decay curves of the $^2H_{11/2}$ (525 nm), $^4S_{3/2}$ (545 nm), and $^4I_{15/2}$ (660 nm) excited states of Er^{3+} in Er:Yb:SrFCl nanocrystals synthesized at 250 °C. Nominal total rare-earth concentrations, red-to-green ratios (R/G), and average lifetimes (τ_{ave}) are indicated. Exponential fits are depicted as solid red lines. Plots are shown in logarithmic scale.

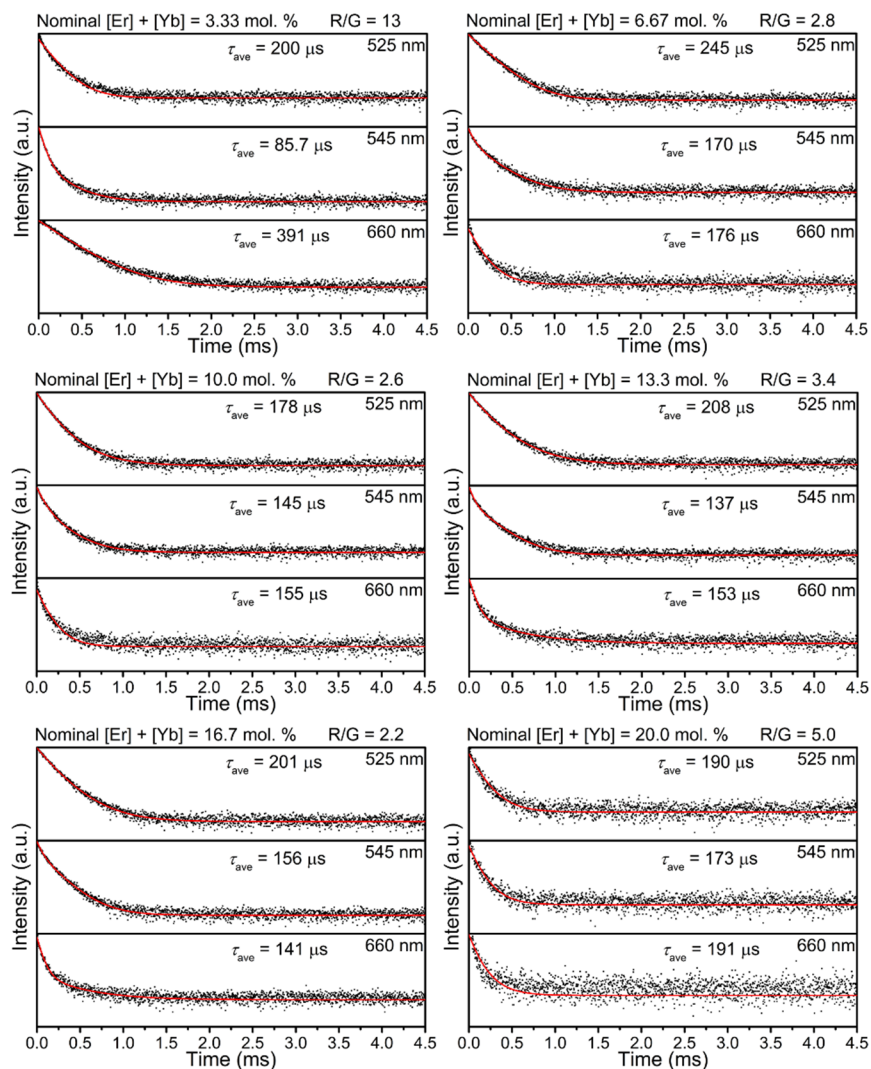


Figure S17. Decay curves of the $^2H_{11/2}$ (525 nm), $^4S_{3/2}$ (545 nm), and $^4I_{15/2}$ (660 nm) excited states of Er^{3+} in Er:Yb:SrFBr nanocrystals synthesized at 225 °C. Nominal total rare-earth concentrations, red-to-green ratios (R/G), and average lifetimes (τ_{ave}) are indicated. Exponential fits are depicted as solid red lines. Plots are shown in logarithmic scale.

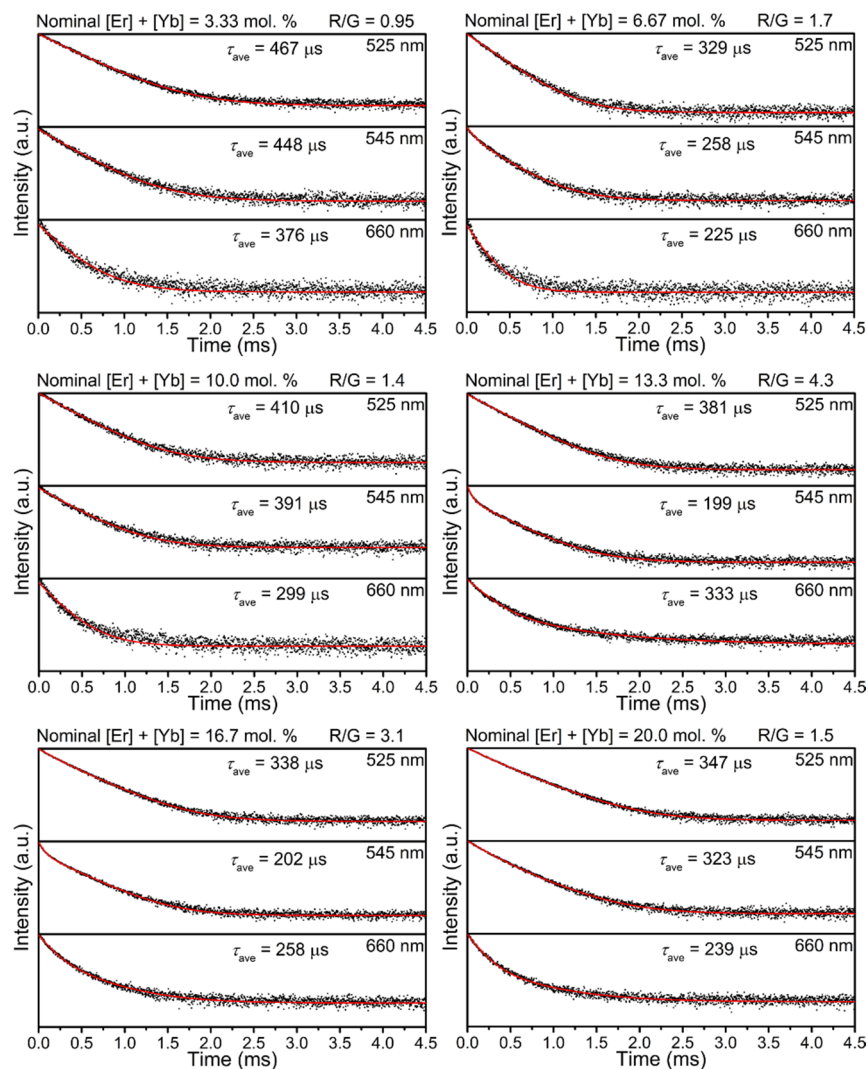


Figure S18. Decay curves of the $^2H_{11/2}$ (525 nm), $^4S_{3/2}$ (545 nm), and $^4I_{15/2}$ (660 nm) excited states of Er^{3+} in Er:Yb:SrFBr nanocrystals synthesized at 250 °C. Nominal total rare-earth concentrations, red-to-green ratios (R/G), and average lifetimes (τ_{ave}) are indicated. Exponential fits are depicted as solid red lines. Plots are shown in logarithmic scale.

Table S4. Red-to-green Ratios (R/G) and Er³⁺ Excited States Average Lifetimes (τ_{average}) in Er:Yb:SrFCl Nanocrystals

Er:Yb:SrFCl – 225 °C						
Er and Yb Concentrations			Photoluminescence			
Nominal	Experimental		R/G	τ_{average} (μs)		
[Er] + [Yb] (mol. %)	[Er] + [Yb] (mol. %)	[Er] / ([Yb] + [Er])		525 nm	545 nm	660 nm
3.33	2.74	0.11	49	101	82	139
6.67	3.14	0.10	48	75	66	130
10.0	4.57	0.11	32	65	51	82
13.3	5.01	0.12	29	53	45	68
16.7	5.05	0.11	23	51	44	56
20.0	5.05	0.11	14	57	42	62

Er:Yb:SrFCl – 250 °C						
Er and Yb Concentrations			Photoluminescence			
Nominal	Experimental		R/G	τ_{average} (μs)		
[Er] + [Yb] (mol. %)	[Er] + [Yb] (mol. %)	[Er] / ([Yb] + [Er])		525 nm	545 nm	660 nm
3.33	2.30	0.10	46	121	113	161
6.67	3.67	0.11	48	85	74	114
10.0	4.25	0.10	32	59	51	76
13.3	4.88	0.11	30	58	47	72
16.7	4.85	0.11	24	53	44	61
20.0	5.02	0.10	8	66	54	63

Table S5. Red-to-green Ratios (R/G) and Er³⁺ Excited States Average Lifetimes (τ_{average}) in Er:Yb:SrFBr Nanocrystals

Er:Yb:SrFBr – 225 °C						
Er and Yb Concentrations			Photoluminescence			
Nominal	Experimental		R/G	τ_{average} (μs)		
[Er] + [Yb] (mol. %)	[Er] + [Yb] (mol. %)	[Er] / ([Yb] + [Er])		525 nm	545 nm	660 nm
3.33	0.161	0.23	13	200	86	391
6.67	0.252	0.20	2.8	245	170	176
10.0	0.352	0.23	2.6	178	145	155
13.3	0.372	0.25	3.4	208	137	153
16.7	0.456	0.25	2.2	201	156	141
20.0	0.455	0.27	5.0	190	173	191

Er:Yb:SrFBr – 250 °C						
Er and Yb Concentrations			Photoluminescence			
Nominal	Experimental		R/G	τ_{average} (μs)		
[Er] + [Yb] (mol. %)	[Er] + [Yb] (mol. %)	[Er] / ([Yb] + [Er])		525 nm	545 nm	660 nm
3.33	0.135	0.27	0.95	467	448	376
6.67	0.200	0.25	1.7	329	258	225
10.0	0.277	0.19	1.4	410	391	299
13.3	0.323	0.24	4.3	381	199	333
16.7	0.345	0.21	3.1	338	202	258
20.0	0.358	0.22	1.5	347	323	239