

Supporting Information

Assessing the Reproducibility and Up-Scaling of Er,Yb-doped NaYF₄-based Upconverting Nanoparticles and Control of the Size, Morphology, and Optical Properties

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1. List of the performed synthesis and nomenclature of the samples

Table S1: List of the performed synthesis and nomenclature of the obtained samples

Series Name	Sample composition	Reaction time and temperature	Solvent composition	Variable parameter	Sample name
Reproducibility	NaYF ₄ : 20 % Yb ³⁺ , 2 % Er ³⁺	30 min (325°C)	40 ml OA : 80 ml ODE	–	STD 1 – STD 10
Robustness	NaYF ₄ : 20 % Yb ³⁺ , 2 % Er ³⁺	30 min (325°C), 60 min (325°C), 30 min (335°C)	40 ml OA : 80 ml ODE	Temperature Time	STD 1 STD 1_60min STD 1_335°C
Scale up	NaYF ₄ : 20 % Yb ³⁺ , 2 % Er ³⁺	30 min (325°C)	20 ml OA: 40 ml ODE 40 ml OA : 80 ml ODE 80 ml OA : 160 ml ODE 200 ml OA : 400 ml ODE	Batch size 0.5x 1x 2x 5x	STD 1_0.5x STD 1 STD 1_2x STD 1_5x
Solvent influence	NaYF ₄ : 20 % Yb ³⁺ , 2 % Er ³⁺	60 min (325°C)	50 ml OA : 70 ml ODE 40 ml OA : 80 ml ODE 30 ml OA : 90 ml ODE 20 ml OA: 100 ml ODE	Ratio OA : ODE 5:7 4:8 3:9 2:10	OA-50 OA-40 (STD 1_60 min) OA-30 OA-20
Dopant influence	NaYF ₄ : x % Yb ³⁺ , 2 % Er ³⁺ (x = 20, 40, 60, 70) NaYbF ₄ : 2 % Er ³⁺	30 min (325°C)	40 ml OA: 80 ml ODE	Yb³⁺ concentration 20 mol% 40 mol% 60 mol% 70 mol% 98 mol%	Yb-20 (STD 1) Yb-40 Yb-60 Yb-70 Yb-98
Precursor concentration influence	NaYF ₄ : 20 % Yb ³⁺ , 2 % Er ³⁺	60 min (325°C), 90 min (325°C)	40 ml OA : 80 ml ODE	Precursor concentration 5 mmol 10 mmol 15 mmol (t=60 min) 15 mmol (t=90 min)	Conc-5 (STD 1_60 min) Conc-10 Conc-15 Conc-15_90min

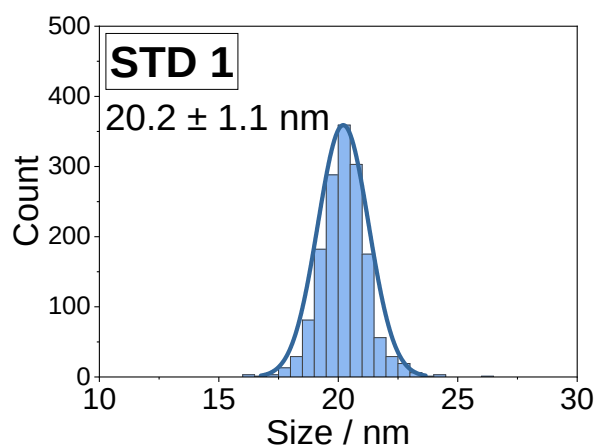
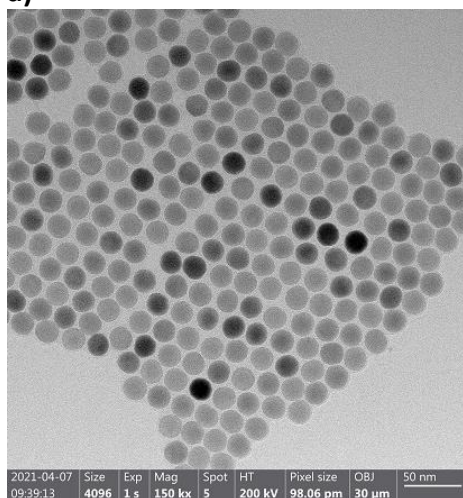
2. Overview of the reactant amounts

Table S2: Overview of the reactant amounts used during the synthesis

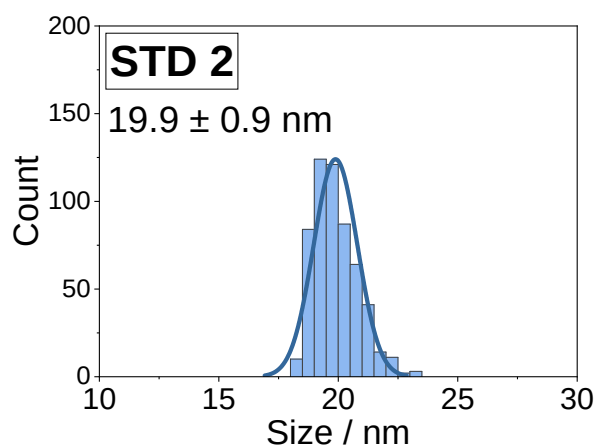
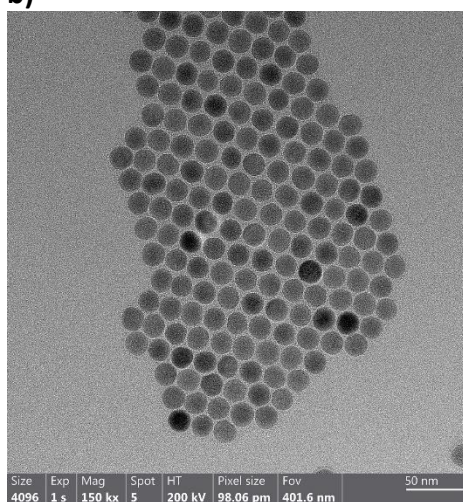
	YCl₃·6H₂O	YbCl₃·6H₂O	ErCl₃·6H₂O	NaOH	NH₄F	Oleic acid	Octadecene
	mg (mmol)	mg (mmol)	mg (mmol)	mg (mmol)	mg (mmol)	mL	mL
STD 1 – STD 10	1183.3 mg (3.90 mmol)	391.7 mg (1.01 mmol)	39.90 mg (0.10 mmol)	519.1 mg (12.98 mmol)	742.4 mg (20.04 mmol)	40	80
STD 1_60min	1183.3 mg (3.90 mmol)	391.7 mg (1.01 mmol)	39.90 mg (0.10 mmol)	519.1 mg (12.98 mmol)	742.4 mg (20.04 mmol)	40	80
STD 1_335°C	1183.5mg (3.90mmol)	387.4 mg (1 mmol)	38.2mg (0.1 mmol)	511 mg (12.78 mmol)	740.8 mg (20 mmol)	40	80
STD 1_0.5x	591.75 mg (1.95 mmol)	193.8 mg (0.5 mmol)	16.0 mg (0.05 mmol)	259.3 mg (6.48 mmol)	370.3 mg (10.01 mmol)	20	40
STD 1_2x	2366.21mg (7.80mmol)	774.98 mg (2 mmol)	76.34 mg (0.20 mmol)	1000 mg (25 mmol)	1481 mg (39.98 mmol)	80	160
STD 1_5x	5920.2 mg (19.52 mmol)	1939.6 mg (5.01 mmol)	192.1 mg (0.50 mmol)	2527.1 mg (63.18 mmol)	3704.0 mg (100 mmol)	200	390
OA-50	1182.1 mg (3.90 mmol)	387.1mg (1 mmol)	38.5 mg (0.10 mmol)	512 mg (12.8 mmol)	740 mg (19.98 mmol)	50	70
OA-30	1183.1 mg (3.90 mmol)	387.49mg (1 mmol)	38.17 mg (0.10 mmol)	518.7 mg (12.97 mmol)	741.4 mg (20.02 mmol)	30	90
OA-20	1183.4 mg (3.90 mmol)	487.7mg (1.26 mmol)	38.4 mg (0.10 mmol)	518.7 mg (12.97 mmol)	740.7 mg (20 mmol)	20	100
Yb-40	439.9 mg (1.45 mmol)	388.4mg (1 mmol)	19.2 mg (0.05 mmol)	258.4 mg (6.46 mmol)	387 mg (10.21 mmol)	20	40
Yb-60	576.4 mg (1.90 mmol)	1162.8mg (3 mmol)	38.2 mg (0.10 mmol)	515 mg (12.88 mmol)	741.4 mg (20.02 mmol)	40	80
Yb-70	84.9 mg (0.28 mmol)	271.6 mg (0.70 mmol)	7.63 mg (0.20 mmol)	101.60 mg (2.54 mmol)	148.20 mg (4 mmol)	6	15
Yb-98	- -	1905.6 mg (4.92 mmol)	39.7 mg (0.10 mmol)	508.4 mg (12.71 mmol)	746.4 mg (20.15 mmol)	40	80
Conc-10	2370.3 mg (7.81 mmol)	779.3 mg (2.01 mmol)	78.0 mg (0.20 mmol)	1037.0 mg (25.93 mmol)	1483.0 mg (40.04 mmol)	40	80
Conc-15	3577.4 mg (11.79 mmol)	1189.7 mg (3.07 mmol)	119.3 mg (0.31 mmol)	1548.3 mg (38.71 mmol)	2222.0 mg (59.99 mmol)	40	80
Conc-15_90min	3569.8 mg (11.77 mmol)	1228.6 mg (3.17 mmol)	120.1 mg (0.31 mmol)	1535.2 mg (38.38 mmol)	2227.6 mg (60.14 mmol)	40	80

3. TEM images and histograms of all samples

a)



b)



c)

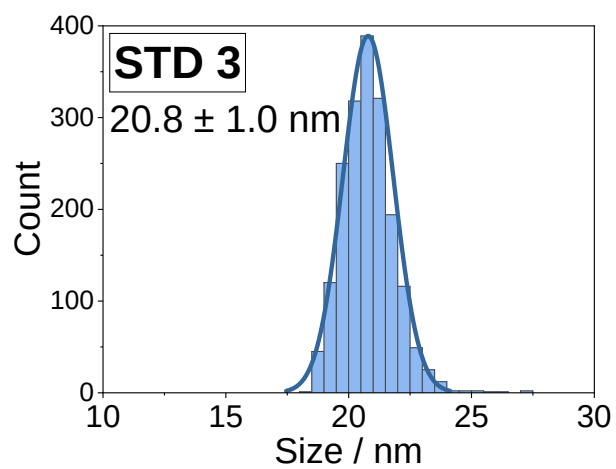
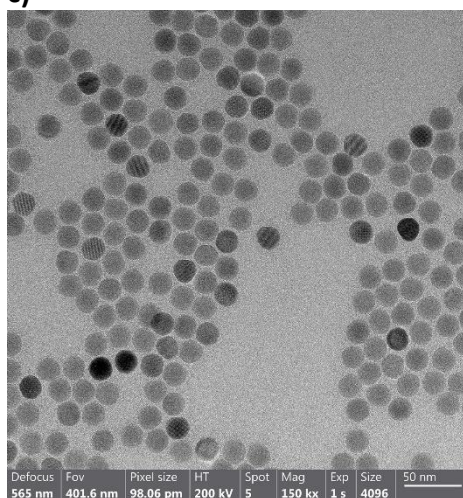
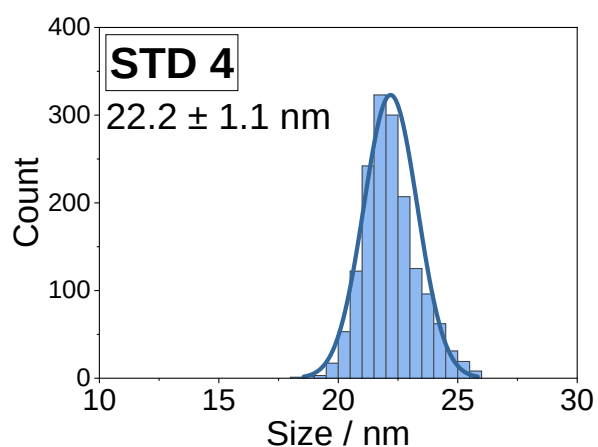
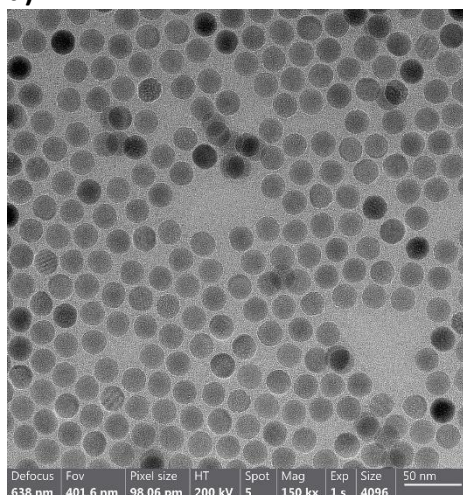
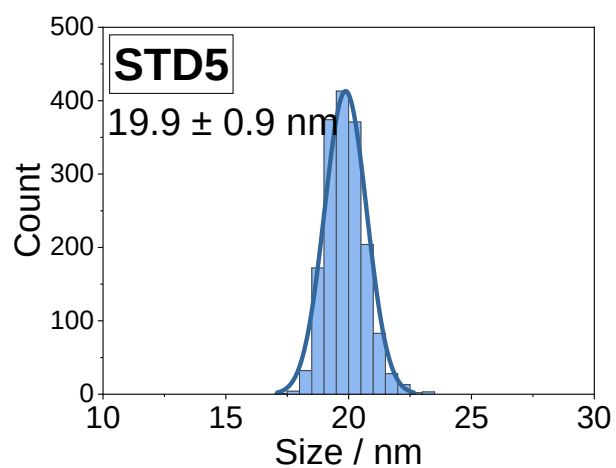
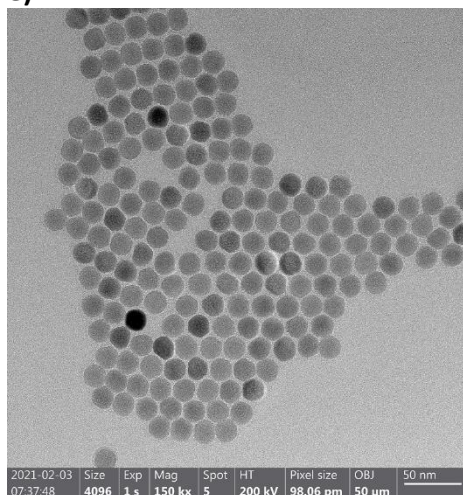


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d)



e)



f)

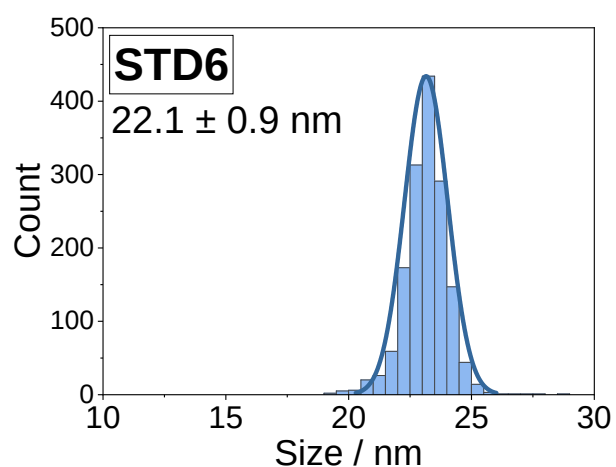
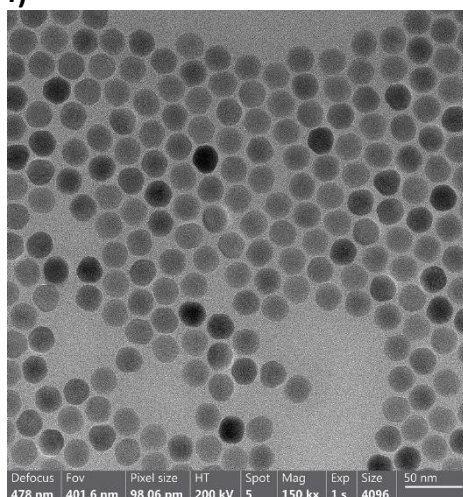
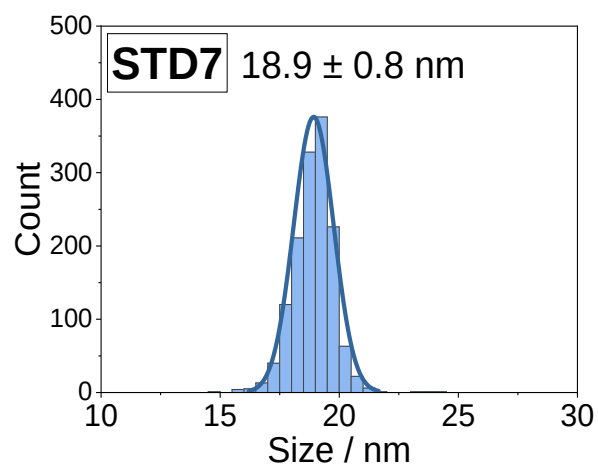
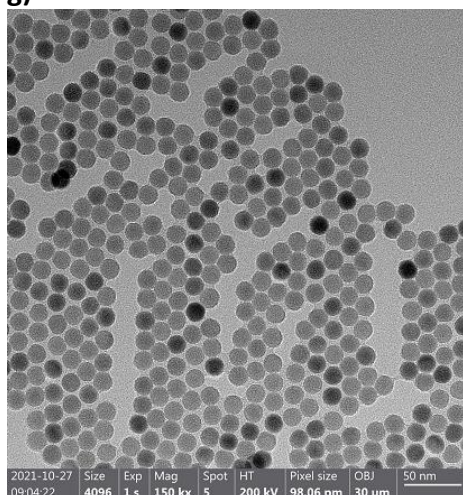
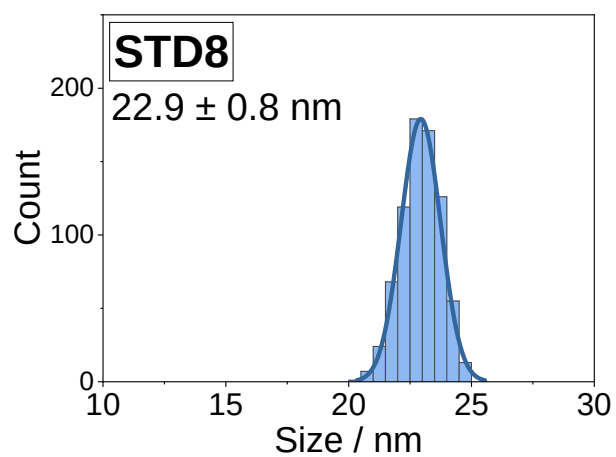
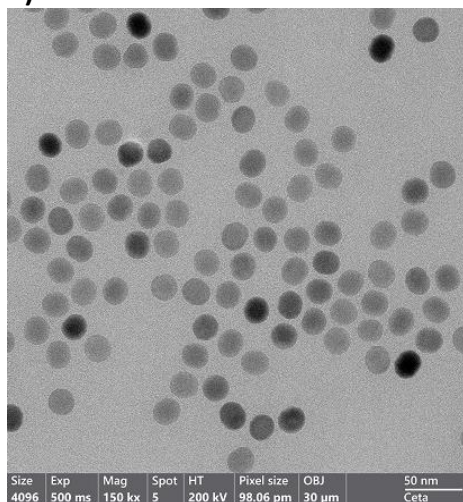


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g)



h)



i)

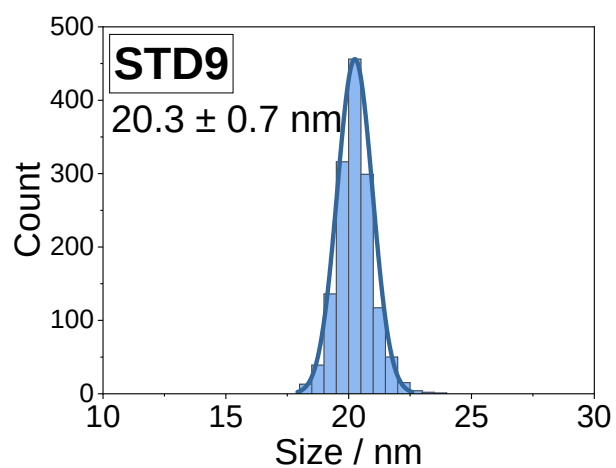
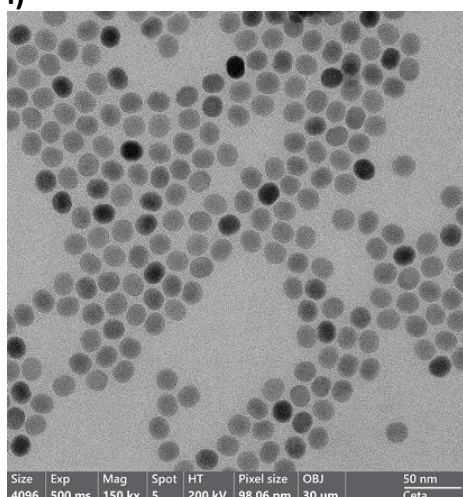
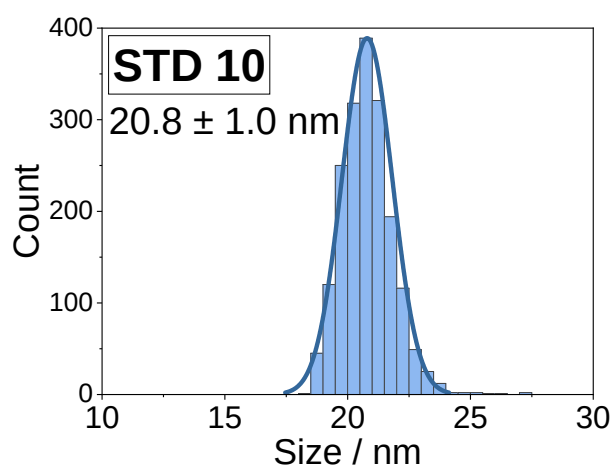
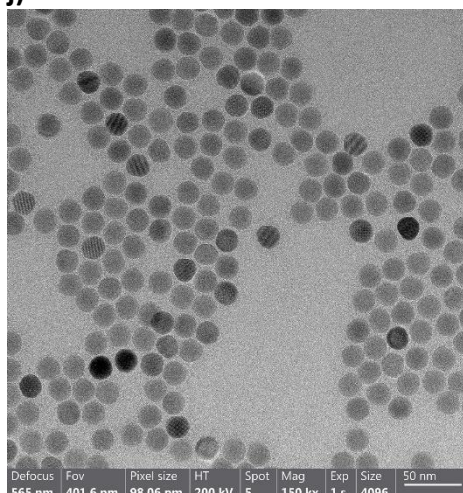
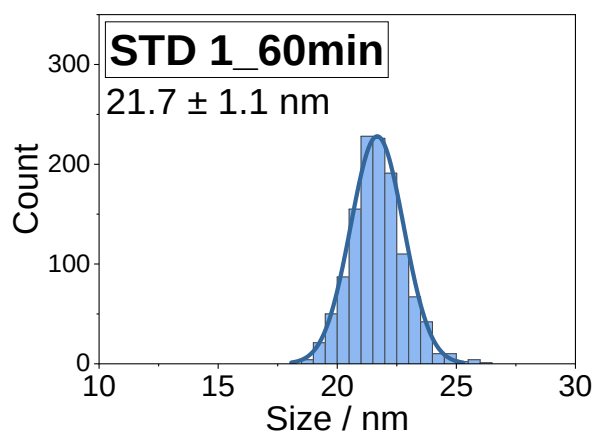
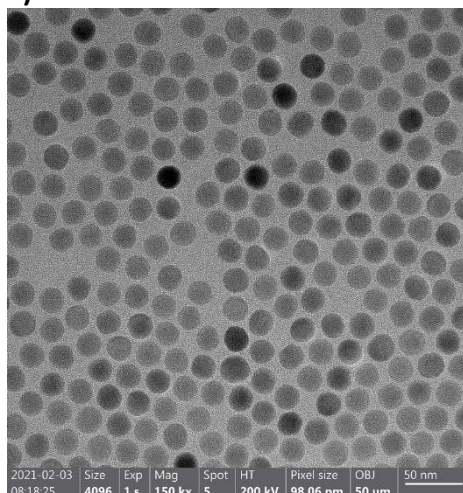


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j)



k)



l)

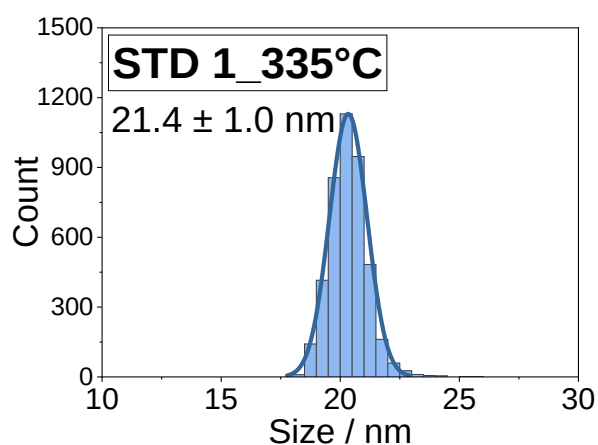
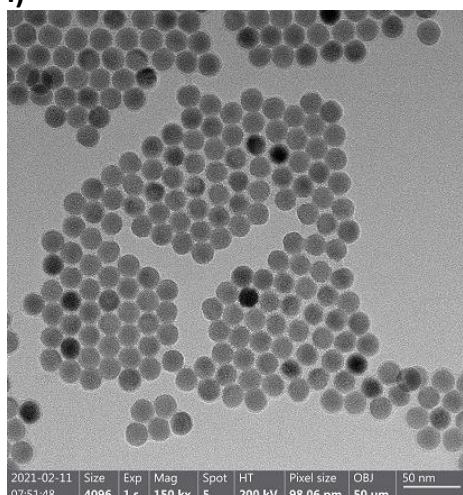
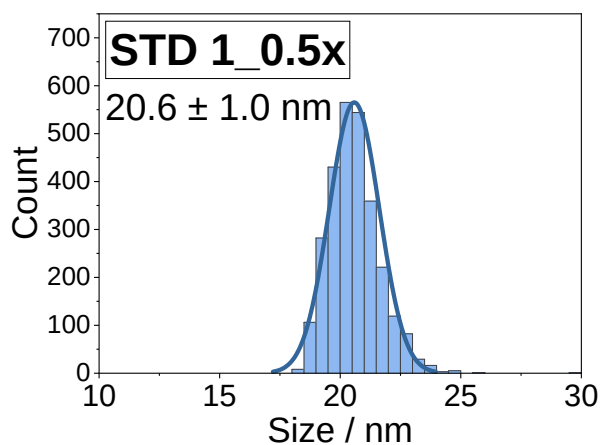
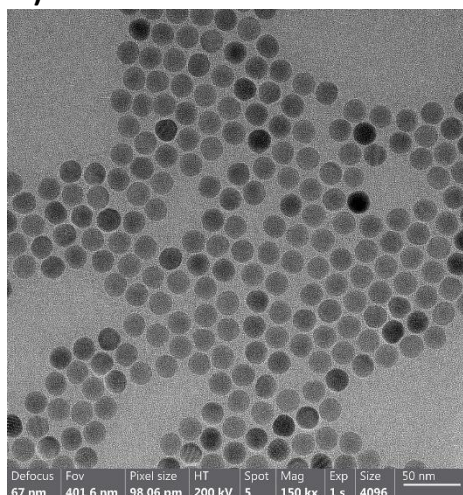
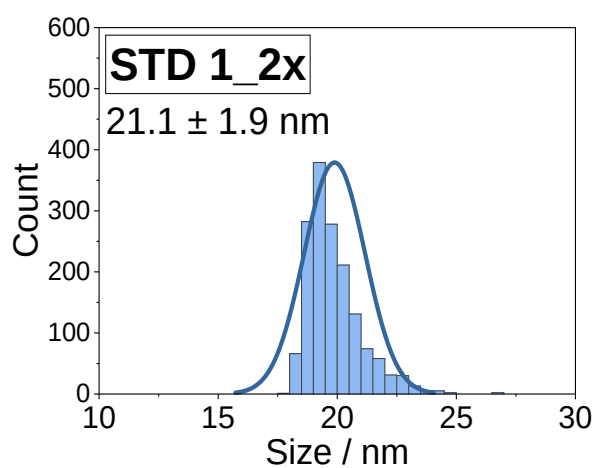
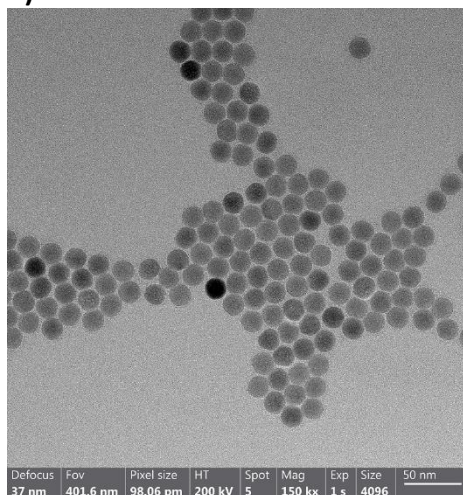


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m)



n)



o)

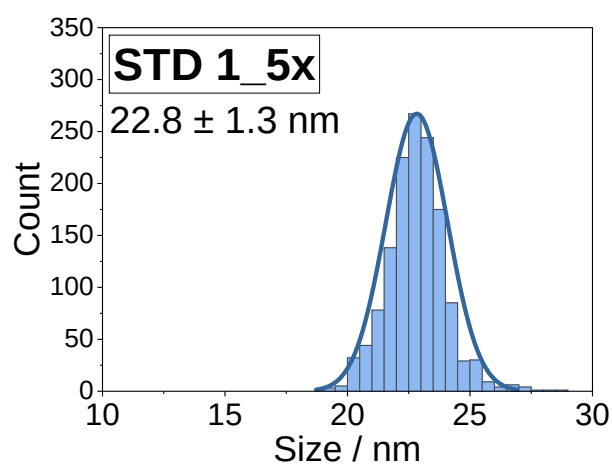
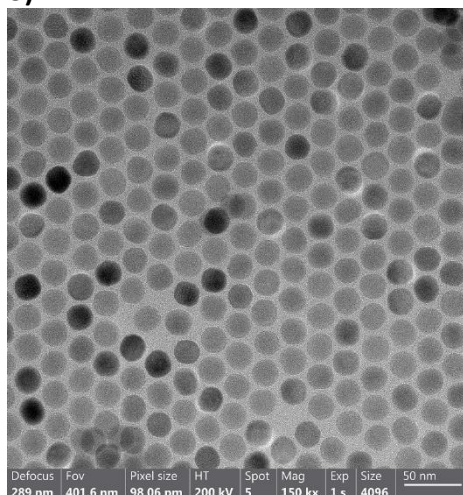
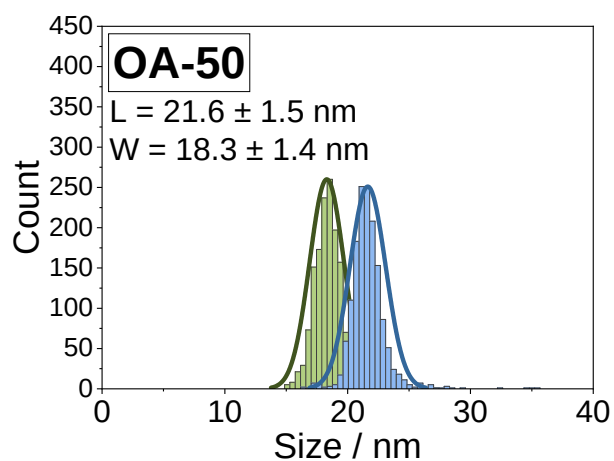
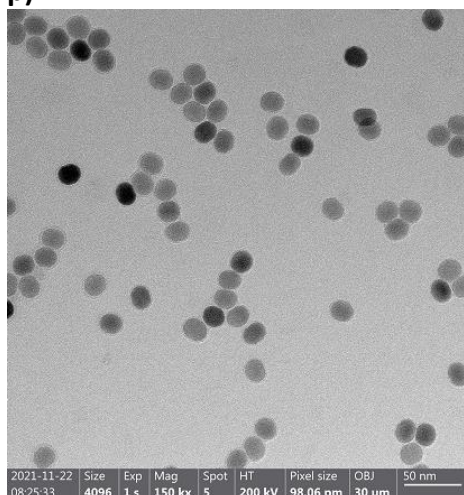
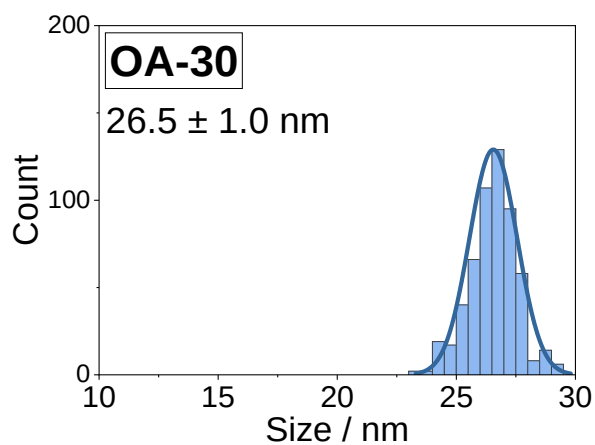
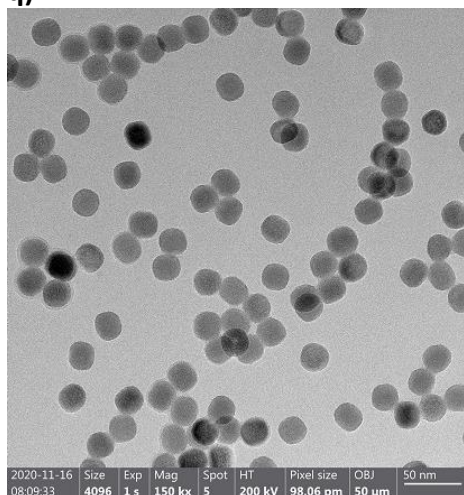


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p)



q)



r)

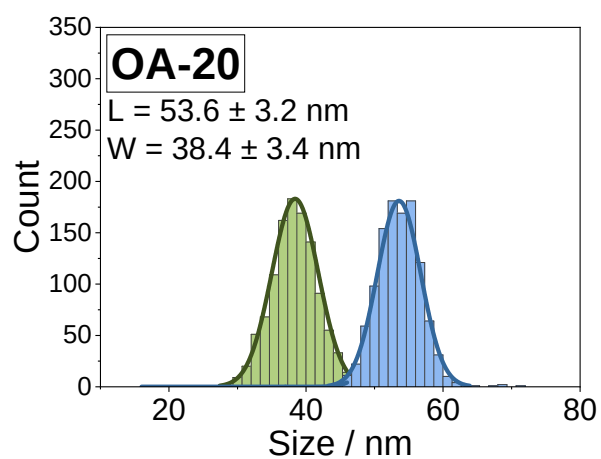
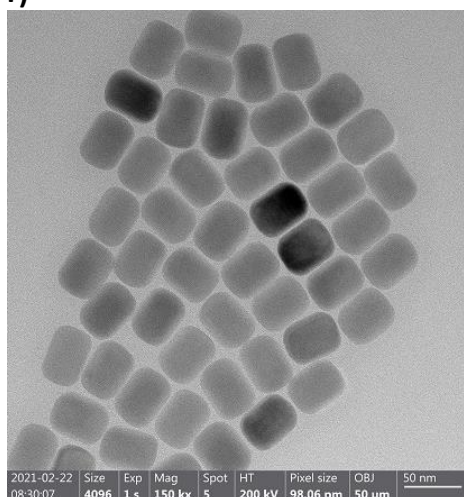
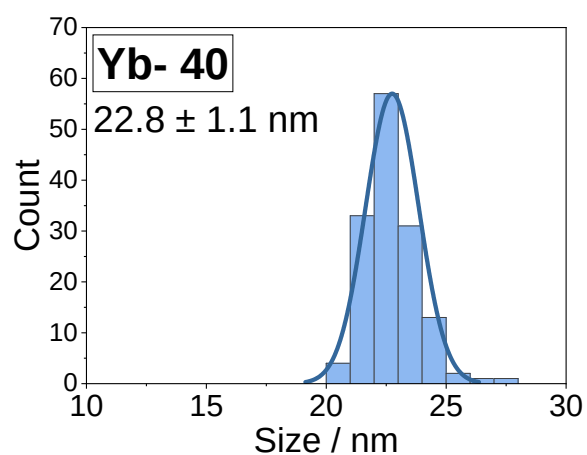
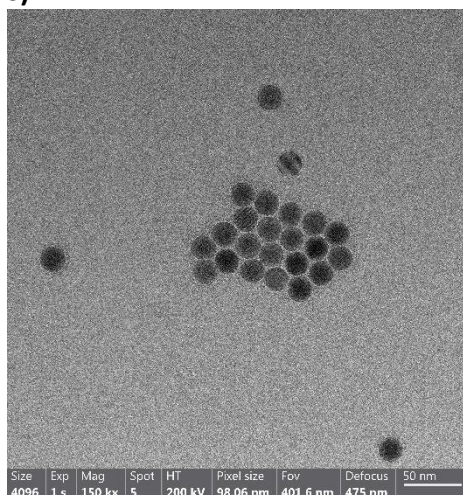
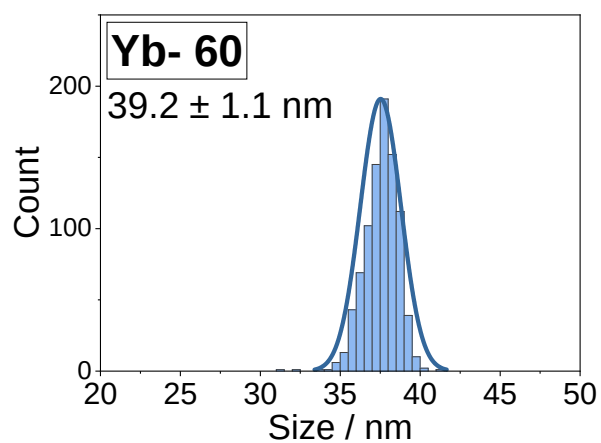
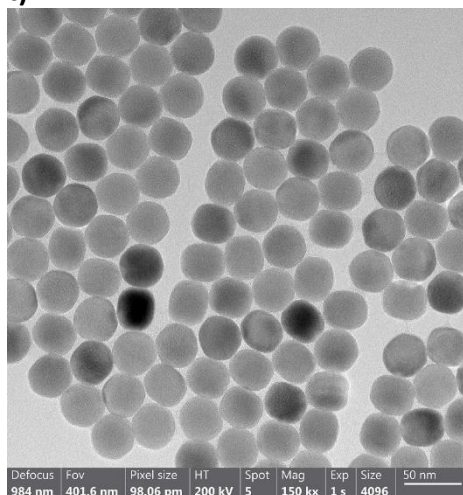


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s)



t)



u)

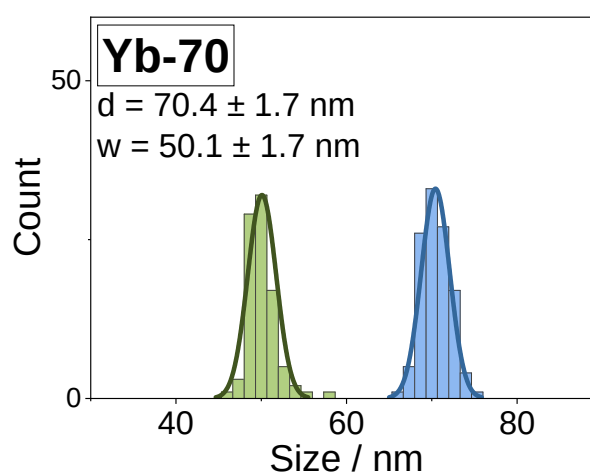
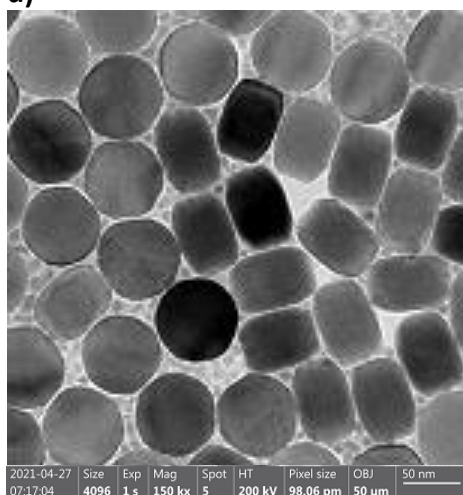
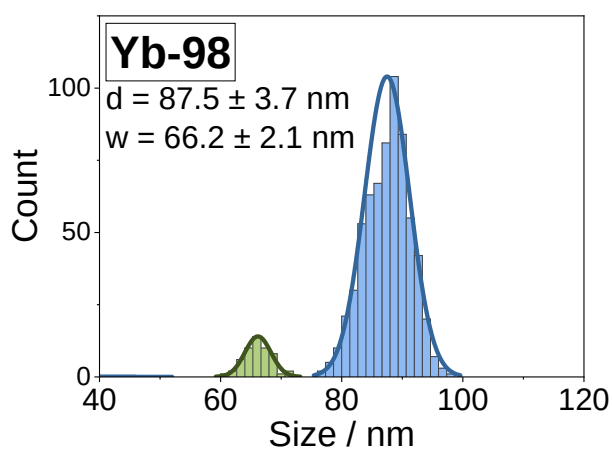
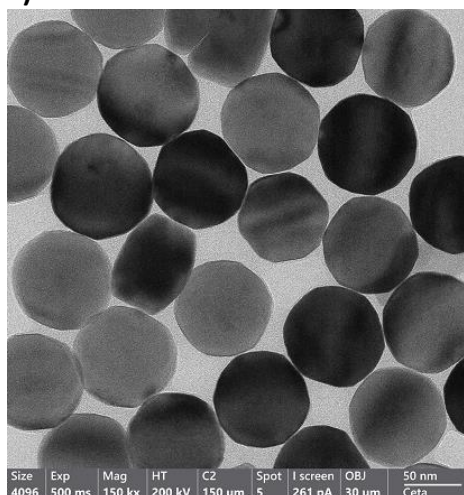
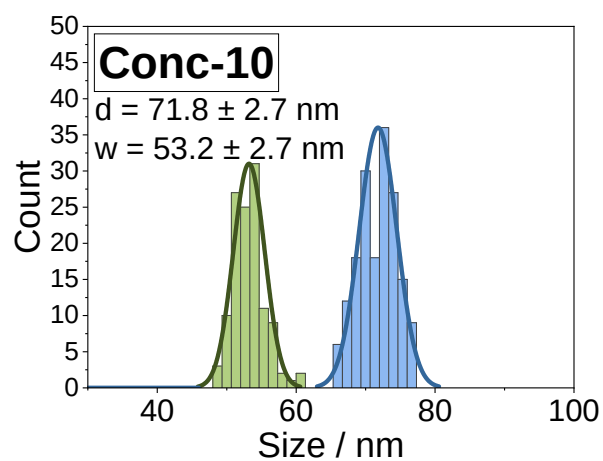
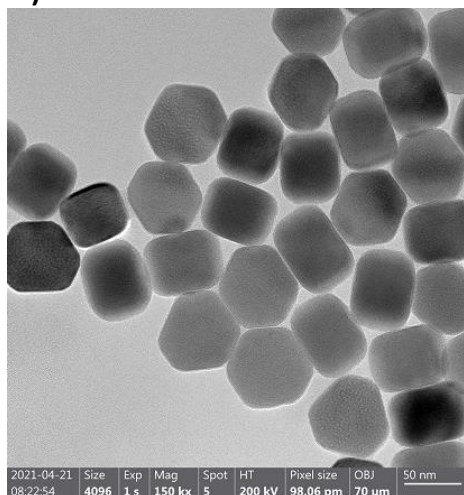


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v)



w)



x)

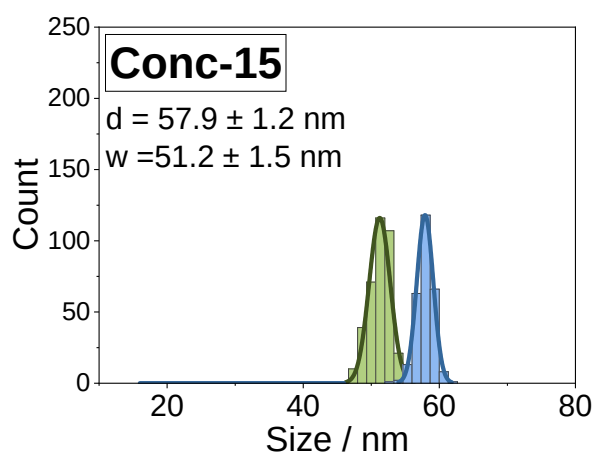
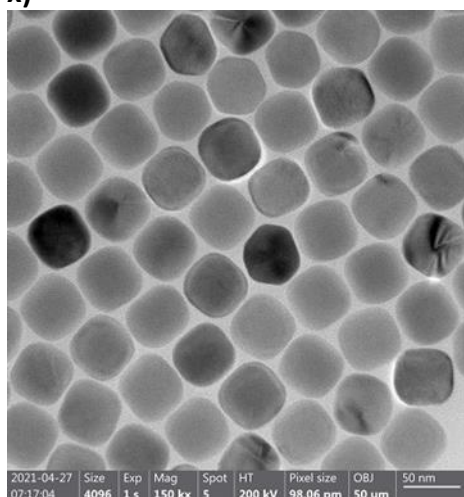
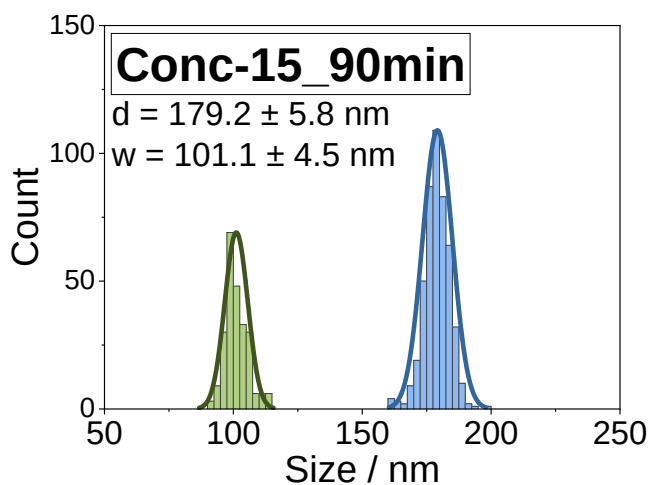
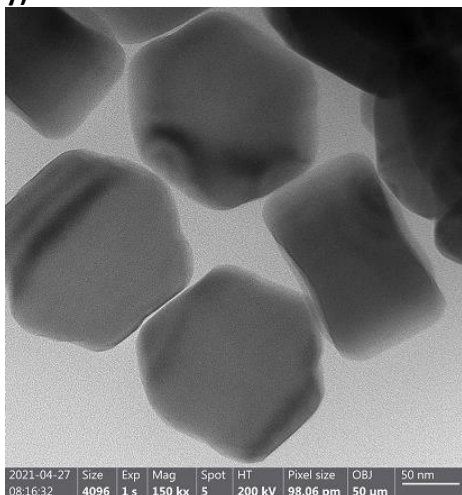


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y)



z)

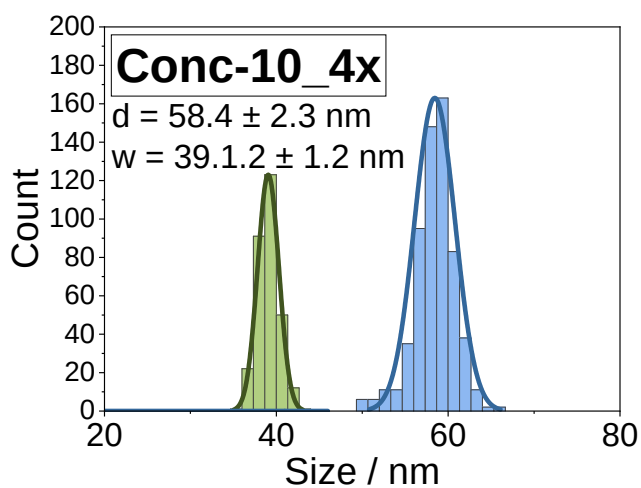
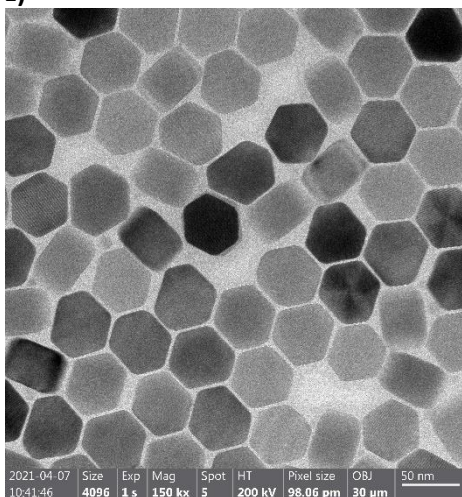


Figure S1: TEM images of as-synthesized oleate-NaYF₄:Yb,Er (magnification 150 kx) with the corresponding size histograms derived from TEM data (size distribution was fitted applying a Gaussian normal distribution)

4. ICP-OES Data

Table S3: Material composition (dopant concentration) of the synthesized UCNPs determined by ICP-OES measurements

Sample name	Expected /mol%			Determined by ICP-OES /mol%		
	Y ³⁺	Yb ³⁺	Er ³⁺	Y ³⁺	Yb ³⁺	Er ³⁺
STD 1	78	20	2	78.65 ± 1.66	19.30 ± 0.37	2.05 ± 0.03
STD 2	78	20	2	78.69 ± 0.47	19.27 ± 0.18	2.04 ± 0.01
STD 3	78	20	2	78.72 ± 1.74	19.25 ± 0.35	2.04 ± 0.03
STD 4	78	20	2	78.24 ± 0.65	19.62 ± 0.25	2.13 ± 0.01
STD 5	78	20	2	78.68 ± 1.11	19.35 ± 0.30	1.98 ± 0.03
STD 6	78	20	2	78.95 ± 0.66	19.01 ± 0.23	2.04 ± 0.02
STD 7	78	20	2	79.00 ± 1.83	18.98 ± 0.31	2.02 ± 0.03
STD 8	78	20	2	78.50 ± 1.06	19.47 ± 0.23	2.02 ± 0.01
STD 9	78	20	2	79.03 ± 0.68	18.95 ± 0.16	2.02 ± 0.01
STD 10	78	20	2	79.07 ± 0.87	19.98 ± 0.19	1.96 ± 0.02
STD 1_60min	78	20	2	78.57 ± 0.87	19.38 ± 0.29	2.06 ± 0.02
STD 1_335°C	78	20	2	78.12 ± 0.60	19.85 ± 0.09	2.04 ± 0.01
STD 1_0.5x	78	20	2	78.53 ± 0.62	19.46 ± 0.44	2.01 ± 0.04
STD 1_2x	78	20	2	77.97 ± 1.36	20.01 ± 0.32	2.02 ± 0.03
STD 1_5x	78	20	2	78.52 ± 1.44	19.45 ± 0.28	2.02 ± 0.02
OA-50	78	20	2	78.51 ± 0.76	19.47 ± 0.16	2.02 ± 0.01
OA-30	78	20	2	78.53 ± 0.62	19.46 ± 0.44	2.01 ± 0.04
OA-20	78	20	2	77.95 ± 1.76	20.07 ± 0.57	1.98 ± 0.03
Yb-40	58	40	2	57.79 ± 1.09	40.27 ± 0.51	1.94 ± 0.04
Yb-60	38	60	2	37.54 ± 1.05	60.34 ± 1.08	2.13 ± 0.04
Yb-70	28	70	2	27.65 ± 0.92	70.21 ± 2.26	2.14 ± 0.05
Yb-98	0	98	2	---	97.85 ± 0.93	2.15 ± 0.05
Conc-10	78	20	2	78.91 ± 0.78	19.06 ± 0.19	2.03 ± 0.01
Conc-15	78	20	2	77.71 ± 1.62	20.23 ± 0.35	2.06 ± 0.03
Conc-15_90min	78	20	2	78.53 ± 0.62	19.46 ± 0.44	2.01 ± 0.04

5. Calculated Red-to-Green ratio and intensity weighted lifetimes of the emissive states of all samples

Table S4: Red-to-Green ratio determined from the emission spectra and intensity weighted lifetimes calculated according to eq. S1 of the emissive states of all samples

Sample name	Red-to-Green ratio	Time-resolved measurements	
		Decay 540 nm	Decay 654 nm
STD 1	0.35	93 μ s	169 μ s
STD 2	0.32	99 μ s	191 μ s
STD 3	0.27	95 μ s	187 μ s
STD 4	0.31	87 μ s	154 μ s
STD 5	0.28	87 μ s	157 μ s
STD 6	0.29	101 μ s	170 μ s
STD 7	0.28	79 μ s	143 μ s
STD 8	0.30	100 μ s	200 μ s
STD 9	0.24	90 μ s	195 μ s
STD 10	0.32	100 μ s	171 μ s
STD 1_60min	0.26	96 μ s	184 μ s
STD 1_335°C	0.29	87 μ s	156 μ s
STD 1_0.5x	0.30	89 μ s	196 μ s
STD 1_2x	0.25	89 μ s	159 μ s
STD 1_5x	0.37	89 μ s	161 μ s
OA-50	0.34	81 μ s	148 μ s
OA-30	0.34	94 μ s	180 μ s
OA-20	1.00	170 μ s	307 μ s
Yb-40	0.53	62 μ s	133 μ s
Yb-60	1.33	56 μ s	264 μ s
Yb-70	2.08	42 μ s	348 μ s
Yb-98	2.68	34 μ s	366 μ s
Conc-10	0.99	236 μ s	430 μ s
Conc-15	1.13	315 μ s	483 μ s
Conc-15_90min	0.86	500 μ s	525 μ s

Intensity weighted lifetime:
$$\tau_{int} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (\text{eq. S3})$$

6. Optical characterization of the samples from the Reproducibility, Scale-up, and Robustness series

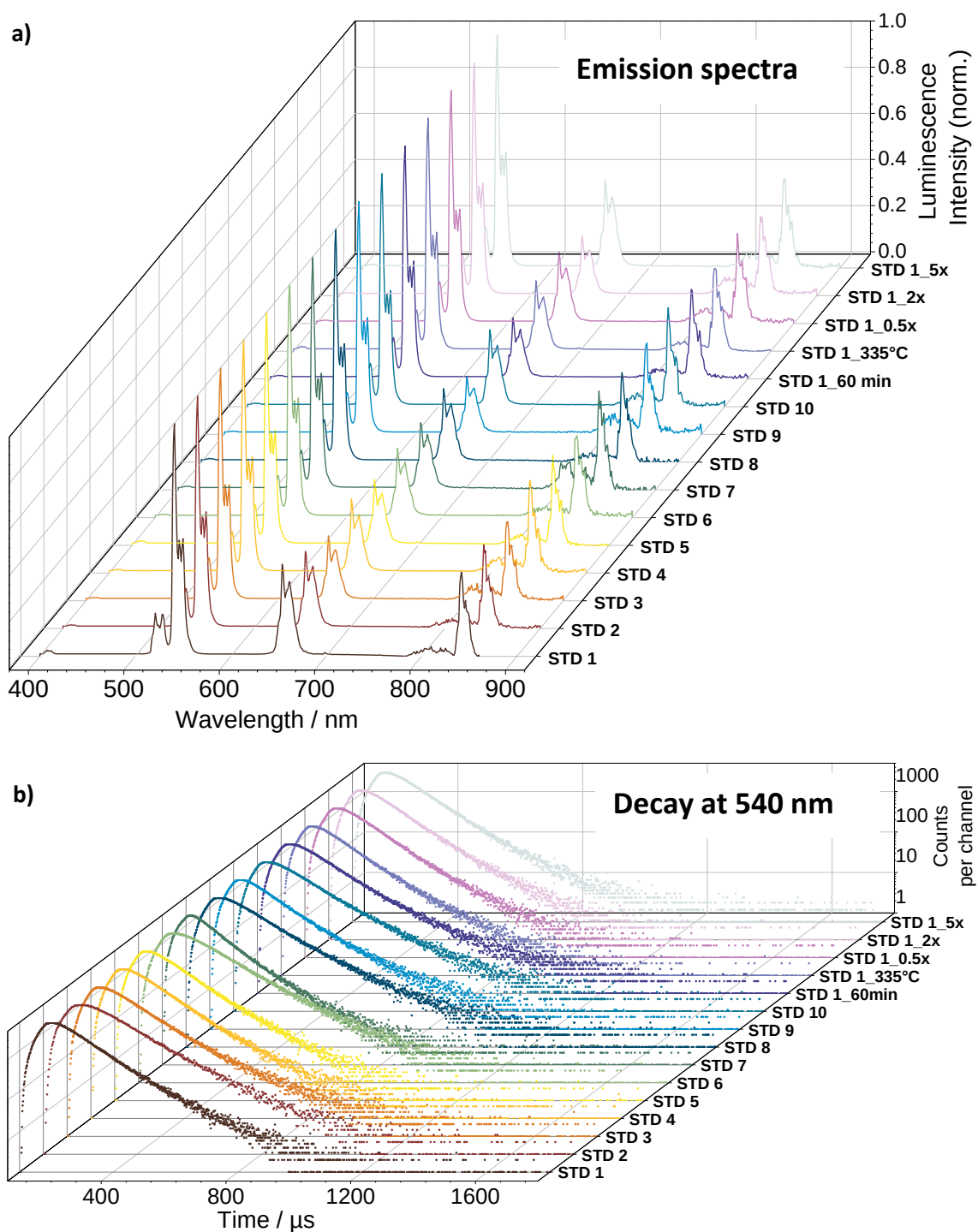


Figure S2: continued next page

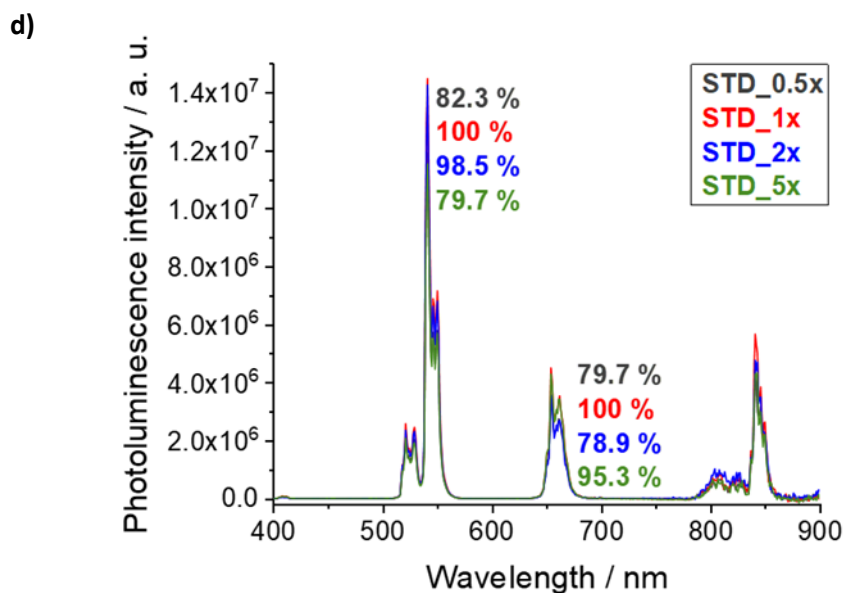
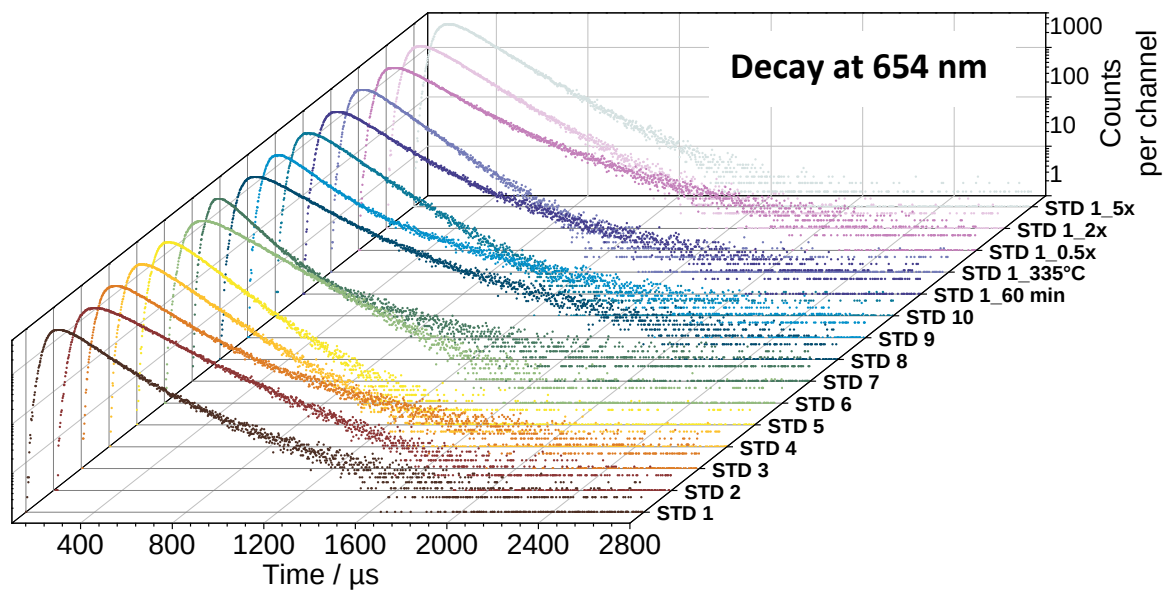


Figure S2: Optical characterization of the samples from the Reproducibility, Scale-up, and Robustness series: a) Normalized emission spectra; b) Decay curves at 540 nm; c) Decay curves at 654 nm and d) As measured photoluminescence spectra of the Scale-up series for sample concentration of 1 mg/mL.

7. X-ray diffraction (XRD) patterns of the samples from the dopant concentration series

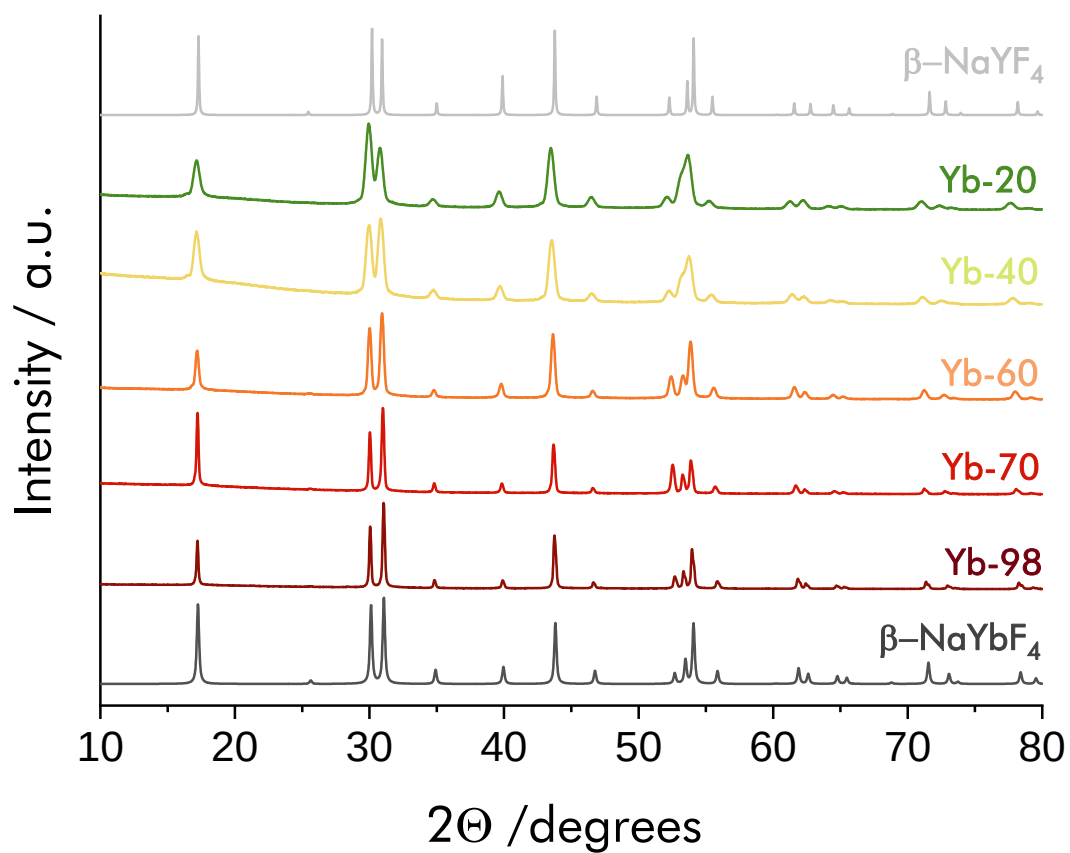


Figure S3: X-ray diffraction (XRD) patterns of samples **Yb-20**, **Yb-40**, **Yb-60**, **Yb-70** and **Yb-98** with references beta (β) phase NaYF₄ and beta (β) phase NaYbF₄.

8. Optical characterization of the samples from the dopant concentration series

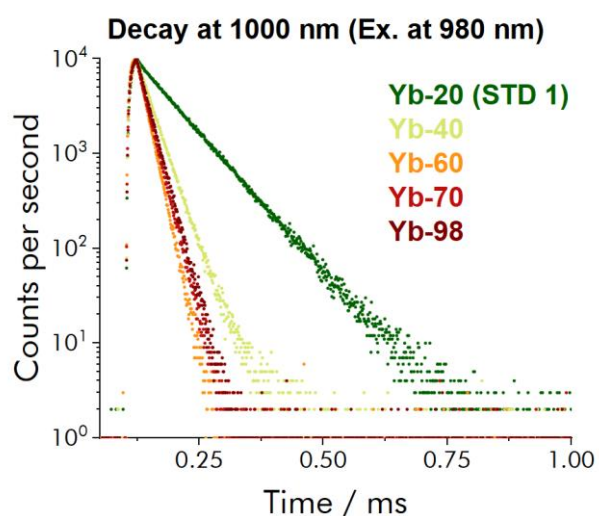


Figure S4: Decay kinetics of down-shifted emission of Yb^{3+} at 1000 nm.

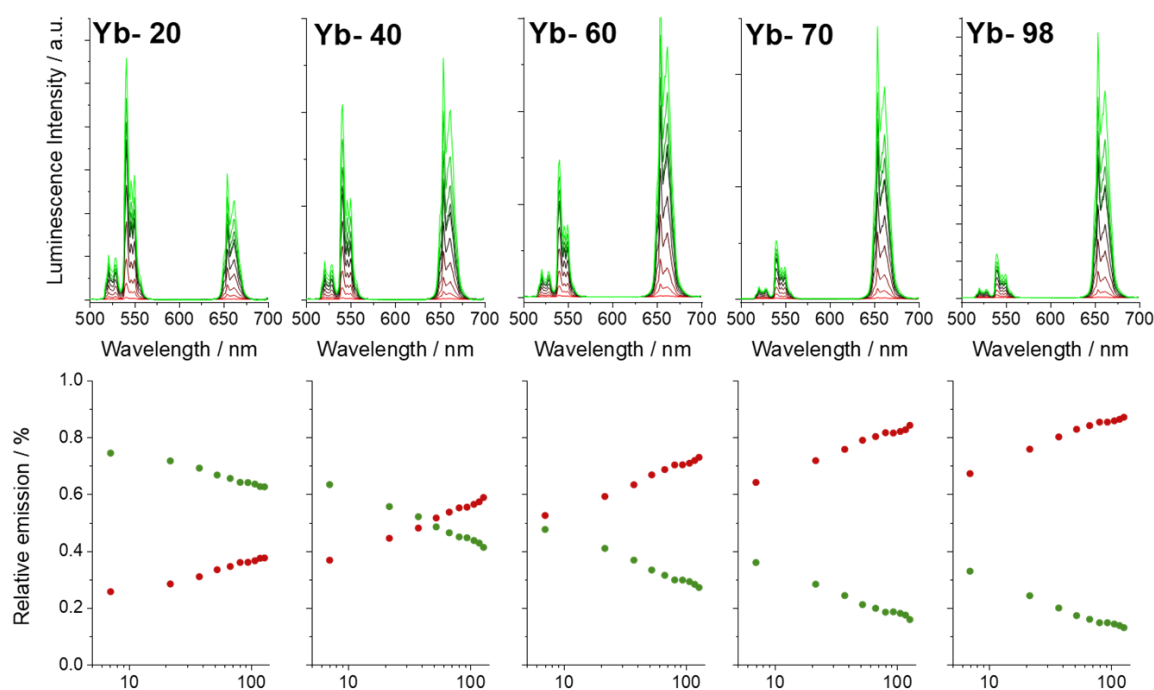
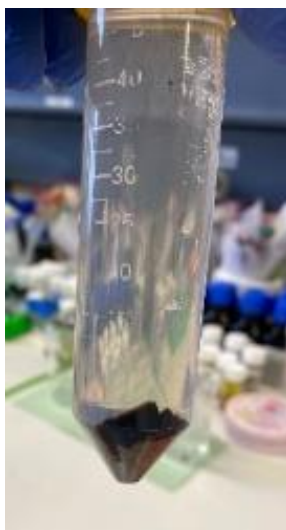


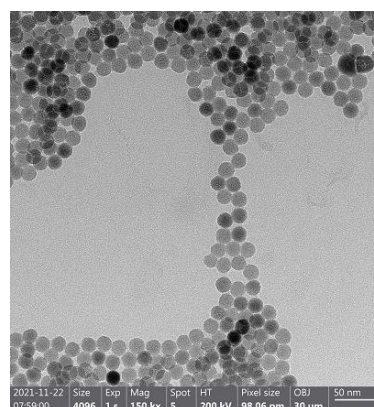
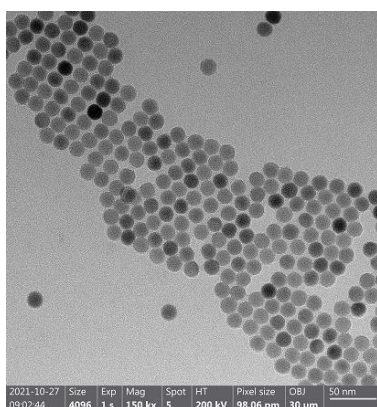
Figure S5: a) Excitation power dependency of the emission spectra of the samples from the Yb-dopant series. The color code represents the increasing excitation powers (red $\rightarrow$ green); b) Relative spectral contribution of the emission at 540 nm (green dots) and at 654 nm (red dots) to overall UCL as function of the excitation power density.

9. Synthesis of UCNPs starting from low-price Ln-precursors

a) As synthesized oleate-capped UCNPs



b) After ligand removal via acid treatment



c)

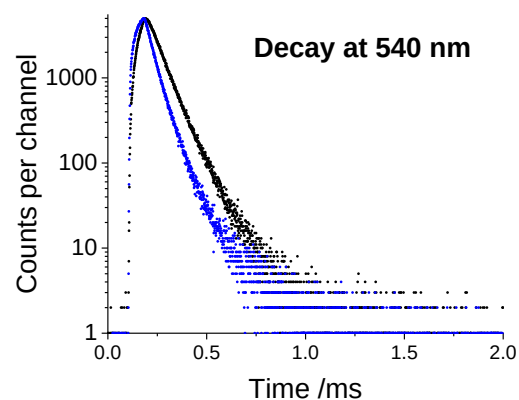
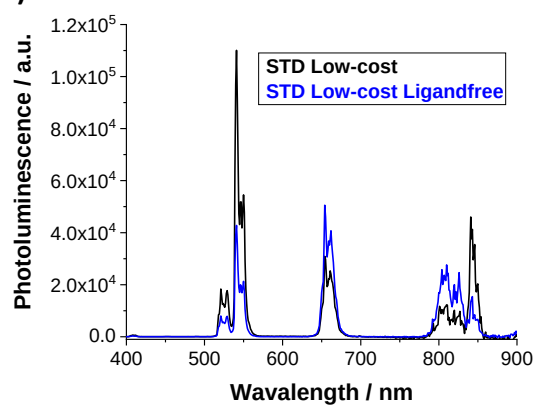


Figure S6: continued next page

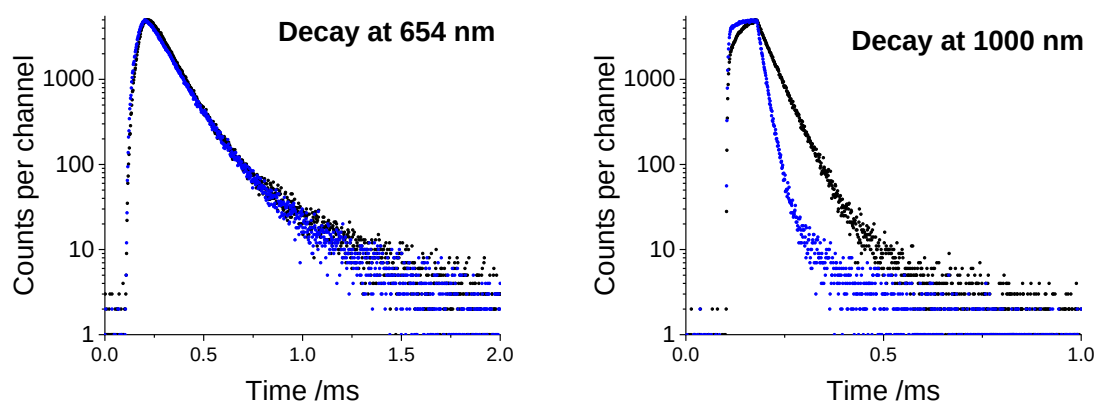


Figure S6: Photographs of a) as-synthesized UCNPs using low-price Ln-chlorides as precursors in dispersion in cyclohexane (left) and as solid (right) and b) after ligand removal via acid treatment and the corresponding TEM images (150kx magnification); c) Spectroscopic characterization of oleate-capped UCNPs prepared from low-cost precursors and after ligand removal.