Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Luminescent properties of europium-doped $(H_3O)Y_3F_{10} \cdot xH_2O$ nanocrystals

Supporting information

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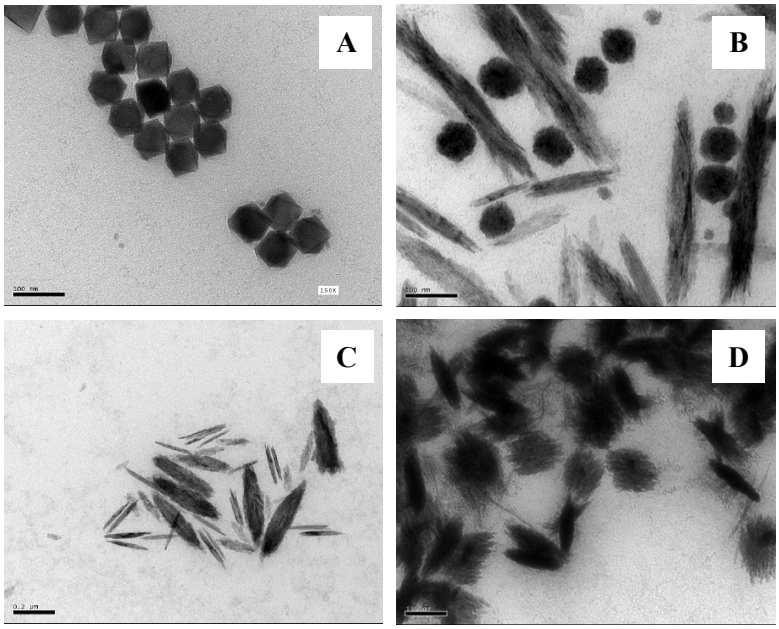

Figure S1: Transmission electron microscopy (TEM) images showing yttrium fluoride nanoparticles synthesized by the reverse microemulsion technique starting from 40 mM ion precursor solutions. The europium doping levels are 5% (A), 10% (B), 50% (C) and 100% (D).

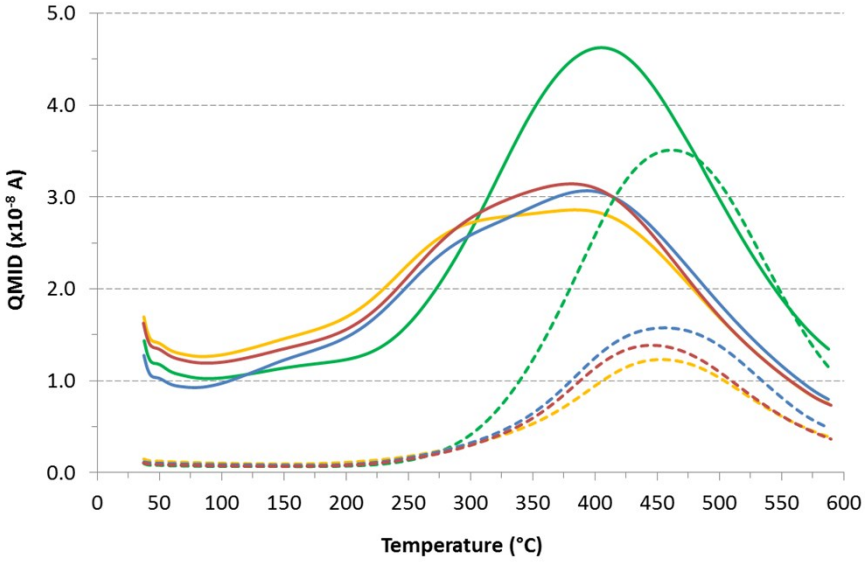

Figure S2: TGA-MS profiles at mass-to-charge ratios (m/z) of 18 (solid lines) and 44 (dashed lines), corresponding to H_2O and CO_2, respectively. Profiles are provided for europium-doped $(H_3O)Y_3F_{10} \cdot xH_2O$ nanocrystals with doping levels of 5% (green), 10% (yellow), 15% (blue) and 20% (red).

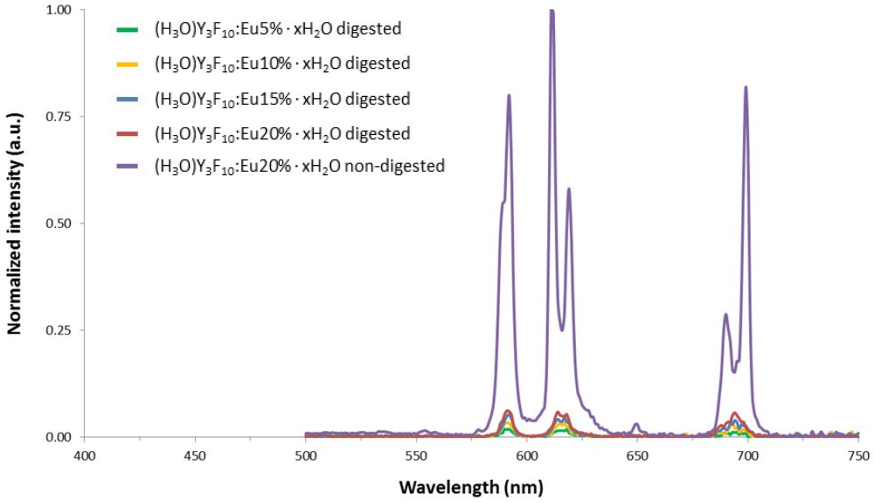

Figure S3: Emisison spectra of digested 5% (green), 10% (yellow), 15% (blue) and 20% (red) europium-doped $(H_3O)Y_3F_{10} \cdot xH_2O$ single crystal nanoparticles. As a reference, the emission spectrum of an aqueous suspension of non-digested $(H_3O)Y_3F_{10}$:Eu20% $\cdot xH_2O$ nanoparticles is provided (purple). (λ_{exc} = 393 nm)

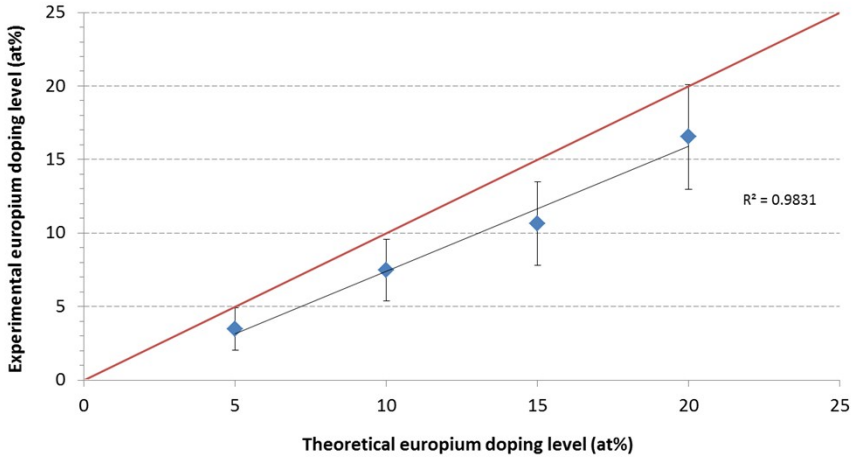

Figure S4: Europium doping levels of $(H_3O)Y_3F_{10} \cdot xH_2O$ nanoparticle samples, as determined by inductively coupled plasma mass spectrometry, as a function the theoretical doping level. The red line represents the ideal case where the experimental doping level is equal to the theoretical one (i.e. that calculated from initial reactant ratios).

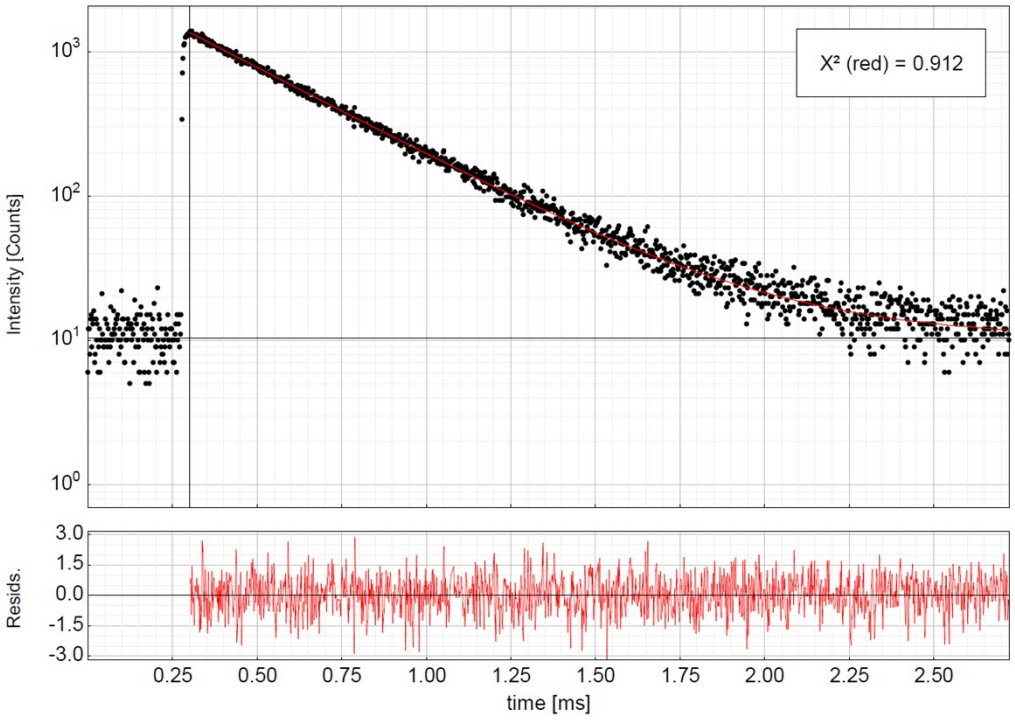

Figure S5: Emission intensity decay curve and residuals plot recorded at 592 nm ($^5D_0 \rightarrow {}^7F_1$) for a 8 mM solution of europium nitrate in methanol fitted with one-decay time tail-fit model.

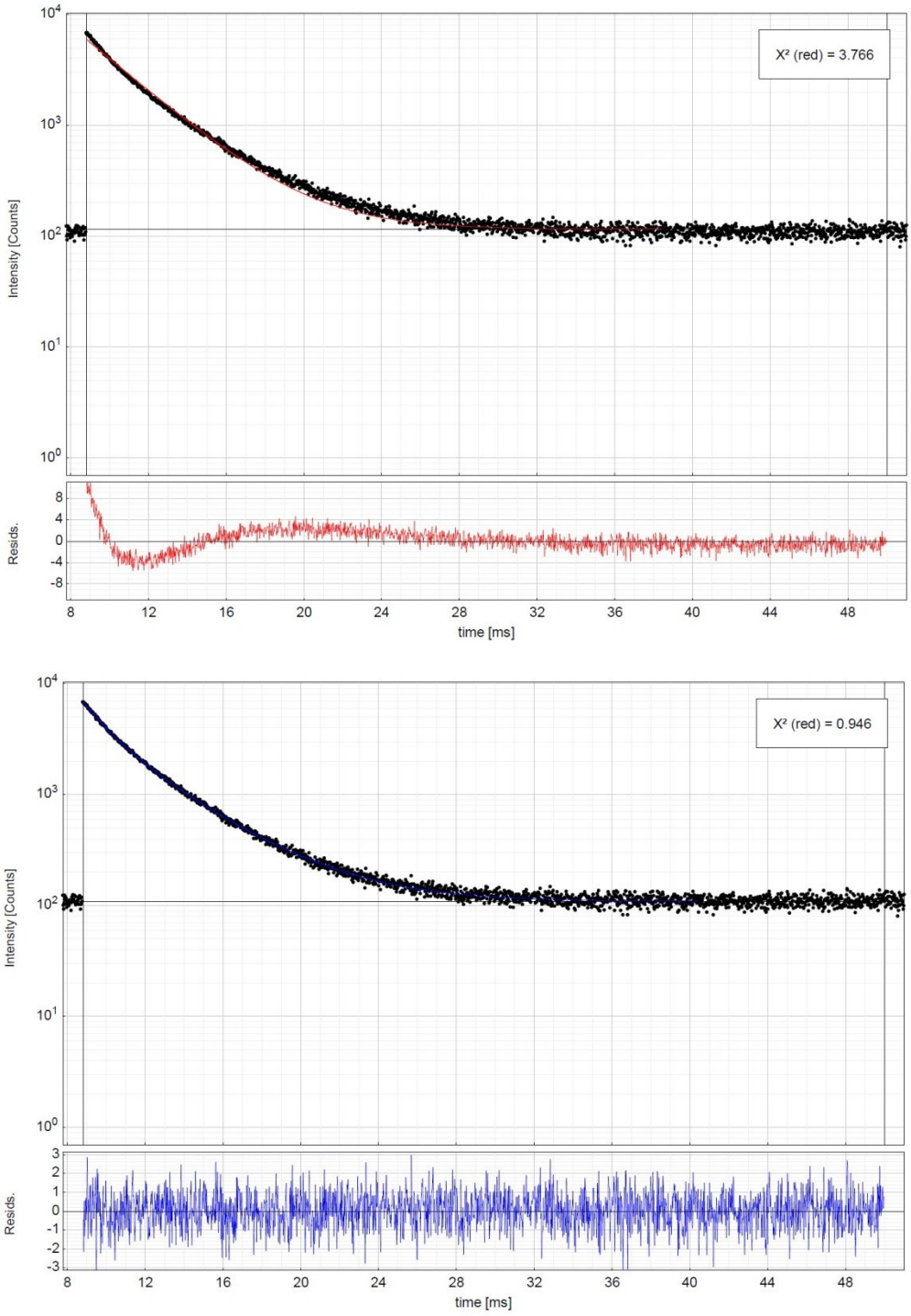

Figure S6: Emission intensity decay curve and residuals plot recorded for 20% europium-doped $(H_3O)Y_3F_{10}$:Eu20% · xH_2O nanoparticles at 592 nm ($^5D_0 \rightarrow {}^7F_1$) fitted with one-decay time (top panel) and two-decay time (bottom panel) tail-fit models. The shape of the residuals plot in the top panel indicates an ill-fitted decay curve using a single-exponential tail-fit.

	Sample composition (at%)							
	$(H_3O)Y_3F_{10}$:Eu5%		$(H_3O)Y_3F_{10}$:Eu10%		$(H_3O)Y_3F_{10}$:Eu15%		$(H_3O)Y_3F_{10}$:Eu20%	
Element	aggregate 1	aggregate 2	aggregate 1	aggregate 2	aggregate 1	aggregate 2	aggregate 1	aggregate 2
Y	18.23	17.33	22.28	15.75	18.22	22.87	21.24	16.48
Eu	0.6	0.64	1.62	1.17	2.06	2.62	3.07	2.91
F	42.85	42.91	65.1	58.57	62.98	58.52	65.01	54.86
C	-----	28.44	-----	16.89	-----	-----	-----	16.71
Si	7.14	4.67	5.14	3.39	9.19	8.61	4.73	5.04
O	22.84	-----	-----	-----	-----	-----	-----	-----
Na	2.7	1.69	-----	-----	-----	-----	-----	-----
K	3.88	3.17	4.49	3.15	4.65	5.11	4.7	2.98
Ca	1.75	1.13	1.37	1.09	2.28	2.26	1.24	1.03
S	-----	-----	-----	-----	0.62	-----	-----	-----

Table S1: Elemental composition of $(H_3O)Y_3F_{10} \cdot xH_2O$ single crystal nanoparticles doped at 5%, 10%, 15% and 20% with europium ions as determined by energy-dispersive X-ray

	Mean doping level (at%)	
Sample	EDX	ICP-MS
$(H_3O)Y_3F_{10}$:Eu5%	3.4 ± 0.3	3 ± 1
$(H_3O)Y_3F_{10}$:Eu10%	6.8 ± 0.1	7 ± 2
$(H_3O)Y_3F_{10}$:Eu15%	10.2 ± 0.1	11 ± 3
$(H_3O)Y_3F_{10}$:Eu20%	14 ± 2	17 ± 4

Table S2: Experimental doping level values for europium-doped $(H_3O)Y_3F_{10} \cdot xH_2O$ nanoparticle samples determined by energy-dispersive X-ray spectroscopy and inductively coupled plasma mass spectrometry.

		$(H_3O)Y_3F_{10}$:Eu5%					
λ (nm)	Transition	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
592	$^5D_0 \rightarrow {}^7F_1$	0.58±0.02	4.38±0.08	0.42±0.02	1.39±0.09	3.1±0.2	1.05
611	$^5D_0 \rightarrow {}^7F_2$	0.78±0.06	4.3±0.1	0.22±0.06	1.9±0.3	3.8±0.5	1.05
619	$^5D_0 \rightarrow {}^7F_2$	0.72±0.06	4.4±0.2	0.28±0.06	1.7±0.3	3.6±0.6	1.07
690	$^5D_0 \rightarrow {}^7F_4$	–	–	–	–	–	–
699	$^5D_0 \rightarrow {}^7F_4$	–	–	–	–	–	–

		$(H_3O)Y_3F_{10}$:Eu10%					
λ (nm)	Transition	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
592	$^5D_0 \rightarrow {}^7F_1$	0.52±0.02	3.97±0.08	0.48±0.02	1.36±0.07	2.7±0.2	1.01
611	$^5D_0 \rightarrow {}^7F_2$	0.71±0.04	3.9±0.1	0.29±0.04	1.4±0.2	3.2±0.3	1.00
619	$^5D_0 \rightarrow {}^7F_2$	0.64±0.05	3.9±0.1	0.36±0.05	1.5±0.2	3.0±0.4	1.01
690	$^5D_0 \rightarrow {}^7F_4$	0.45±0.07	3.8±0.3	0.55±0.07	1.2±0.2	2.3±0.6	1.04
699	$^5D_0 \rightarrow {}^7F_4$	0.6±0.2	4.0±0.3	0.4±0.1	1.8±0.4	3±1	1.06

		$(H_3O)Y_3F_{10}$:Eu15%					
λ (nm)	Transition	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
592	$^5D_0 \rightarrow {}^7F_1$	0.55±0.01	3.90±0.04	0.45±0.01	1.26±0.04	2.7±0.1	1.03
611	$^5D_0 \rightarrow {}^7F_2$	0.73±0.03	3.95±0.06	0.27±0.03	1.6±0.2	3.3±0.3	1.08
619	$^5D_0 \rightarrow {}^7F_2$	0.64±0.02	3.93±0.06	0.36±0.02	1.35±0.08	3.0±0.2	1.08
690	$^5D_0 \rightarrow {}^7F_4$	0.43±0.04	3.8±0.2	0.57±0.04	1.2±0.1	2.3±0.4	1.05
699	$^5D_0 \rightarrow {}^7F_4$	0.7±0.1	4.0±0.2	0.3±0.1	1.6±0.4	3.3±0.9	1.07

		$(H_3O)Y_3F_{10}$:Eu20%					
λ (nm)	Transition	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
592	$^5D_0 \rightarrow {}^7F_1$	0.56±0.02	3.62±0.05	0.44±0.02	1.25±0.06	2.6±0.2	0.95
611	$^5D_0 \rightarrow {}^7F_2$	0.73±0.03	3.58±0.07	0.27±0.03	1.4±0.1	3.0±0.2	1.13
619	$^5D_0 \rightarrow {}^7F_2$	0.71±0.03	3.52±0.07	0.29±0.03	1.0±0.1	2.8±0.2	0.99
690	$^5D_0 \rightarrow {}^7F_4$	0.44±0.05	3.6±0.2	0.56±0.04	1.1±0.1	2.2±0.4	1.02
699	$^5D_0 \rightarrow {}^7F_4$	0.79±0.05	3.7±0.1	0.21±0.05	1.4±0.3	3.2±0.4	1.03

Table S3: Phosphorescence lifetime values measured for methanol suspensions of europium-doped $(H_3O)Y_3F_{10} \cdot xH_2O$ nanoparticles (λ_{exc} = 393 nm). Lifetime values calculated using two-exponential local tail-fit. Fitting ranges for all data sets were set to identical boundaries. Uncertainties indicated for A_1, τ_1, A_2, τ_2 calculated using support plane error analysis (P=0.68). Decay curves for 690-nm and 699-nm emission lines of 5% Eu-doped nanoparticles not measured due to long signal accumulation times required to achieve two-decay fits with acceptable S/N ratios.

	$^5D_0 \rightarrow {}^7F_1$ (592 nm)					
λ (nm)	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
5%	0.66±0.01	4.07±0.04	0.34±0.02	1.48±0.04	3.20±0.09	1.26
10%	0.49±0.01	4.07±0.04	0.51±0.01	1.48±0.04	2.75±0.08	1.02
15%	0.49±0.01	4.07±0.04	0.51±0.01	1.48±0.04	2.76±0.08	1.07
20%	0.44±0.01	4.07±0.04	0.56±0.01	1.48±0.04	2.62±0.07	1.12

	$^5D_0 \rightarrow {}^7F_2$ (611 nm)					
λ (nm)	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
5%	0.82±0.03	4.21±0.06	0.18±0.03	2.06±0.07	3.8±0.2	1.13
10%	0.55±0.03	4.21±0.06	0.45±0.03	2.06±0.07	3.2±0.2	1.03
15%	0.60±0.03	4.21±0.06	0.40±0.03	2.06±0.07	3.4±0.2	1.10
20%	0.46±0.03	4.21±0.06	0.54±0.03	2.06±0.07	3.0±0.2	1.24

	$^5D_0 \rightarrow {}^7F_2$ (619 nm)					
λ (nm)	A_1	τ_1	A_2	τ_2	τ_{ave}	χ^2
5%	0.80±0.03	4.16±0.07	0.20±0.03	1.68±0.08	3.7±0.2	1.12
10%	0.56±0.03	4.16±0.07	0.44±0.03	1.68±0.08	3.1±0.2	1.02
15%	0.60±0.03	4.16±0.07	0.40±0.03	1.68±0.08	3.2±0.2	1.05
20%	0.43±0.03	4.16±0.07	0.51±0.02	1.68±0.08	2.9±0.2	1.08

Table S4: Phosphorescence lifetime values measured for methanol suspensions of europium-doped $(H_3O)Y_3F_{10} \cdot xH_2O$ nanoparticles (λ_{exc} = 393 nm) for 3 strongest emission lines (592, 610 and 619 nm). Lifetime values calculated using double-exponential global tail-fit. Fitting ranges for all data sets were set to identical boundaries. Uncertainties indicated for A_1, τ_1, A_2, τ_2 calculated using support plane error analysis (P=0.68).

λ (nm)	Transition	τ	χ^2
592	$^5D_0 \rightarrow {}^7F_1$	0.355±0.003	0.93
617	$^5D_0 \rightarrow {}^7F_2$	0.354±0.002	1.02
685	$^5D_0 \rightarrow {}^7F_4$	0.349±0.008	0.95
694	$^5D_0 \rightarrow {}^7F_4$	0.351±0.009	1.06

Table S5: Phosphorescence lifetime values for 8-mM methanol solution of europium nitrate (λ_{exc} = 393 nm). Lifetime values calculated using single-exponential local tail-fit. Uncertainties are asymptotic standard errors.