

Supporting Information

The Effect of Surface-Capping Oleic Acid on the Optical Properties of Lanthanide-Doped Nanocrystals

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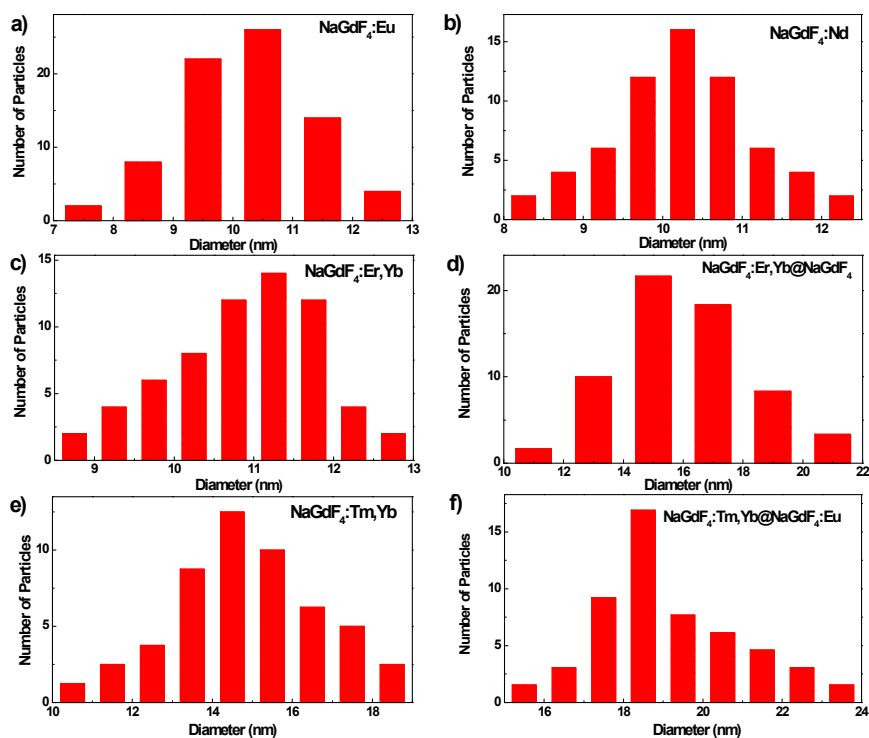


Figure S1. Particle size distribution of OA-capped a) $\text{NaGdF}_4:\text{Eu}$, b) $\text{NaGdF}_4:\text{Nd}$, c) $\text{NaGdF}_4:\text{Er, Yb}$, d) $\text{NaGdF}_4:\text{Er, Yb}@NaGdF_4$, e) $\text{NaGdF}_4:\text{Tm, Yb}$, and f) $\text{NaGdF}_4:\text{Tm, Yb}@NaGdF_4:\text{Eu}$ nanocrystals obtained from the TEM images

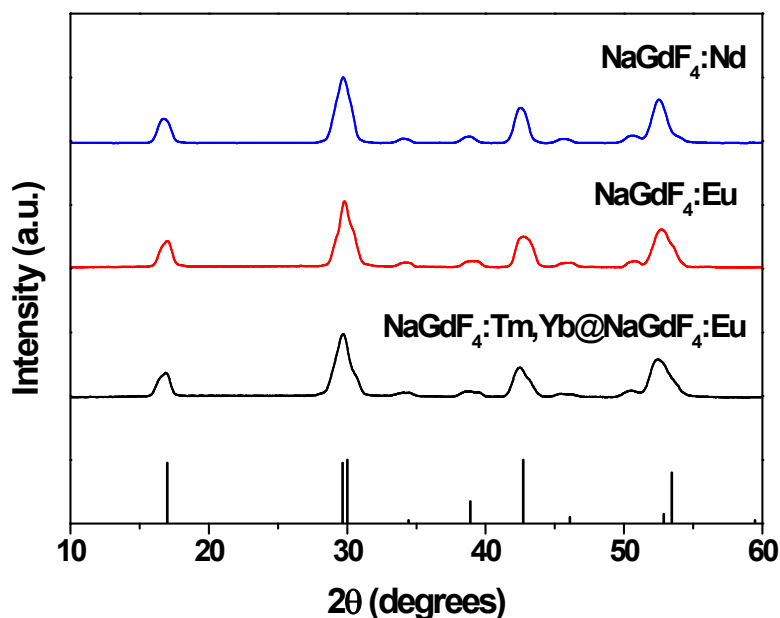


Figure S2. XRD patterns of $\text{NaGdF}_4:\text{Tm, Yb}@NaGdF_4:\text{Eu}$, $\text{NaGdF}_4:\text{Eu}$, and $\text{NaGdF}_4:\text{Nd}$ nanocrystals, and the corresponding line pattern of hexagonal phase NaGdF_4 (JCPDS standard card no. 27-0699).

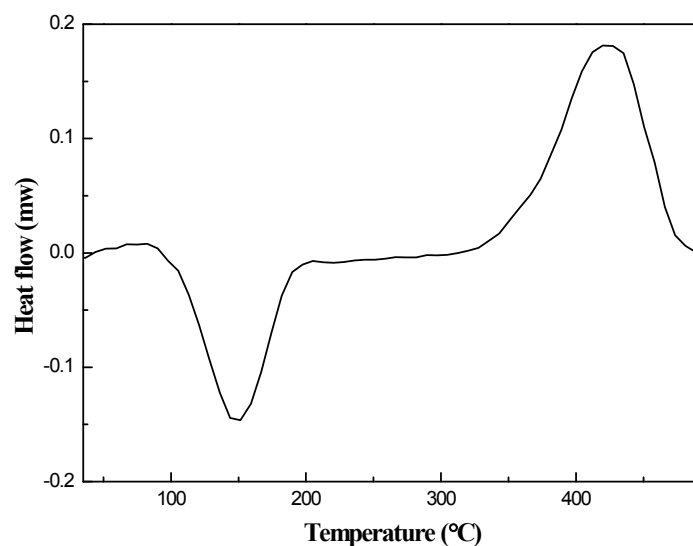


Figure S3. Differential Thermal Analysis OA-capped NaGdF₄: Eu nanocrystals. The result indicates that the OA starts to leave the nanocrystals at 330 °C.

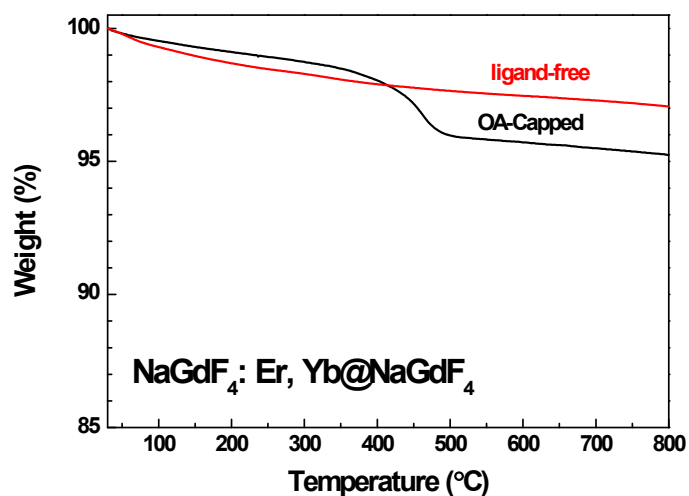


Figure S4. Thermal gravity analysis (TGA) of OA-capped (black) and ligand-free (red) NaGdF₄: Er, Yb@NaGdF₄ core-shell nanocrystals. The weight losses for OA-capped and ligand-free samples are calculated to be 5.5% and 2.1%, respectively.

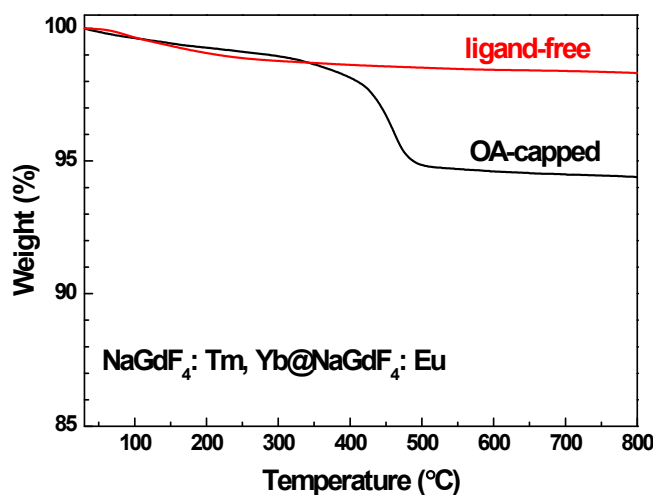


Figure S5. Thermal gravity analysis (TGA) of OA-capped (black) and ligand-free (red) NaGdF₄: Tm, Yb@NaGdF₄: Eu core-shell nanocrystals. The weight losses for OA-capped and ligand-free samples are calculated to be 5.3% and 1.5%, respectively.

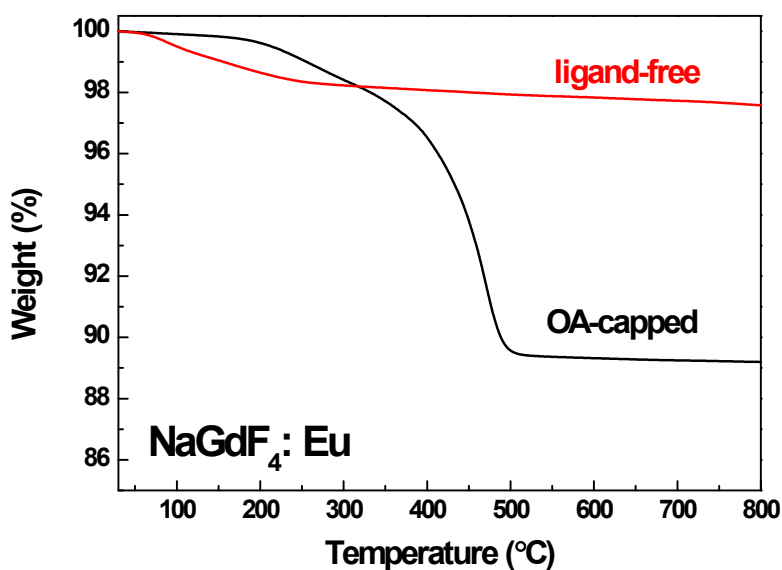


Figure S6. Thermal gravity analysis (TGA) of OA-capped (black) and ligand-free (red) NaGdF₄: Eu nanocrystals. The weight losses for OA-capped and ligand-free samples are calculated to be 11.2% and 2.2%, respectively.

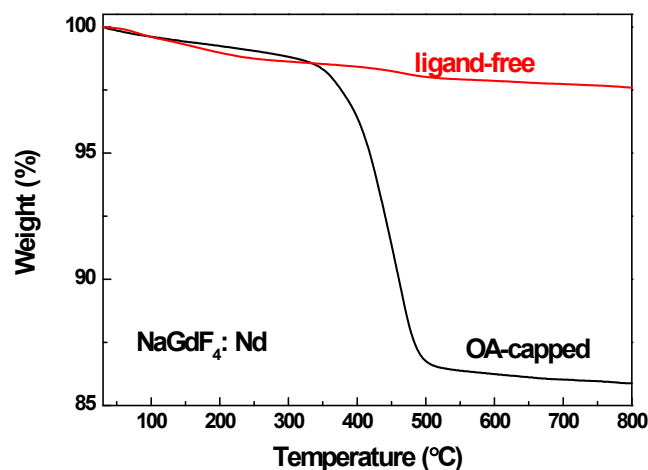


Figure S7. Thermal gravity analysis (TGA) of OA-capped (black) and ligand-free (red) $\text{NaGdF}_4:\text{Nd}$ nanocrystals. The weight losses for OA-capped and ligand-free samples are calculated to be 13.5% and 3.0%, respectively.

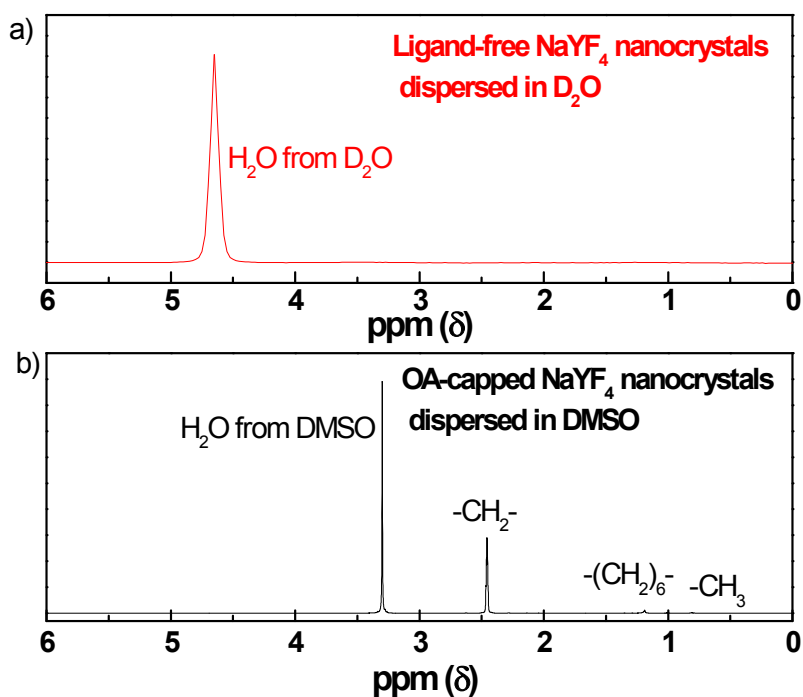


Figure S8. The ^1H NMR spectrum of a) ligand-free NaYF_4 nanocrystals dispersed in D_2O and b) OA-capped NaYF_4 nanocrystals dispersed in DMSO were recorded on a JEOL JNM-ECZ400S spectrometer. Chemical shifts are reported in parts-per-million (δ , ppm): a) 4.64 (H_2O from D_2O) and b) 3.30 (H_2O from DMSO), 2.0-2.5 ($-\text{CH}_2-$), 1.0-1.4 ($-(\text{CH}_2)_6-$) and 0.5-1.0 ($-\text{CH}_3$).

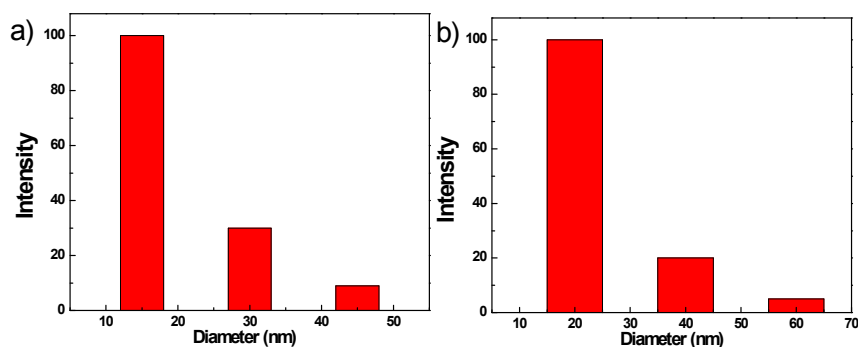


Figure S9. Hydrodynamic diameter distribution of a) ligand-free and b) OA-capped nanocrystals obtained from dynamic light scattering (DLS).

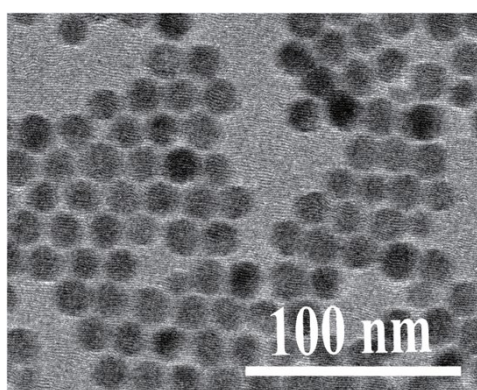


Figure S10. TEM image of ligand-free NaGdF₄: Eu, illustrating that ligand-free nanocrystals are still monodispersed after removing OA ligand.

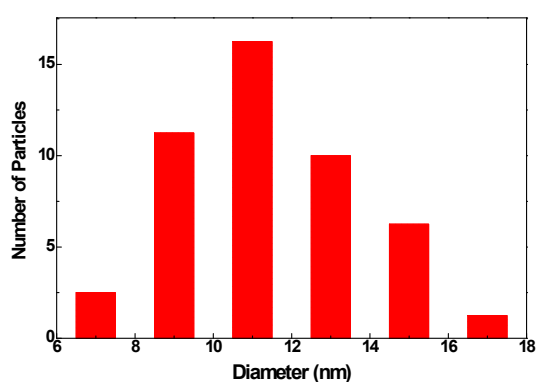


Figure S11. Particle size distribution of ligand-free NaGdF₄: Eu nanocrystals obtained from the TEM images

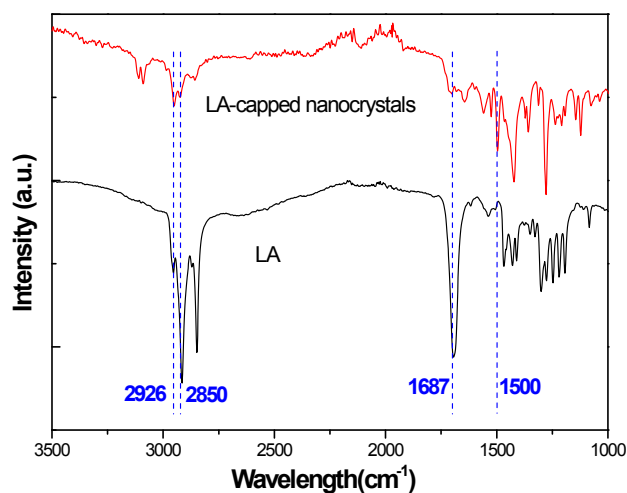


Figure S12. FTIR spectra of lauric acid (LA, black line) and LA-capped NaGdF₄: Eu (red line). The absorption bands peaked at 2926 and 2850 cm⁻¹ can be assigned to the stretching vibration of -CH₂-, and the bands peaked at 1687 and 1468 cm⁻¹ are attributed to stretching vibrations of COO in LA.

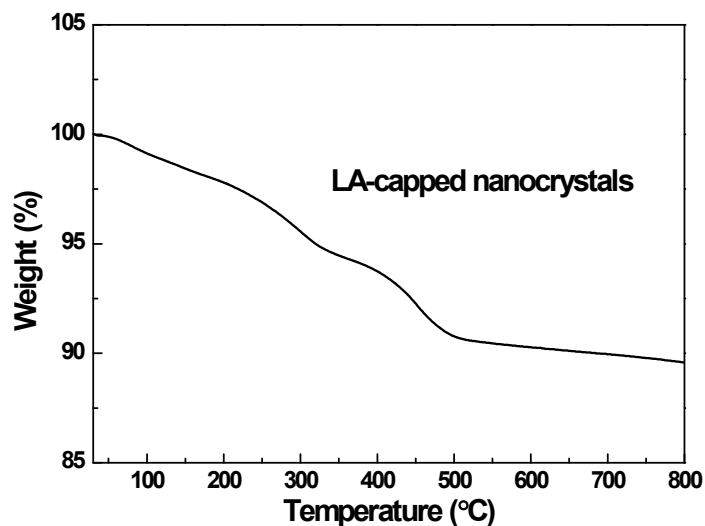


Figure S13. Thermal gravity analysis (TGA) of LA-capped NaGdF₄: Er, Yb nanocrystals.

Table 1. The fitting parameters for the lifetime of emissive lanthanides in this work with the fitting equation to be $y=a_1 \cdot \exp(-x/t_1)+y_0$.

Samples in solid state				
	a₁	y₀	t₁ (ms)	Standard error
Er in OA-capped core	4258.1	0	0.161	0.000275
Er in ligand-free core	3998.4	0	0.170	0.00031
Er in OA-capped core-shell	3651.3	0	0.189	0.00044
Er in ligand-free core-shell	3497.8	0	0.196	0.00048
Tm in OA-capped	3296.6	0	0.46	0.00074
Tm in ligand-free	3941.7	0	0.47	0.00096
Eu in OA-capped upconversion	1144.0	0	3.96	0.00479
Eu in ligand-free upconversion	1056.1	0	4.02	0.0059
Eu in OA-capped downshifting	1204.1	0	6.04	0.0090
Eu in ligand-free downshifting	1301.6	0	6.22	0.014
Nd in OA-capped	3962.9	0	0.20	0.00054
Nd in ligand-free	3593.2	0	0.22	0.00074
Samples in colloidal solution				
	a₁	y₀	t₁	Standard error
Er in OA-capped core	4258.1	0	0.051	0.000085
Er in ligand-free core	16574.0	0	0.026	0.000042
Er in OA-capped core-shell	2089.3	0	0.105	0.00018
Er in ligand-free core-shell	2198.7	0	0.094	0.00016
Tm in OA-capped	7154.3	0	0.26	0.00042
Tm in ligand-free	8630.1	0	0.21	0.00029
Eu in OA-capped upconversion	1147.6	0	2.90	0.0087
Eu in ligand-free upconversion	1219.7	0	2.72	0.0078
Eu in OA-capped downshifting	865.3	0	3.49	0.021
Eu in ligand-free downshifting	1099.5	0	3.78	0.010
Nd in OA-capped	1649.5	0	0.12	0.0008
Nd in ligand-free	1350.0	0	0.08	0.00065

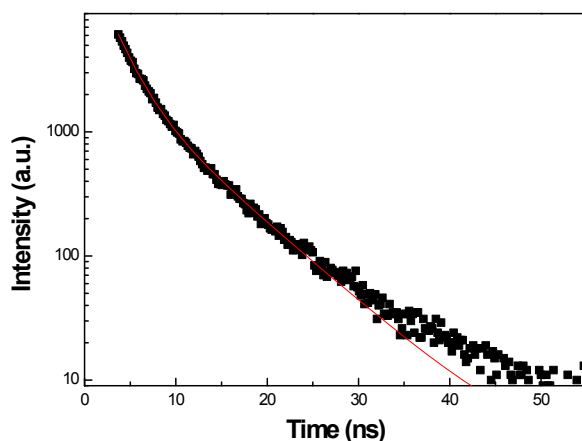


Figure S14. Luminescence decays of emission band peaked at 490 nm of NaGdF₄: 5 mol% Eu nanocrystals. The decay curve fits to a dual-exponential function, and the average lifetime is calculated to be 2.52 ns, indicating that this emission band could not be attributed to the emission of Eu³⁺.

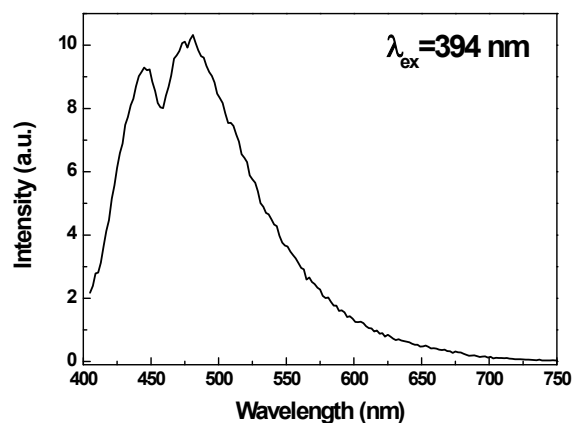


Figure S15. The downshifting spectra of left OA after acid treatment of OA-capped nanocrystals. The presence of broad emission band unambiguously confirm that the broad band in OA-capped NaGdF₄: 5 mol% Eu belong to the emission of surface-capped OA.

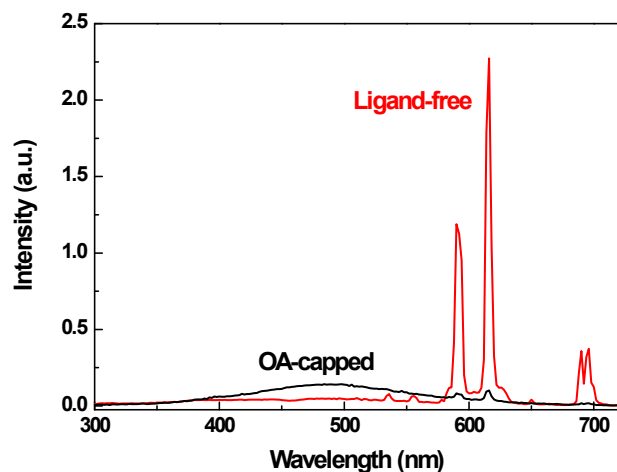


Figure S16. The downshifting spectra of OA-capped (black) and ligand-free (red) NaGdF₄: 5 mol% Eu nanocrystals in solid states under the excitation of 272 nm. In contrast to the excitation at 394 nm, more enhancement in emission intensity of Eu³⁺ between OA-capped and ligand-free samples excited at 272 nm, which should be attributed to the increased screening effect of OA from 394 nm to 272 nm.

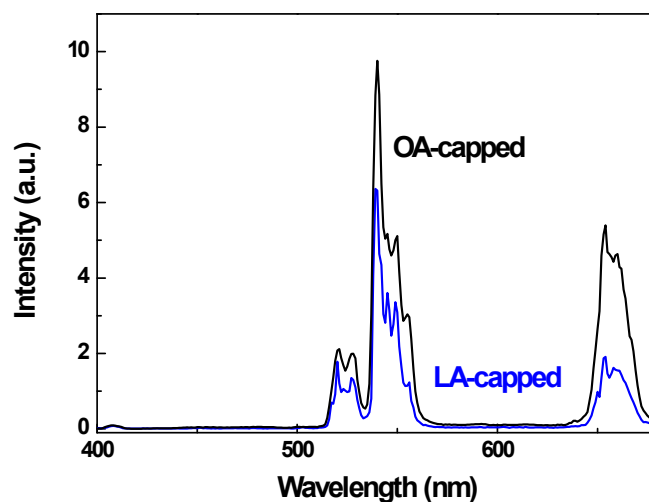


Figure S17. The emission spectra of OA-capped (black) and LA-capped (blue) NaGdF₄: 2 mol%Er, 18 mol% Yb nanocrystals in PDMS colloidal solutions. The emission intensity of LA-capped nanocrystals in solutions can only arrive 0.68 time as strong as that of OA-capped nanocrystals, which is stronger than that of ligand-free samples due to the presence of short-chain LA.

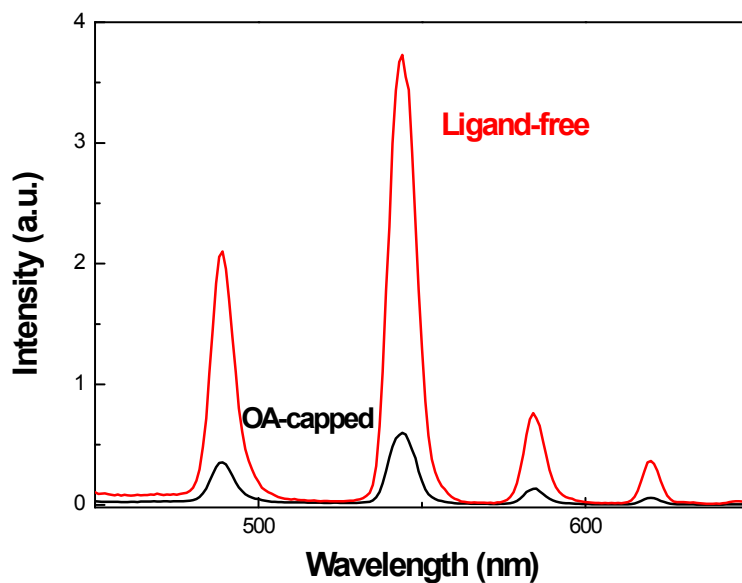


Figure S18. The emission spectra of NaGdF₄: 5 mol% Tb, 15 mol% Ce nanocrystals with OA-capped surface (black line) or ligand-free surface (red line) in PDMS solution. The excitation is 254 nm, and the concentrations for OA-capped and ligand-free nanocrystals in PDMS are 21.9 mg/mL and 20.0 mg/mL, respectively.

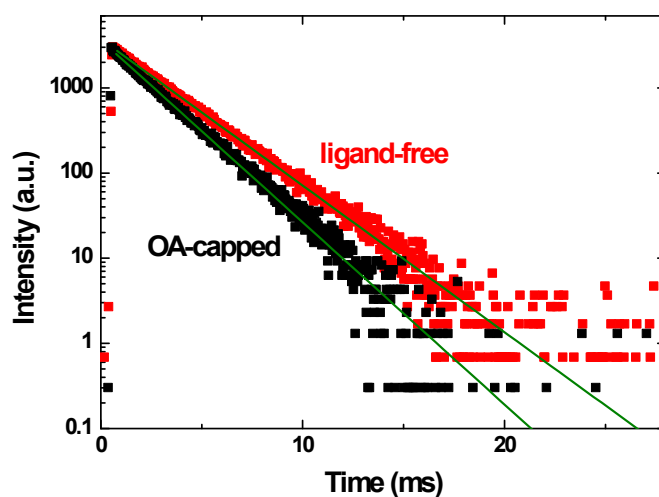


Figure S19. Time-dependent photoluminescence measurement of ${}^5D_4 \rightarrow {}^7F_5$ transition of Tb³⁺ for NaGdF₄: 5 mol% Tb, 15 mol% Ce nanocrystals with OA-capped (black) or ligand-free (red) surface. The lifetimes for OA-capped and ligand-free nanocrystals are calculated to be 2.02 and 2.52 ms, respectively.

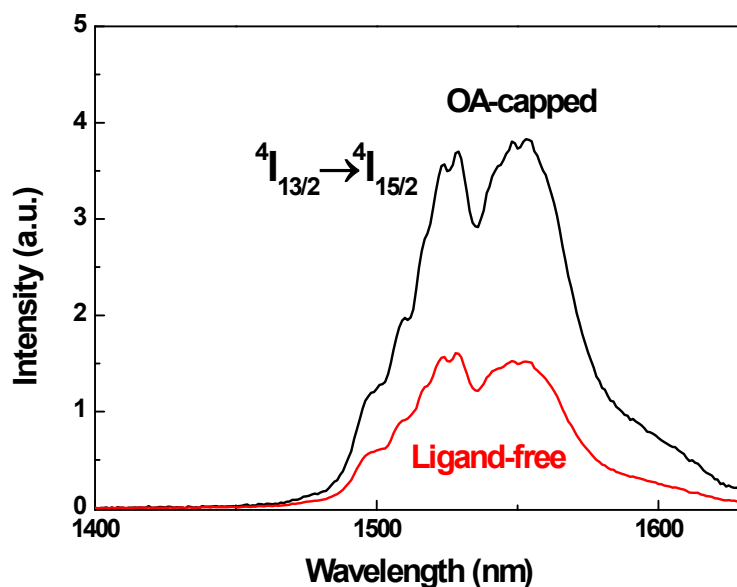


Figure S20. The emission spectra of NaGdF₄: 2 mol% Er, 20 mol% Yb nanocrystals with the surface being OA-capped (black line) or ligand-free (red line). The concentrations for OA-capped and ligand-free nanocrystals in PDMS are 23.3 and 20.0 mg/mL, respectively.

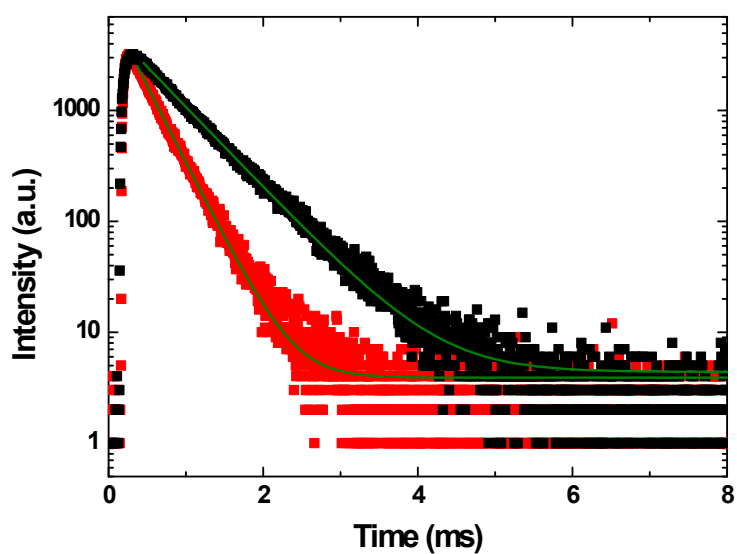


Figure S21. Time-dependent photoluminescence measurement of ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of NaGdF₄: 2 mol% Er, 20 mol% Yb nanocrystals with OA-capped (black) or ligand-free (red) surface. The lifetimes for OA-capped and ligand-free nanocrystals are calculated to be 0.60 and 0.35 ms, respectively.