Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ho^{3+}-Yb^{3+} doped $NaGdF_4$ nanothermometers emitting in BW-I and BW-II. Insight into the particle growth intermediate steps.

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Experimental details

The CF_3COONa was prepared according to a previously reported procedure.[1] All other chemicals were commercially purchased and used without further purification.

Synthesis of the $NaGdF_4$ and $NaGdF_4$:Ho,Yb nanoparticles

In a typical synthesis 0.5 mmol $GdCl_3$ was mixed with 4 mL of oleic acid and 6 mL of 1-octadecene in a 50 mL three-necked round-bottom flask. The mixture was heated to 120 °C under vacuum for 30 min with constant stirring. Subsequently, it was heated to 120 °C under N_2 flow with constant stirring for 30 min until a clear solution was formed. Afterwards, it was cooled down to 50 °C. Next, 1.25 mmol of CF_3COONa (powder) was added to the flask. The mixture was stirred for a few minutes and heated to 120 °C under vacuum for a few minutes to remove any present water. Afterwards the resulting solution was heated to 300 °C under N_2 flow and vigorous stirring for 40, 60 or 120 min. The obtained $NaGdF_4$ nanoparticles were precipitated by adding acetone and isolated by centrifugation. They were washed two times with acetone, and finally redispersed in cyclohexane.

Synthesis of the $NaGdF_4$:Ho,Yb nanoparticles

For the synthesis of doped $NaGdF_4$:Ho,Yb nanoparticles the same procedure was employed as above, but $LnCl_3$ (where Ln^{3+} = Gd, Ho, Yb used as different ratios) was used. The employed reaction time was 40 min.

Oleate ligand removal from $NaGdF_4$:Ho,Yb nanoparticles

The synthesis of oleate-free $NaGdF_4$:Ho,Yb nanoparticles was carried out according to previously reported protocol.[2] Briefly, oleate-capped nanoparticles dispersed with cyclohexane were mixed with 10 mL water and the pH was maintained at 4 by adding a 0.1 M HCl solution. The mixture was vigorously stirred for 2 h at room temperature. During the reaction the carboxylate groups of the oleate ligand were protonated and yielded oleic acid. The uncapped nanoparticles were recuperated by centrifugation after precipitation with acetone. The product was redispersed several times in acetone and centrifugated. After this the nanoparticles were dispersed in water forming a stable colloidal suspension.

Characterization

Bright-Field Transmission Electron Microscopy (BFTEM) images were taken using a Cs-corrected JEOL JEM2200FS device operated at 200 kV. The samples were prepared using holey carbon copper grids. Powder XRD patterns were recorded using a Thermo Scientific ARL X'TRA diffractometer equipped with a Cu Kα (l = 1.5405 Å) source, a goniometer and a Peltier cooled Si (Li) solid-state detector. The

XRD patterns were measured on nanoparticles coated with oleic acid. A few drops of a suspension of the nanoparticles in cyclohexane was placed on a Si plate and left to dry at ambient atmosphere. X-ray fluorescence (XRF) was measured using an XRF Supermini200 Rigaku to analyze the relative lanthanide (Gd, Ho, Yb) content. The room temperature and temperature dependent photoluminescence of nanoparticle colloidal suspensions was recorded. Colloidal suspensions were measured in quartz cuvettes (Starna cuvette type 23/Q/10) with a path length of 10 mm (at a concentration of 1 mg of the sample dispersed in 1 mL distilled water). Luminescence measurements were performed on an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup. A 640 nm CW laser (100 mW) was used as the steady state excitation source. A Hamamatsu R5509−72 photomultiplier was used to detect emission in the NIR region. The temperature-dependent luminescent measurements were performed using a Julabo refrigerated and heating F-25 circulator in a temperature range of 10 °C to 50 °C with steps of 5 °C, which was circulating through the cuvette holder supplied by the Edinburgh Instruments. Between every temperature step we waited 20 minutes for the temperature to stabilize. The temperature was controlled through the Julabo circulator sensor as well as sensor in the FLSP920 sample holder. All thermometric calculations were carried out using the *TeSenCalculator* software.

Table S1. Gd/Ho/Yb ratio in nanoparticles based on XRF analysis

Sample	% Gd	% Ho	% Yb
NP1	75.45	20.65	3.90
NP2	74.30	23.73	1.97
NP3	74.15	24.30	1.55

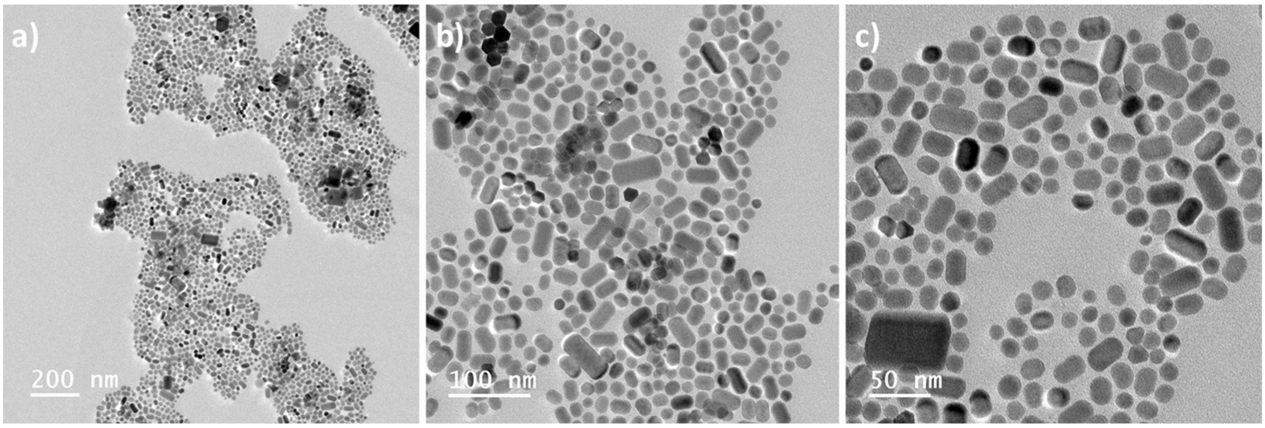

Fig. S1 BFTEM images of NP3 dispersing in distilled water after oleate ligand removal, indicating no change in morphology and no aggregations.

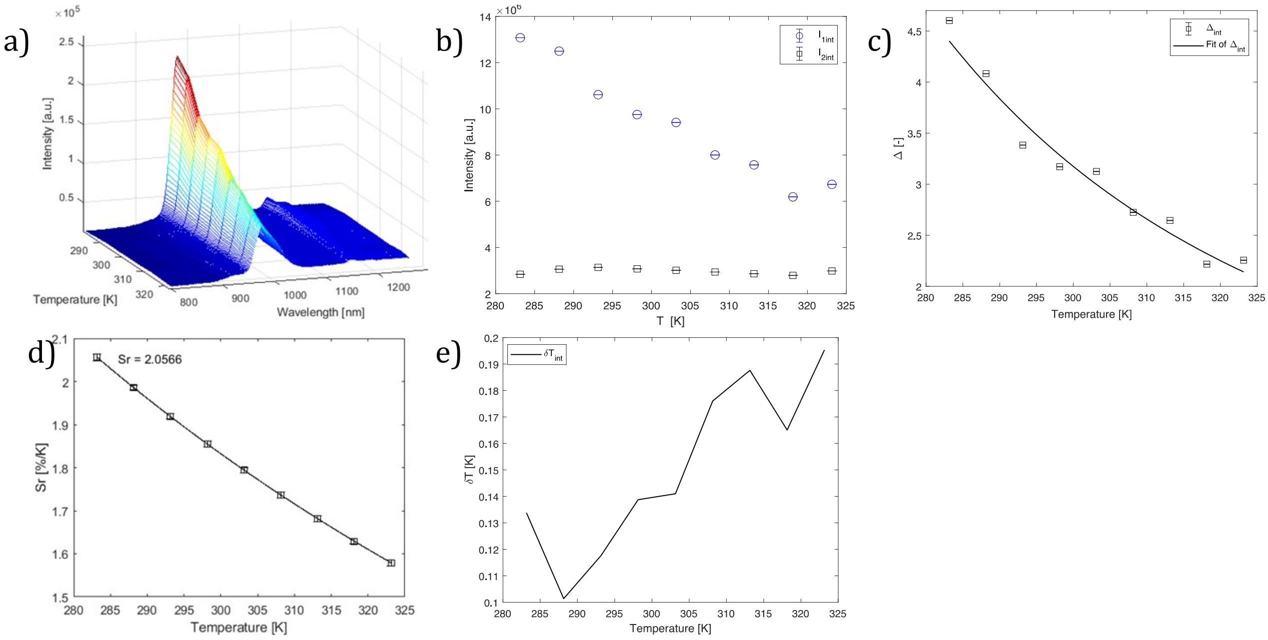

Fig. S2 (a) Emission map on NP2 recorded in cyclohexane at 283.15 – 323.15 K (10 – 50 ºC); (b) plot showing the emission intensity (based on integrated areas under the peak) of the 974 nm peak (blue circles) and 1181 nm peak (black squares); (c) plot showing the calibration curve for NP2 in cyclohexane upon usage of equation 2. The points show the experimental delta parameters and the solid line shows the least-squares fit of the experimental points (R^2 = 0.96686); (d) plot of the relative sensitivity (S_r) at varying temperatures, the solid line is a guide for the eyes; (e) graph depicting the temperature uncertainty over the regarded temperature range.

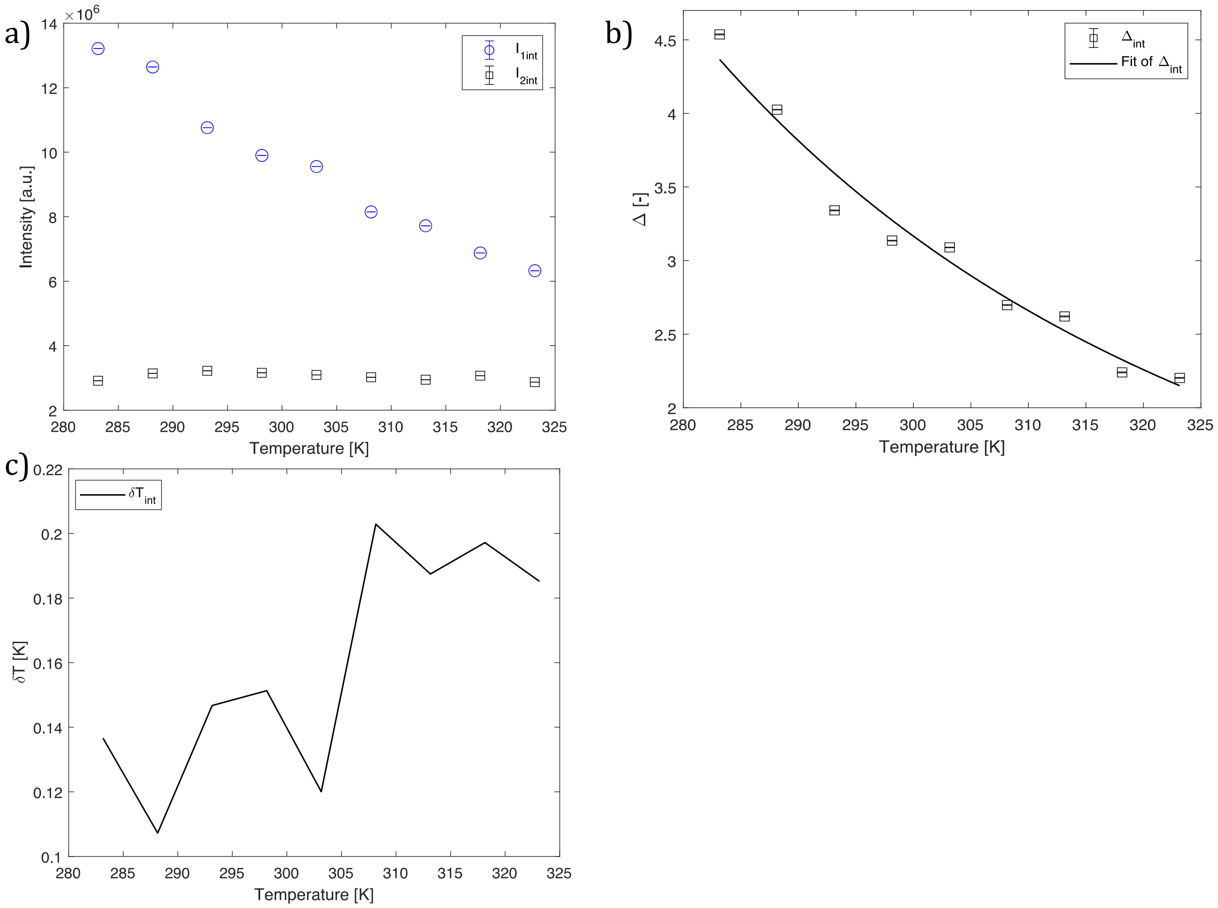

Fig. S3 (a) Plot showing the emission intensity (based on integrated areas under the peak) of the 974 nm peak (blue circles) and 1181 nm peak (black squares) recorded in H_2O at 283.15 – 323.15 K (10 – 50 ºC); (b) plot showing the calibration curve for NP2 in H_2O upon usage of equation 2. The points show the experimental delta parameters and the solid line shows the least-squares fit of the experimental points (R^2 = 0.97008); (c) graph depicting the temperature uncertainty over the regarded temperature range.

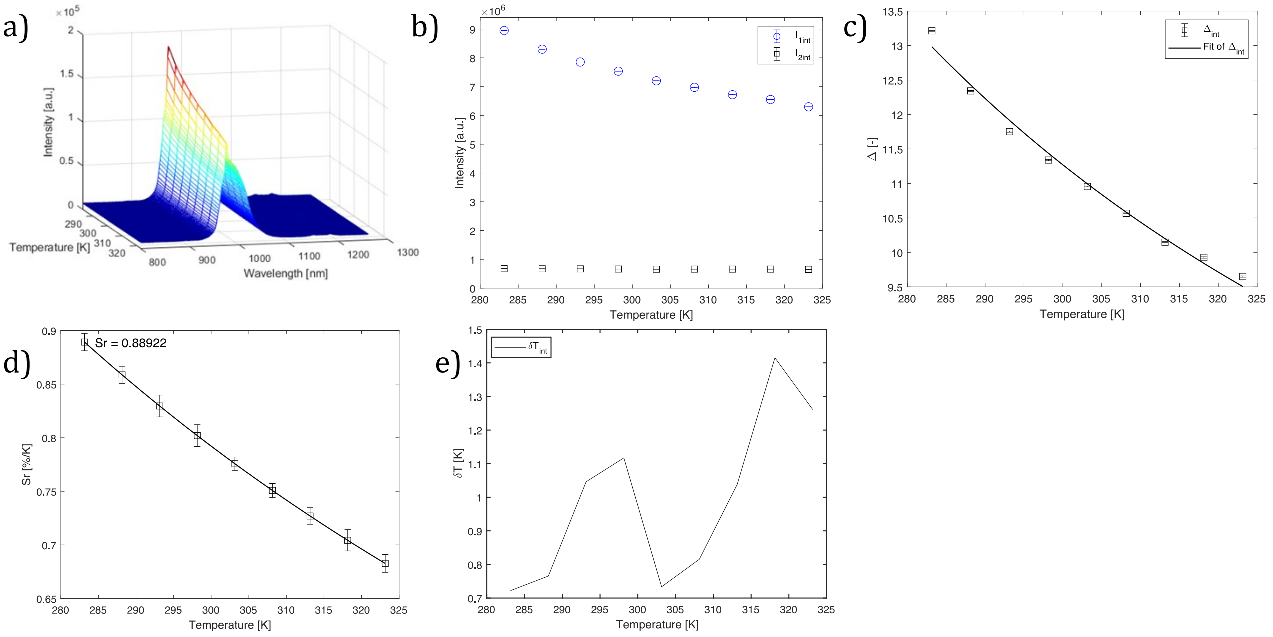

Fig. S4 (a) Emission map on NP3 recorded in H_2O at 283.15 – 323.15 K (10 – 50 ºC); (b) plot showing the emission intensity (based on integrated areas under the peak) of the 974 nm peak (blue circles) and 1181 nm peak (black squares); (c) plot showing the calibration curve for NP3 in H_2O upon usage of equation 2. The points show the experimental delta parameters and the solid line shows the least-squares fit of the experimental points (R^2 = 0.98445); (d) plot of the relative sensitivity (S_r) at varying temperatures, the solid line is a guide for the eyes; (e) graph depicting the temperature uncertainty over the regarded temperature range.

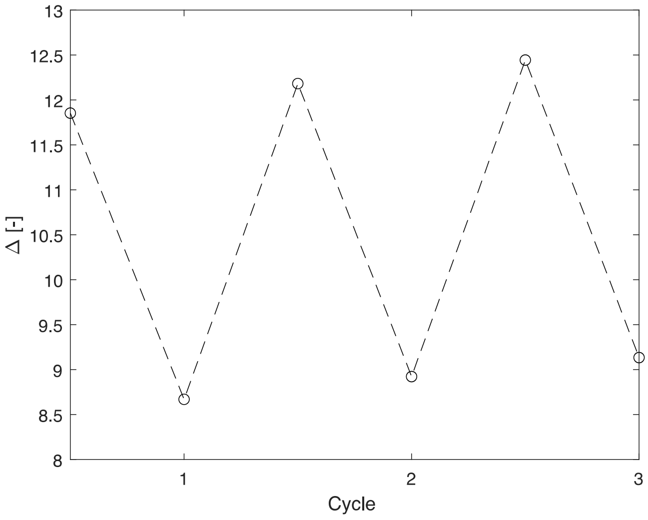

Fig. S5 Cycle test for NP3 carried out in H_2O.

References:

1. J. Liu, H. Rijckaert, M. Zeng, K. Haustraete, B. Laforce, L. Vincze, I. Van Driessche, A. M. Kaczmarek, R. Van Deun, Adv. Funct. Mater., 2018, 17, 1707365.
2. J. Liu, W. Bu, L. Pan, J. Shi, Angew. Chem. Int. Ed. 2013, 16, 4375.