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Electronic Supporting Information

Covering the optical spectrum through collective rare-earth doping of $NaGdF_4$ nanoparticles: 806 and 980 nm excitation routes

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Detailed experimental procedures

Precursor synthesis. Precursors for the core were prepared by mixing 0.9125 mmol Gd_2O_3 (99.99+ %), 0.25 mmol Yb_2O_3 (99.99+ %), 0.025 mmol Er_2O_3 (99.99+ %) and 0.0625 mmol Ho_2O_3 (99.99+ %) with 5 ml trifluoroacetic acid (99 %) and 5 ml of distilled water in a 50 ml three-neck round bottom flask. The mixture was then refluxed under vigorous stirring at 80 °C until a clear solution was obtained, at which point the temperature was decreased to 60 °C in order to slowly evaporate residual trifluoroacetic acid and water. Shell #1 and shell #2 precursors were prepared separately in analogous way as core precursors. However, 0.975 mmol Gd_2O_3 (99.99+ %), 0.25 mmol Yb_2O_3 (99.99+ %) and 0.0625 mmol Nd_2O_3 (99.99+ %) were used for shell #1, whereas 1.25 mmol Gd_2O_3 (99.99+ %) was used for the undoped shell #2. Precursors were obtained as solid dried materials and were used for the rare-earth nanoparticle (RENP) synthesis without further purification. All materials involved in precursor synthesis were obtained from Alfa Aesar, USA and used without further purification.

Synthesis of RENPs. An initial mixture of 12.5 ml each of oleic acid (90 %, Alfa Aesar, USA) and 1-octadecene (90 %, Alfa Aesar, USA) was prepared in a 100 ml three-neck round bottom flask (Solution A). Aside, 2.5 mmol of sodium trifluoroacetate (98 %, Alfa Aesar, USA) was added to the dried core precursors together with 7.5 ml each of oleic acid and 1-octadecene (Solution B). Both Solutions A and B were degassed at a temperature of 145 °C under vacuum with magnetic stirring for 30 min. After degassing, Solution A was placed under inert Ar atmosphere and the temperature was slowly raised to 315 °C. Solution B was then injected into the reaction vessel containing solution A using a syringe and pump system (Harvard Apparatus Pump 11 Elite, USA) at a 1.5 ml/min injection rate. The mixture was left at 315 °C

temperature under vigorous stirring for 60 min to form the $NaGdF_4$:Er^{3+}, Ho^{3+}, Yb^{3+} core. Subsequently, in order to initiate the growth of the Yb^{3+} and Nd^{3+} doped shell, a solution of shell #1 precursors and 2.5 mmol of sodium trifluoroacetate dissolved in 7.5 ml each of oleic acid and 1-octadecene (Solution C, degassed at 145 °C under vacuum with magnetic stirring for 30 min) was injected into the reaction vessel at the same 1.5 ml/min injection rate. The mixture was left at 315 °C under vigorous stirring for 60 min to form the $NaGdF_4$:Nd^{3+}, Yb^{3+} shell #1 around the previously formed $NaGdF_4$:Er^{3+}, Ho^{3+}, Yb^{3+} core. Finally, Solution D (undoped shell #2 precursor, 2.5 mmol sodium trifluoroacetate, 7.5 ml oleic acid, 7.5 ml 1-octadecene, degassed at 145 °C under vacuum with magnetic stirring for 30 min) was also injected at 1.5 ml/min injection rate resulting in the growth of the outer passivating shell #2 consisting of the undoped $NdGdF_4$. Fig. 1A summarizes the steps of the multilayered RENP synthesis. After a total of 3 h of reaction time, the final mixture was allowed to cool down to room temperature. Subsequently, oleate-capped core/shell/shell RENPs were precipitated with ethanol and recollected via centrifugation at 6000 RPM for 15 min. The obtained RENPs were washed twice with a mixture of hexane/ethanol (1/4 v/v) and precipitated via centrifugation. Finally, the oleate-capped RENPs were redispersed in hexane for storage, structural characterization and optical studies.

RENP transfer to water via phospholipid coating. The obtained RENPs were transferred into an aqueous environment following a modified phospholipid coating method. 50 mg of RENPs were redispersed in 4 ml of chloroform (99.9 %, Sigma Aldrich, Germany) together with 5.6 mg (2 μmol) of 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethylene glycol)-2000] (PEG-DOPE) phospholipids (Avanti Polar Lipids, Inc., USA). The content was swirled by hand, following chloroform evaporation at 45 °C under inert Ar atmosphere resulting in a dry phospholipid film containing the RENPs. Subsequently, distilled water (5 ml) was added in order to hydrate the dry film under sonication at 65 °C temperature for 60 min. Finally, the mixture was passed through 0.45 μm and 0.2 μm filters step-wise to remove large phospholipid and RENP-phospholipid structures.

Structural characterization of RENPs. The crystallinity and phase of the core-only, core/shell and core/shell/shell RENPs were determined via X-ray powder diffraction (XRD) analysis with a Bruker D8 Advance Diffractometer using CuKα radiation. The morphology and size distribution of the core-only, core/shell, core/shell/shell RENPs were further investigated by transmission electron microscopy (TEM, Philips Tecnai 12). The particle sizes were determined from TEM images using ImageJ analysis software with set sizes of 300 particles per core, core/shell and core/shell/shell samples. Fourier transform infrared (FTIR) spectra of oleate-capped RENPs, pure PEG-DOPE and RENPs encapsulated in PEG-DOPE micelles (*aq*RENPs) were recorded with a ThermoFisher Scientific Nicolet 6700 FTIR spectrometer using a mixture of dried samples with KBr as a reference.

Optical characterization of RENPs in the visible and NIR spectral regions. Visible and NIR emission spectra of core-only, core/shell and core/shell/shell RENPs in hexane and water were obtained at room temperature under laser diode excitation of 806 nm (Lumics, Germany) or 980 nm (BTW, China). Both 806 and 980 nm laser power densities on the target varied between 14 and 140 W/cm^2 (between 20 and 180 mW in terms of absolute laser power) for upconversion and NIR emission excitation studies. The visible upconversion emission was collected using a lens at a 90^o angle from the excitation beam and recorded with an Avaspec-ULS2048L spectrometer (Avantes, Netherlands). Maintaining the same optical path configuration, the NIR emission was recorded separately with a Shamrock 500i monochromator (Andor, Ireland) equipped with an iDus InGaAs 1.7 NIR detector (Andor, Ireland). In order to remove any stray light from the excitation source, a short pass 785 nm filter (Semrock, Inc., USA) was used for the visible range spectrum acquisition under both wavelengths of excitation. For the NIR detection, long pass (LP) 830 or 980 nm filter (Semrock, Inc., USA) was used when samples were excited by 806 or 980 nm wavelengths, respectively. Core-only, core/shell and core/shell/shell RENPs in hexane and *aq*RENPs in water were maintained at approximate 1 wt% of concentration for all optical measurements. All of upconversion and NIR emission spectra presented in the main text were recorded under 140 W/cm^2 power density for both 806 and 980 nm wavelengths of laser excitation.

Complex formation with chlorin e_6 (Ce_6) and NIR emission transmission through tissue. The interaction between *aq*RENPs and Ce_6 (Frontier Scientific Inc., USA) was facilitated by adding a small amount of Ce_6 stock solution to *aq*RENPs (~1 wt%) dispersed in phosphate buffer solution of pH 7, resulting in a final molar concentration of Ce_6 of around 10 μM. Upconversion spectrum of *aq*RENPs was recorded under 806 nm (140 W/cm^2) wavelength of excitation before and after the addition of Ce_6. Direct fluorescence of Ce_6 (alone and in the presence of *aq*RENPs) was recorded under 440 nm LED excitation (Thorlabs, USA).

NIR images were acquired with an InGaAs NIR imaging camera (XEVA-1781, Xenics, Belgium) after the excitation (806 nm; 140 W/cm^2) of *aq*RENPs sample in quartz cuvette of 1 cm optical path. A 90^o optical geometry was maintained between the excitation beam and the NIR camera objective. Chicken breast tissues of various thicknesses (1 to 10 mm) were placed between the excitation trace and the NIR camera. Specific LP filters (830LP, 980LP, 1150LP or 1450LP) were placed in front of the NIR camera objective in order to systematically limit the collection of the NIR emitted light to the specific NIR spectral range.

RENP characterization: X-ray powder diffraction analysis and size distribution

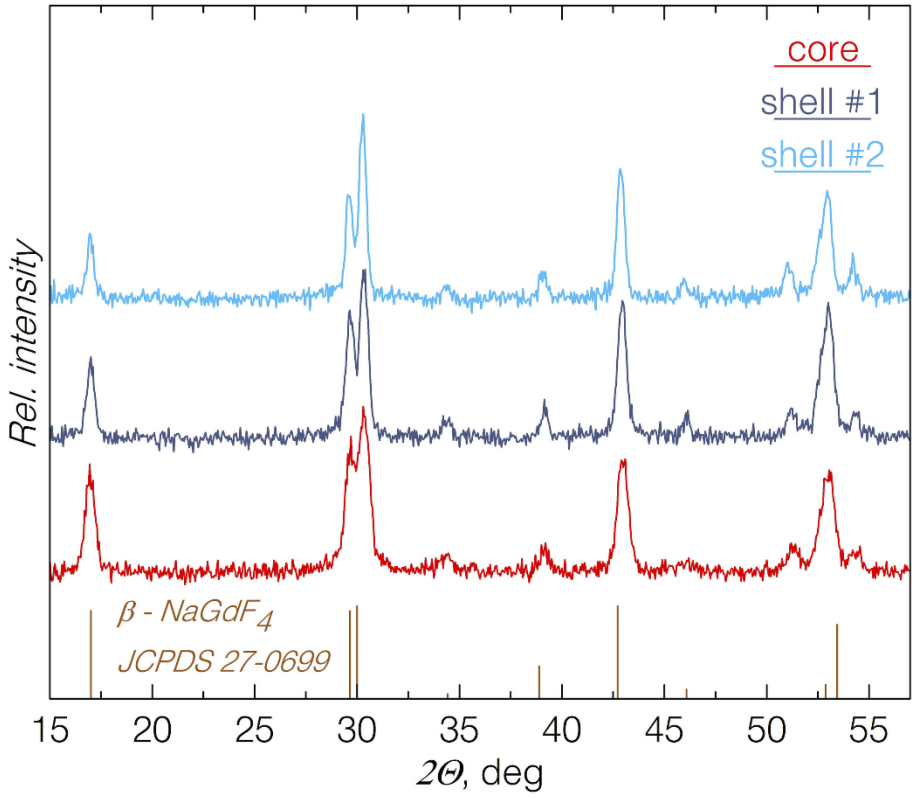

Figure S1. X-ray powder diffraction analysis of core-only, core/shell and core/shell/shell $NaGdF_4$: 2% Er^{3+}, 5% Ho^{3+}, 20% Yb^{3+} / $NaGdF_4$: 5% Nd^{3+}, 20% Yb^{3+} / $NaGdF_4$ RENPs. Hexagonal (β) phase crystallinity of the core and subsequently grown shells (#1 and #2) is observed.

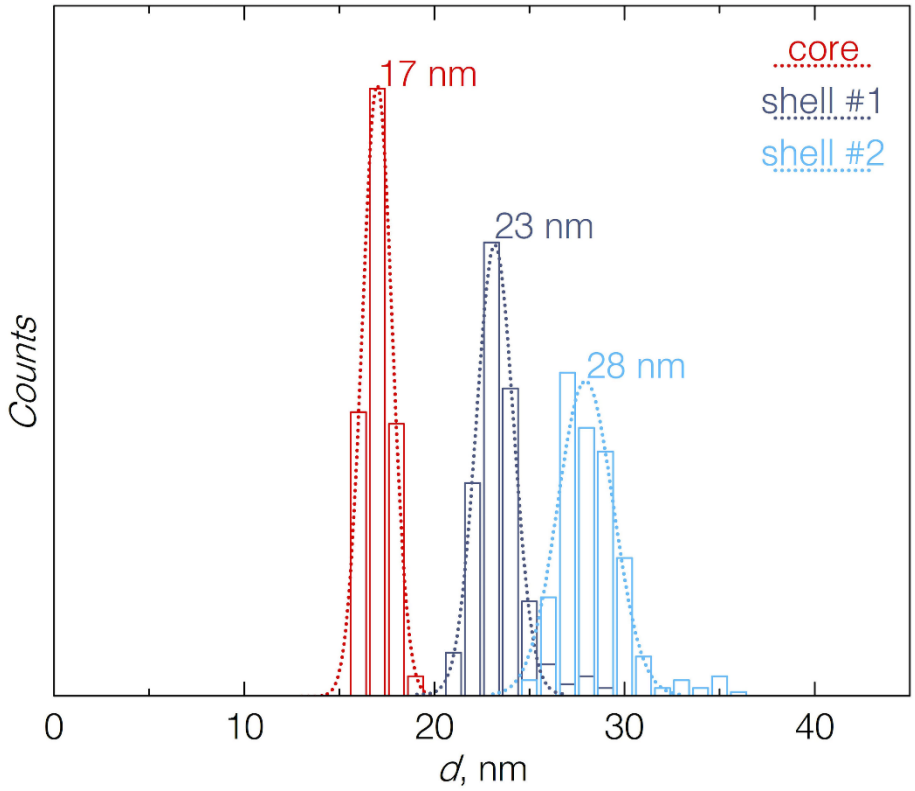

Figure S2. Size of core-only (17.0±0.8 nm), core/shell (23.0±1.0 nm) and core/shell/shell (28.0±1.5 nm) RENPs determined from respective TEM images (set size of 300 particles per each sample).

Direct water heating by 806 and 980 nm laser irradiation

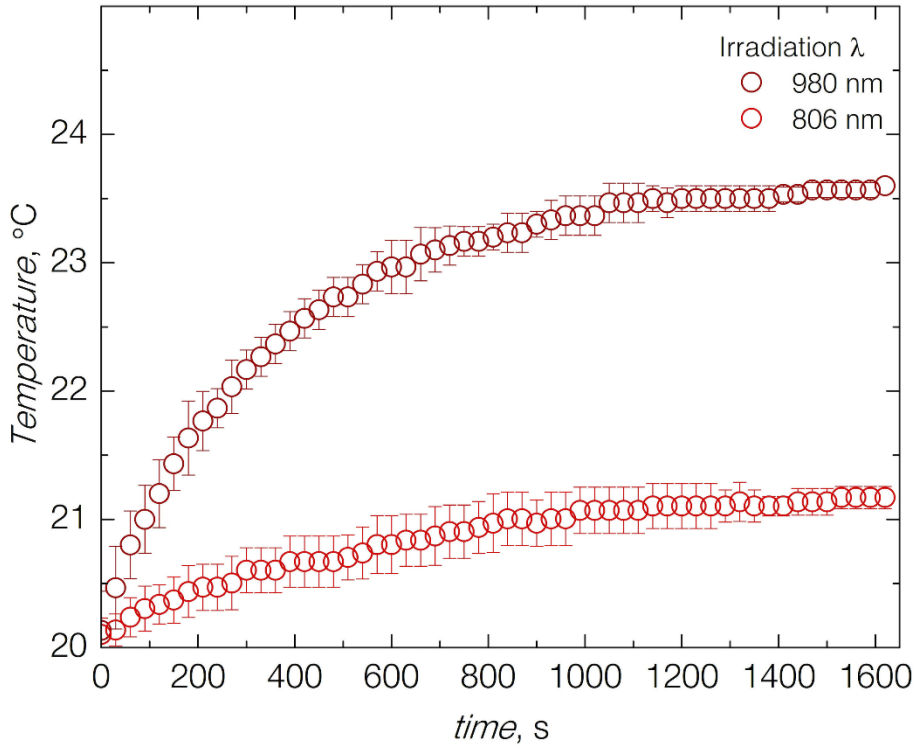

Figure S3. Temperature change in 1 ml of distilled water under 980 or 806 nm wavelength of laser irradiation (140 W/cm^2). The water temperature increased to 23.5 °C from the ambient room temperature of around 20 °C after a little more than 15 min of 980 nm laser irradiation, while only minor temperature elevation to 21 °C was determined when 806 nm wavelength of irradiation was used.

Surface Modification: FTIR Spectroscopy

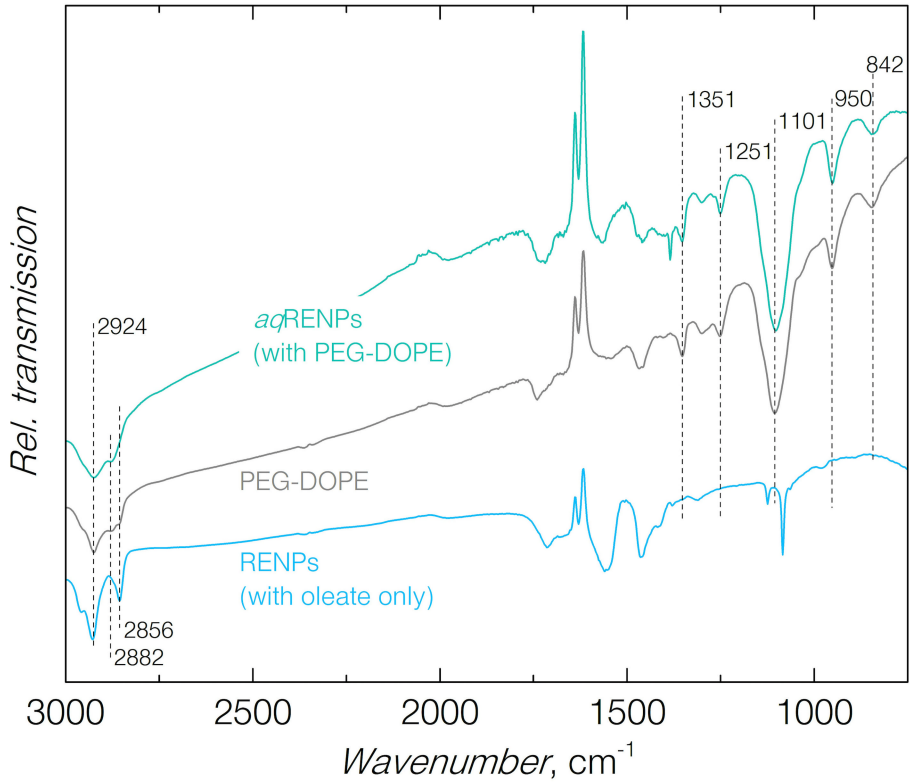

Figure S4. FTIR spectra of PEG-DOPE phospholipids, RENPs (oleate-capped), and *aq*RENPs (modified with PEG-DOPE). PEG-DOPE specific infrared absorption bands are observed in the *aq*RENPs. These are located respectively at 2924 and 2882 cm^{-1} (aliphatic C-H_2 stretching) and 1737 cm^{-1} (symmetrical C=O stretching) while those located in the region 850 - 1350 cm^{-1} are a distinctive feature of phospholipids since they mainly stem from the phosphate group (PO_4).