

## Supporting Information

### *Dual light emitting nanoparticles: second harmonic generation combined with rare-earth photoluminescence*

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### Experimental section

**Chemicals.** Titanium(IV) butoxide (Ti(OBut)<sub>4</sub>), potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), hydrochloric acid (HCl) (37 %), europium(III) chloride hexahydrate (EuCl<sub>3</sub>·6H<sub>2</sub>O), sodium triphosphate pentabasic (TPP - Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>), lanthanum(III) nitrate hexahydrate (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), europium(III) nitrate pentahydrate (Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), were purchased from Sigma-Aldrich and used as received.

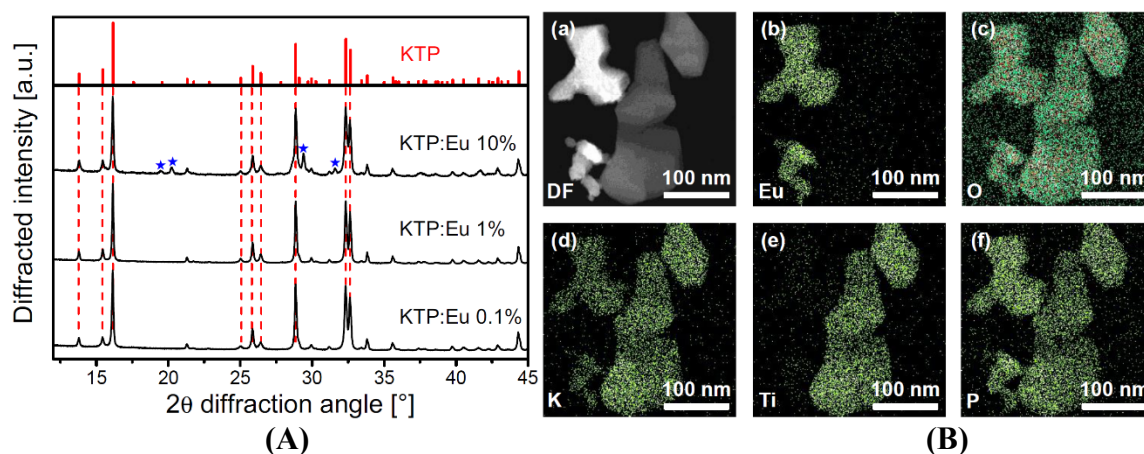
**Synthesis of KTP:Eu nanoparticles.** This process is adapted from [13] assuming Eu ions occupy the Ti sites in the KTP lattice. For a 1 % substitution, 9.9 mmol of Ti(OBut)<sub>4</sub> and 0.1 mmol of EuCl<sub>3</sub>·6H<sub>2</sub>O dissolved in 10 mL of water were added to 10 mL of HCl dissolved in 40 mL of water. After 10 minutes of stirring, 10 mmol of KH<sub>2</sub>PO<sub>4</sub> dissolved in 30 mL of water were added. A white precipitate appeared instantly. Finally a saturated solution of K<sub>2</sub>CO<sub>3</sub> was added until pH ~6. The mixture was left under stirring for 24 h. The precipitate was retrieved by a 20 minute centrifugation at 15500 rpm and then dried at 80 °C for 24 h. The ground white amorphous powder was annealed during 2 hours at 700 °C. Finally the powder was washed 5 times with water to completely remove potassium chloride and then dispersed into 20 mL of water.

**Synthesis of KTP@LaPO<sub>4</sub>:Eu nanoparticles.** For a LaPO<sub>4</sub>:Eu 5 % shell, 600 μL of a ~150 nm KTP nanoparticles solution (c ~ 80g/L) previously prepared [13], were diluted in 10 mL of water. Then 67 mg (149 μmol) of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 3 mg (7 μmol) of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O dissolved in 10 mL of water were added followed by 61 mg (157 μmol) of TPP dissolved in 10 mL of water. The temperature was constantly held at 70 °C during 3 h. The nanoparticles were retrieved by a 20 minute centrifugation at 25000 rpm then washed 5 times with water and finally dispersed in 10 mL of water. The same process was applied a second time to this solution to obtain a thicker shell.

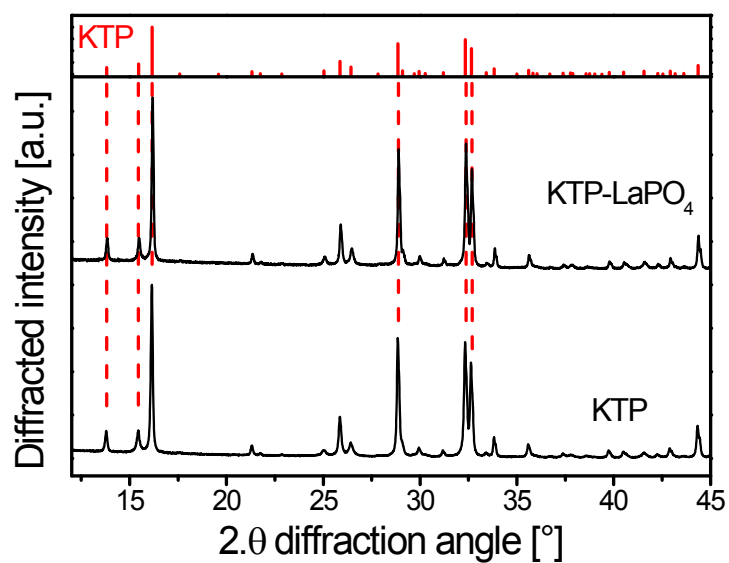
**Structural characterizations.** X-ray powder diffraction (PXRD) was achieved using a Phillips X-pert equipment with Cu K $\alpha$  radiation. The reference used for crystalline phase identification is the JCPDS file n° 01-078-1342 (KTiOPO<sub>4</sub>). Dynamic Light Scattering measurements were performed on Malvern Instruments (Zetasizer). Structural studies and chemical analysis by Scanning Transmission Electron Microscopy (STEM) have been done with a spherical aberration corrected Jeol 2200 FS TEM/STEM microscope operating at 200 keV and equipped with an energy dispersive X-ray analysis (EDX) system. The probe current was 150 pA with a probe size (FWHM) of 0.12nm. The convergence half angle of the probe was 30 mrad, and the inner and outer half angles for the annular dark-field (ADF) detector were 100mrad, and 170mrad, respectively. The High Angle Annular Dark Field (HAADF) STEM images are realized with the same probe than the EDX measurements. The EDX elemental maps are obtained from the K $\alpha$  lines for O, P, K, Ti and L $\alpha$  lines for the La and Eu.

**Optical characterizations.** Photoluminescence properties of colloidal suspensions were recorded using a commercial spectrofluorimeter (Jobin-Yvon Horiba, Fluoromax 4). The photoluminescence and SHG characteristics of individual nanoparticles were recorded using a home-made confocal microscope, equipped with an AFM head to determine simultaneously the particle size (Figure S4). For SHG, the particles previously deposited onto a quartz substrate were excited using a femto-second pulsed laser (Tsunami, Spectra-Physics) at 990 nm, with a repetition rate of 80 MHz and a pulse duration of 100 fs. The excitation beam was focused onto the sample using a x60 objective (Olympus) with a numerical aperture of 1.35. The sample was scanned and its fluorescence collected via the same objective, filtered and recorded using avalanche photodiodes (APD) in the photon-counting regime. For photoluminescence, the sample was excited at 532 nm using a commercial CW laser via the objective. Similarly the sample was scanned and its fluorescence was collected via the objective, filtered, sent through a pinhole and recorded onto an APD.

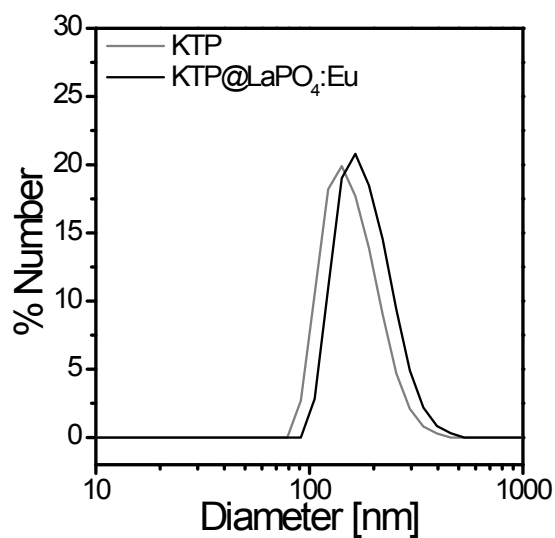
## Figures



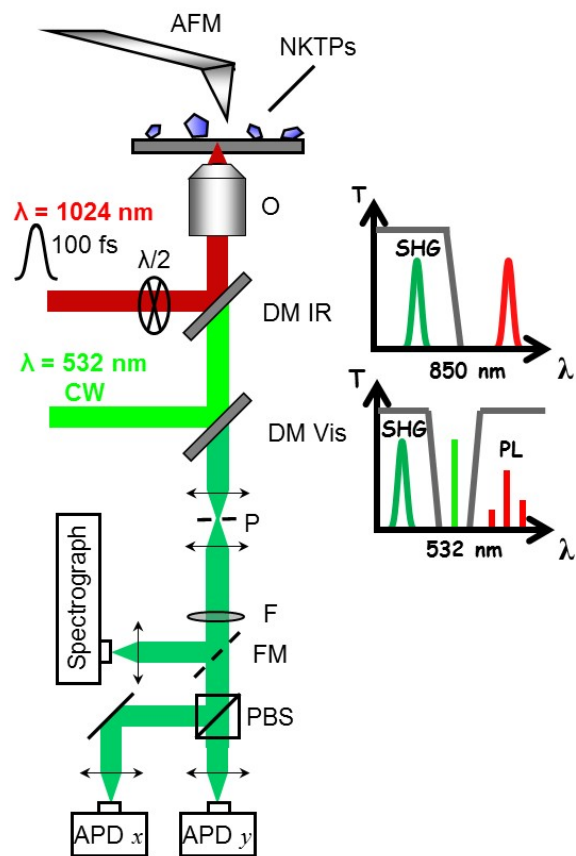
**Figure S1.** A) Powder X-Ray diffraction patterns of pure KTP and KTP doped with 10, 1, 0.1 % Eu nanoparticles. All peaks correspond to the KTiOPO<sub>4</sub> phase (JCPDS file n°01-078-1342) except those marked with an asterisk, corresponding to a parasitic phase. B) STEM images of several KTP:10%Eu nanoparticles. (a) HAADF image (b) EDX Eu (c) EDX O (d) EDX K (e) EDX Ti and (f) EDX P chemical maps.



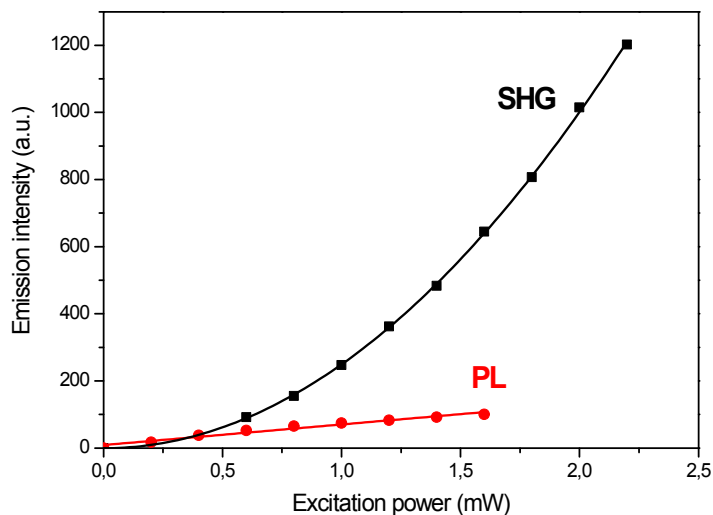
**Figure S2.** Powder X-Ray diffraction pattern of KTP@LaPO<sub>4</sub>:Eu nanoparticles and those of KTP nanoparticles and the reference JCPDS file n°01-078-1342.



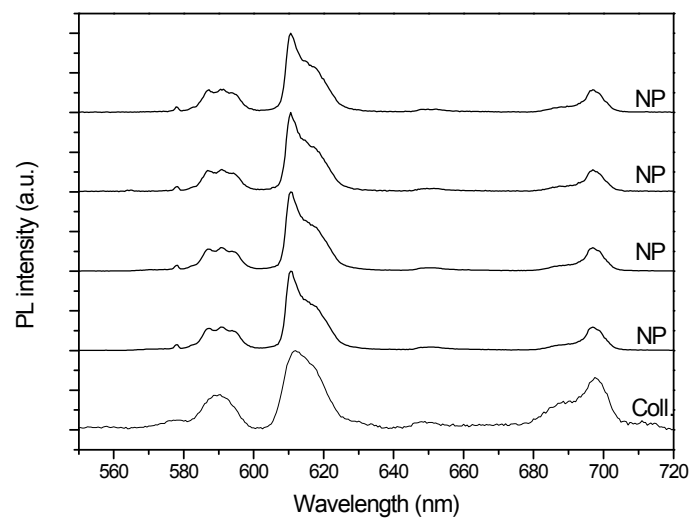
**Figure S3.** DLS size distribution curves of colloidal suspension of KTP nanoparticles before (grey line) and after the growth of LaPO<sub>4</sub>:Eu shell (black line).



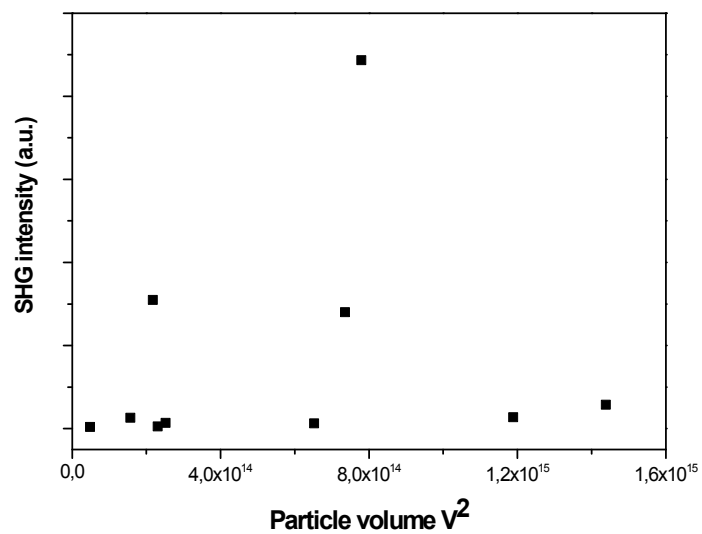
**Figure S4:** Experimental setup to determine SHG and PL signals of individual  $\text{KTP@LaPO}_4\text{:Eu}$  nanoparticles, as well as their size.



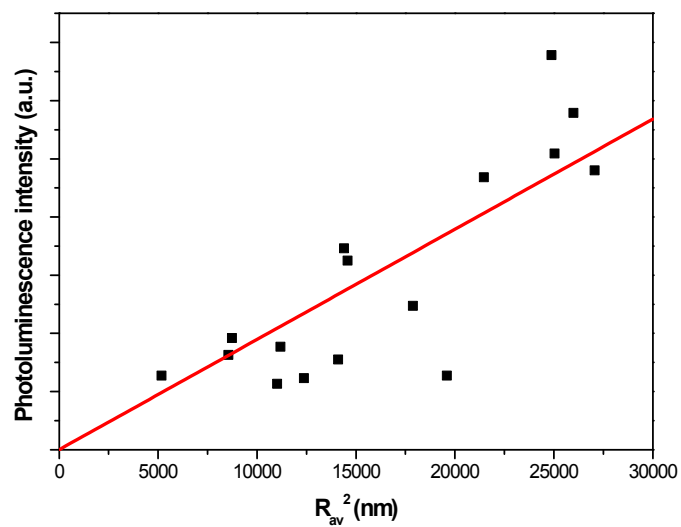
**Figure S5:** Evolution of SHG and PL intensities as a function of the pump power. The fits show a linear trend for the PL signal and a quadratic evolution for the SHG signal.



**Figure S6:** Few PL spectra of individual nanoparticles (NP) under a 532-nm excitation and the spectrum of the colloidal solution (Coll.) under a 395-nm excitation.



**Figure S7.** Evolution of the SHG intensity as a function of  $V^2$  where  $V$  is the volume of the  $\text{KTP@LaPO}_4\text{:Eu}$  nanoparticles.



**Figure S8.** Evolution of the photoluminescence intensity as a function of  $R^2$  where  $R$  is the radius of the KTP@LaPO<sub>4</sub>:Eu nanoparticles. The linear curve has a regression coefficient of 0.91 and intercepts zero.