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Control of upconversion luminescence by gold nanoparticle size: from quenching to enhancement

Electronic Supplementary Information (ESI)

Diego Mendez-Gonzalez,[a] Sonia Melle,*[b] Oscar G. Calderón,[b] Marco Laurenti,[a] E. Cabrera-Granado,[b] Ana Egatz-Gómez,[c,d] Enrique López-Cabarcos,[a] Jorge Rubio-Retama,[a] and Elena Díaz[e]

Contents

[a] *Department of Chemistry in Pharmaceutical Sciences, Complutense University of Madrid, E-28040 Madrid, Spain*
[b] *Department of Optics, Complutense University of Madrid, E-28037 Madrid, Spain. E-mail: smelle@fis.ucm.es*
[c] *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, United States.*
[d] *Center for Applied Structural Discovery, The Biodesign Institute, Arizona State University, Tempe, Arizona 85281, United States*
[e] *GISC, Department of Materials Physics, Complutense University of Madrid, E-28040 Madrid, Spain*

S1. Analysis of the luminescence decay signals.

Luminescence decay time was obtained by fitting the decay curve to a single exponential function. We consider a fitting time window from t_{ini} to t_{final} where the final time was set to $t_{final} = 1.2$ ms. For each experimental decay curve, we calculated around 25 fits by changing the initial fitting time t_{ini} within the range where the luminescence intensity varies from 70% to 30% of its maximum value (shadowed area). This fitting procedure gives us an average lifetime with its standard error.

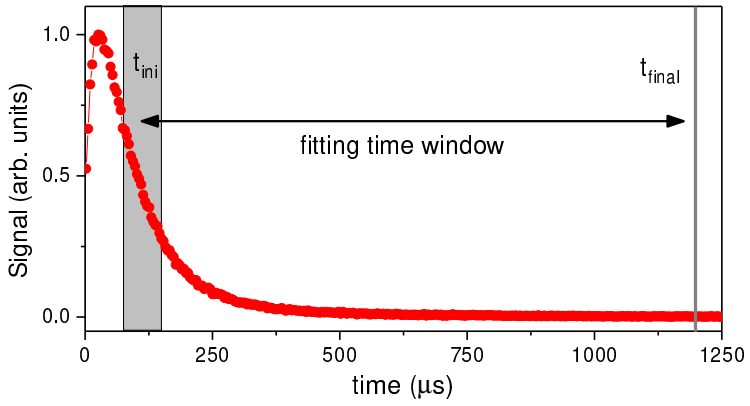

Fig. S1. Exponential decay luminescence curve showing the fitting procedure.

S2. Luminescence rise time measurements for samples with Au_{66nm} NPs and UCNPs.

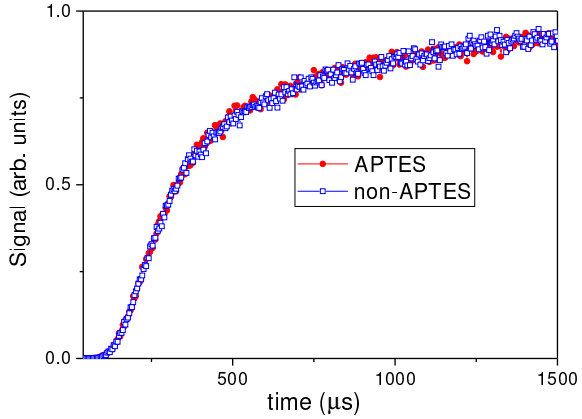

Fig. S2. Normalized luminescence rise curves at 540 nm (transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions) for 100 μL of UCNPs ethanol dispersion after adding 8 μL of Au_{66nm} NPs aqueous dispersion, for APTES-UCNPs (solid red circles) and non-APTES-UCNPs (open blue squares). Both signals follow the same temporal behavior which, in principle, rules out the excitation enhancement phenomenon. Excitation laser at 976 nm with 2 ms pulses at 125 Hz repetition rate.

S3. Absorbance spectra for samples with Au_{66nm} NPs and UCNPs.

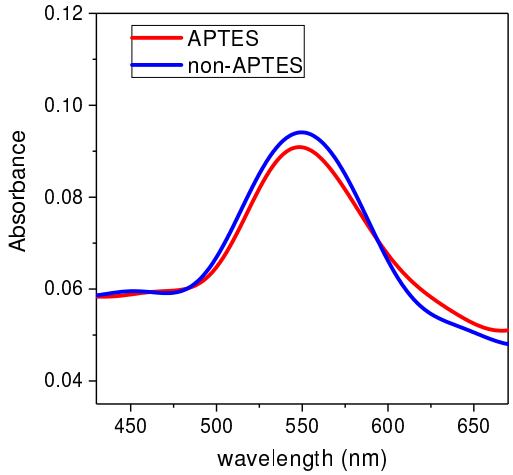

Fig. S3. Absorbance spectrum for 100 μL of APTES-UCNPs (red lines) and non-APTES-UCNPs (blue lines) dispersion after adding 8 μL of Au_{66nm} NPs dispersion. This result rules out a change of plasmon resonance due to the interaction of AuNPs with the UCNPs mediated by APTES.

S4. Luminescence efficiency for 34 nm-diameter UCNPs.

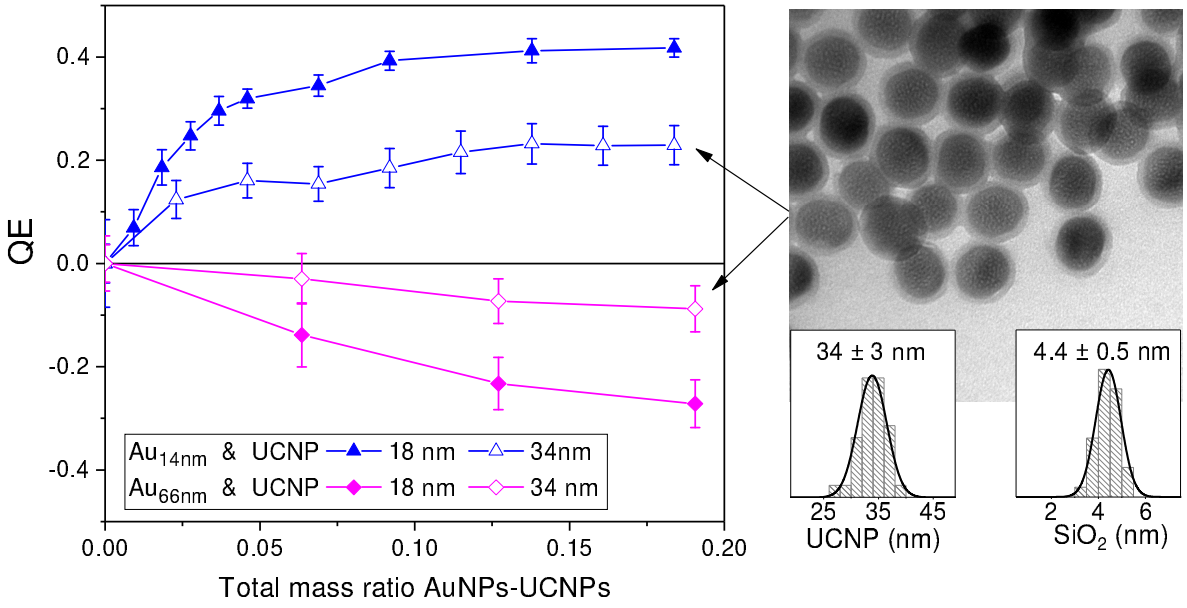

Fig. S4. (Left) Upconversion luminescence quenching efficiency, QE (from Eq. 1), as a function of the total mass of AuNPs normalized to the total mass of UCNPs. UCNPs with 34 nm-diameter (open symbols), and 18 nm-diameter (solid symbols). (Right) TEM from $NaYF_4$:Yb,Er@SiO_2 UCNPs with particle diameter (34 $\pm$ 3 nm) and silica shell thickness (4.4 $\pm$ 0.5 nm). Experiments were performed in the same conditions as those in Fig. 5, 100 μL of an ethanol dispersion of UCNPs@SiO_2-NH_2 (APTES-UCNPs) at 0.1 g/L is mixed with an increasing volume of an AuNPs aqueous dispersion. An ethanol dispersion containing UCNPs@SiO_2 (non-APTES-UCNPs) was used as a reference.

S5. Detailed description of the simulated luminescence decay curves of UCNPs interacting with AuNPs.

We describe the parameter values used in the simulations of the luminescence decay. The energy level scheme of the system is shown in Fig. S5.

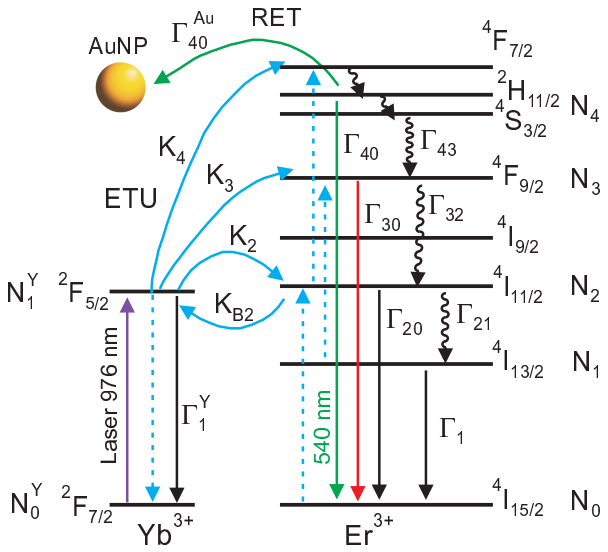

Fig. S5. Energy level diagram for Yb^{3+} and Er^{3+} ions. Blue lines represent the ETU mechanism that populates the green emission levels $^2H_{11/2}$ and $^4S_{3/2}$ by a 976 nm laser. The luminescence emission from these levels is represented by a solid green line. Solid lines represent the radiative decays while wavy lines are the non-radiative decays to next lower level. The RET process to the AuNP is also shown

The metastable level 1 ($^4I_{13/2}$) of Er^{3+} ions decays radiatively to the ground state $^4I_{15/2}$ with a decay time of $1/\Gamma_1 = 10$ ms. The same occurs for level 1 of Yb^{3+} ions with a decay time of $1/\Gamma_1^Y = 2$ ms. The rest of energy levels of Er^{3+} ions present two contributions, a radiative decay rate to the ground sate in the millisecond range ($1/\Gamma_{20} = 10$ ms, $1/\Gamma_{30} = 1$ ms, and $1/\Gamma_{40} = 1$ ms) and a faster nonradiative decay rate to the next lower level (partially due to multiphonon relaxation). Here, we used as a parameter the intrinsic quantum yield for the green level 4 $\eta_0 = \Gamma_{40}/(\Gamma_{40}+\Gamma_{43})$. We choose a value in accordance with the ones used in the simulations of the quenching efficiency (see Fig. 7) and with the aim of obtaining a N_4 population lifetime similar to the upconversion green luminescence lifetime found in the experiments ($\simeq 85$ μs). We took $\eta_0 = 0.04$, which leads to $\Gamma_{43} = 2.4\times10^4$ s^{-1}. We considered the same value for the two upper levels $\Gamma_{32} = \Gamma_{43}$ and a lower value for level 2 according to the larger energy to the next lower level ($\Gamma_{21} = 0.7\Gamma_{43}$). K_2, K_3 and K_4 are the coefficients of the Förster resonance energy transfer from the Yb^{3+} ion (donor) to the Er^{3+} ion (acceptor) in the energy levels 2, 3, and 4, respectively[1,2]. K_{B2} is the coefficient of back energy transfer from the Er^{3+} ion in level 2 to the Yb^{3+} ion. We took the value $K_2 = 4\times10^{-16}$ cm^{3}s^{-1} and a lower value for the other energy transfer coefficients $K_{B2} = K_3 = K_4 = 0.17K_2$ to obtain a N_4 population lifetime close to experimental one around 85 μs. Last, I/I_{sat} is the excitation laser intensity normalized to the saturation intensity of the transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ for the Yb^{3+} ions, whose value was estimated in the Experimental Section: Optical characterization, $I_{sat} \simeq 3$ kW/cm^2. By considering a laser power around 1 W we achieve a laser intensity nearly $I \simeq 0.5I_{sat}$. The interaction of the Er^{3+} ions with the AuNP was introduced by means of a new decay rate for the green level 4 to the ground level 0 which simulates the global effect of both the non-radiative energy transfer to the AuNP and the increase of the radiative decay rate due to Purcell effect.

References

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2 X. P. Jiang, Z. M. Yang, T. Liu and S. H. Xu, *Journal of Applied Physics*, 2009, **105**, 103113.