Supporting information for: Cascaded plasmon-enhanced emission from a single upconverting nanocrystal

Amirhossein Alizadehkhaledi,[†,‖] Adriaan L. Frencken,[‡,‖] Mohsen Kamandar Dezfouli,[¶] Stephen Hughes,[§] Frank C.J.M. van Veggel,[‡,‖] and Reuven Gordon[*,†,‖]

†*Department Electrical and Computer Engineering, University of Victoria, Victoria, British Columbia V8P 5C2, Canada*

‡*Department of Chemistry, University of Victoria, British Colombia V8W 3V6, Canada*

¶*Advanced Electronics and Photonics Research Centre, National Research Council Canada, 1200 Montreal Rd., Ottawa, ON K1A 0R6, Canada*

§*Department of Physics, Engineering Physics and Astronomy, Queen's University, Kingston, Ontario K7L 3N6, Canada*

‖*Centre for Advanced Materials & Related Technologies (CAMTEC), University of Victoria, Victoria, British Columbia V8W 2Y2, Canada*

E-mail: rgordon@uvic.ca

Phone: +1 250 472 5179 . Fax: +1 250 721 6052

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Author Information

Corresponding Author

*E-mail (R. Gordon): rgordon@uvic.ca

ORCID

Reuven Gordon: 0000-0002-1485-6067

A. Upconverting nanocrystals (UCNCs)

Transmission electron microscopy (TEM) was used to characterize the morphological and structural properties of the UCNCs. Figure S1(a),(b) show TEM images of UCNCs with 50 k and 250 k magnification respectively.

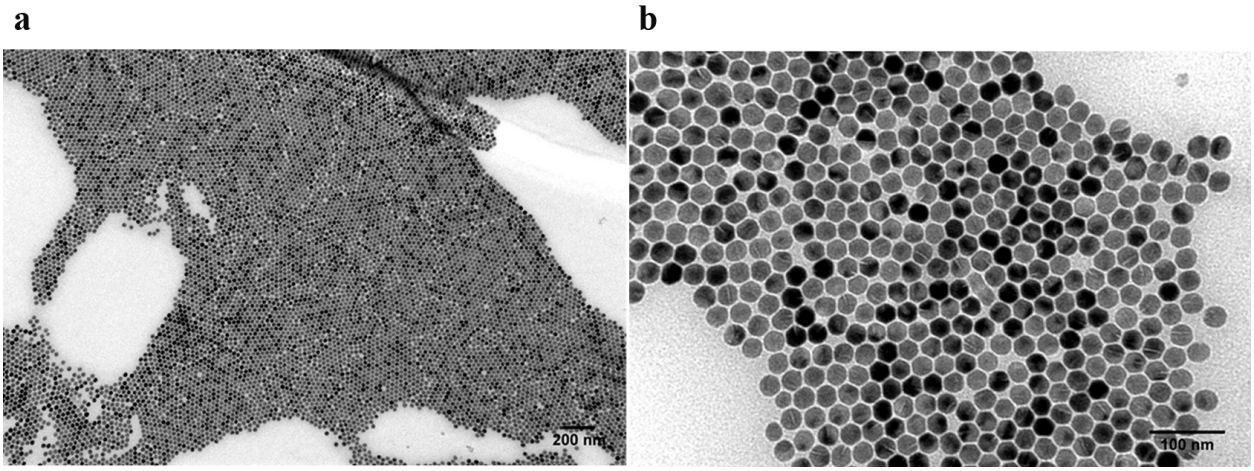

Figure S1: TEM images of $NaYF_4$: 2% Er nanoparticles magnified 50k times (a) and 250k times (b).

Figure S2 shows size analysis of UCNCs from the TEM images by measuring the surface area of at least 300 particles. The UCNCs mean diameter is 26.17 nm with standard deviation 2.65 nm.

Figure S3 shows an x-ray diffractogram of $NaYF_4$: 18 % Yb, 2% Er UCNCs comparing to a reference pattern of hexagonal $NaYF_4$.[1]

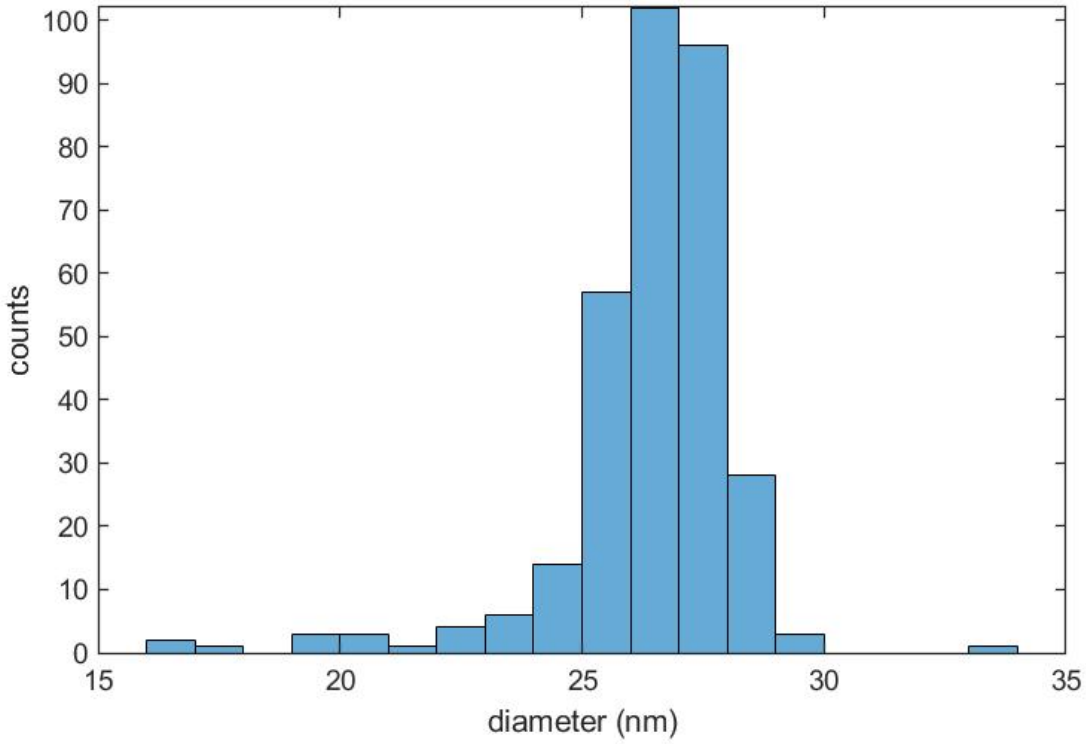

Figure S2: Size distribution of measured UCNCs.

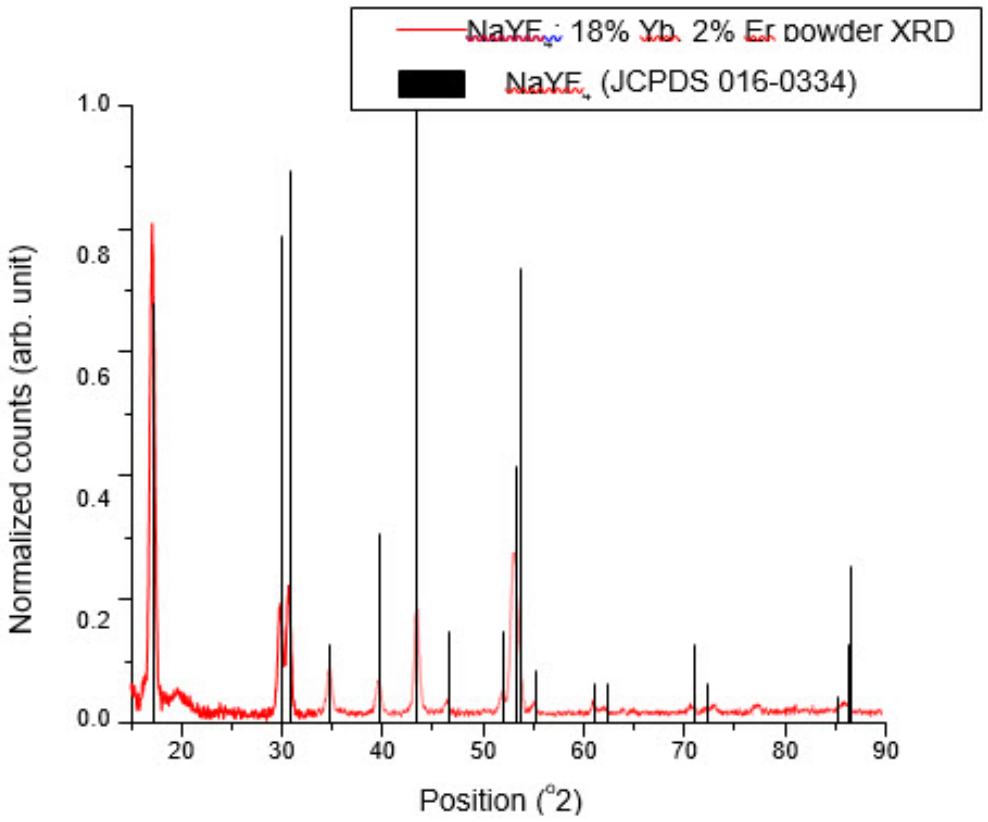

Figure S3: Experimental x-ray diffractogram of UCNCs and a reference pattern of hexagonal $NaYF_4$ [1]

B. Optical trapping setup

Figure S4 shows the schematic of optical trapping setup used for trapping UCNCs and detecting emission.

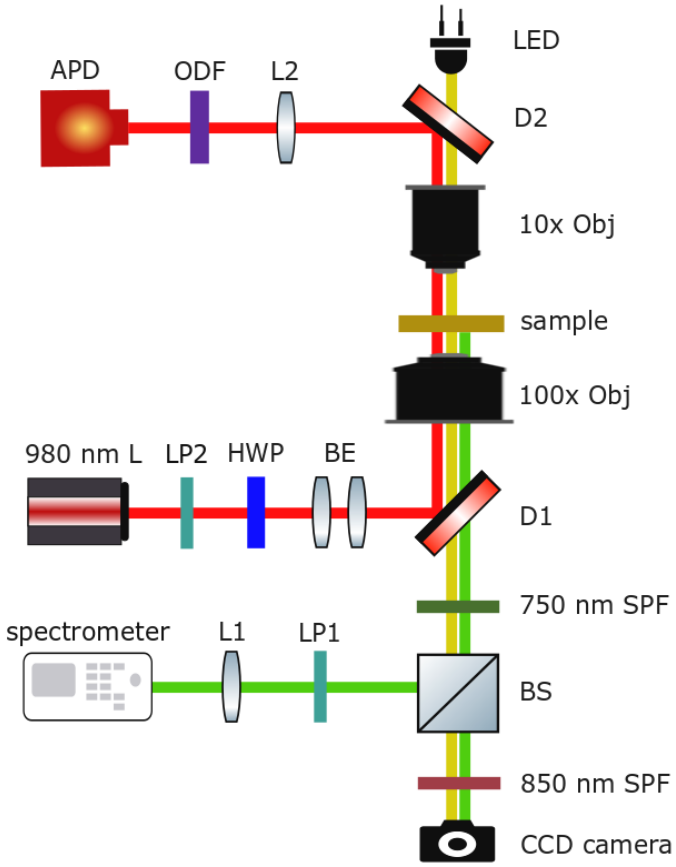

Figure S4: Schematic of the optical trapping setup. Abbreviations used: CCD camera = charge coupled device camera, SPF = short pass filter, BS= beam splitter, LP = linear polarizer, L=lens, D=dichroic mirror, HWP = half wave plate, BE = beam expander, 980 nm L=980 nm laser, Obj= objective lens ODF = optical density filter and APD = avalanche photodetector.

C. Particle diffusion

Using the Stokes-Einstein equation, we estimate that the time for a 26 nm particle to diffuse to the trapping site in hexane for $3 \times 10^{10}/\text{cm}^3$ concentration is 140 ms. Figure S5 shows optical transmission through a 100 nm $\times$ 100 nm aperture for several trapping events in one second. Laser is turned on at time t = 0 s. Trapping occurred consistently within 0.01 s of turning on the laser. Figure S6 depicts the avalanche photodetector (APD) signal for the the first 0.1 s of the trapping event shown in Fig. S5.

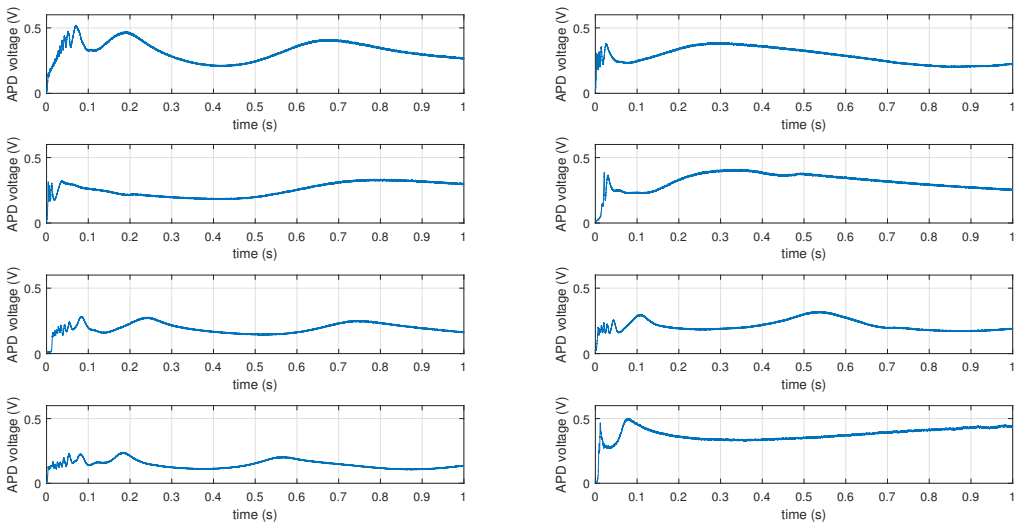

Figure S5: Optical transmission for several trapping events with one second interval (laser turned on at time zero).

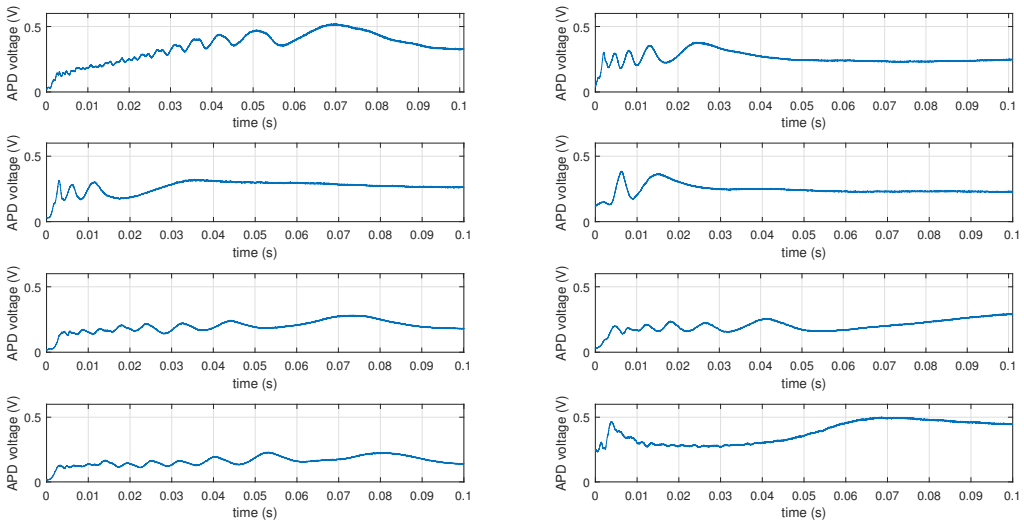

Figure S6: Optical transmission for several trapping events with 100 ms span (laser turned on at time zero).

D. Single particle emission

Figure S7 shows upconversion emission for three different cases of single particle trapping, multiple particle trapping and no trapping, for the same aperture. When trapping multiple particles, the emission spectrum increases. To be sure that we measured a stable single particle emission, five separate emission spectrums were recorded from the sample from five separate trapping events. As we can see from Figure S8, all the measurements were approximately the same. The standard deviation of this measurement for 550 nm and 650 nm is 3.3 and 7.1 photons (3.1 % and 3.3 % normalized standard deviation).

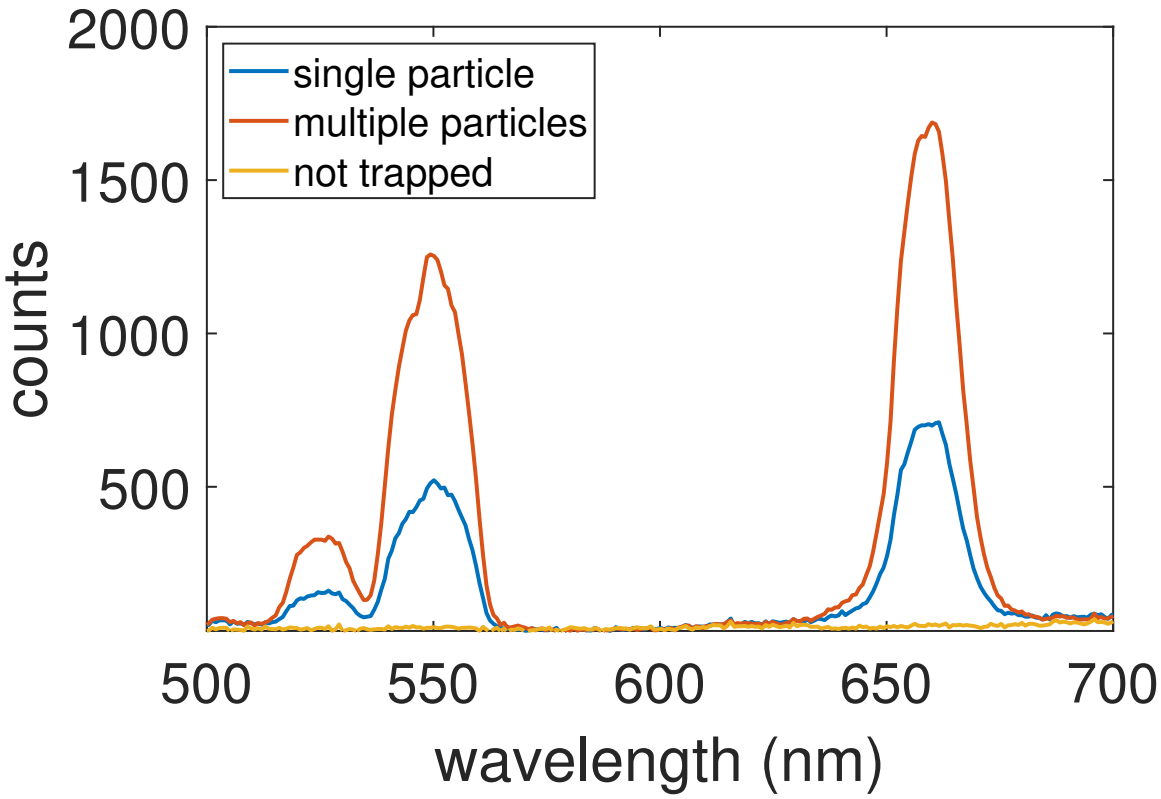

Figure S7: Luminescence emission spectrum from a single aperture for (blue) single particle trapping, (red) multiple particle trapping and (yellow) no particle trapping.

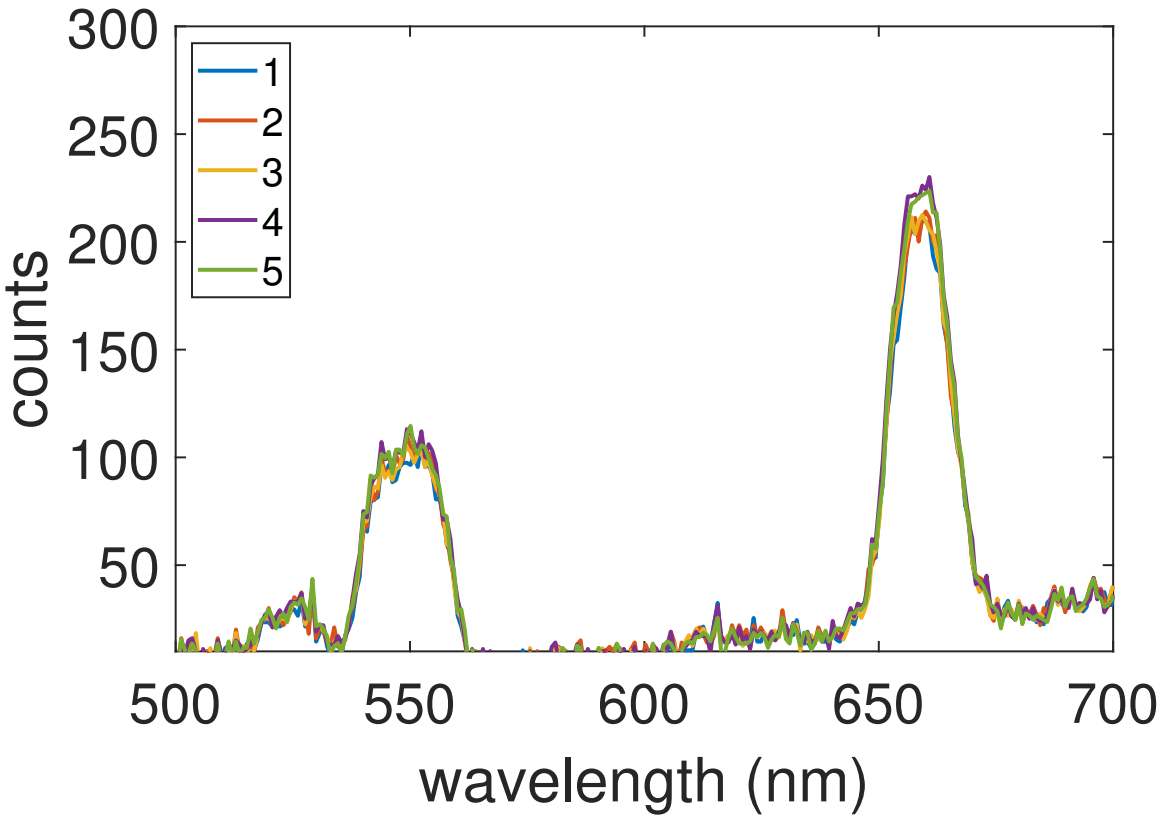

Figure S8: Luminescence emission spectrum from a single aperture for five different trapping events of single UCNCs.

E. Power dependence

Figure S9 shows the 650 nm and 550 nm emission counts with varying the incident power. With high pumping power at 980 nm, the 650 nm and 550 nm increase linearly with the incident power. Since the incident power in this paper for all measurements is 30 mW, where we are in the linear regime.[2]

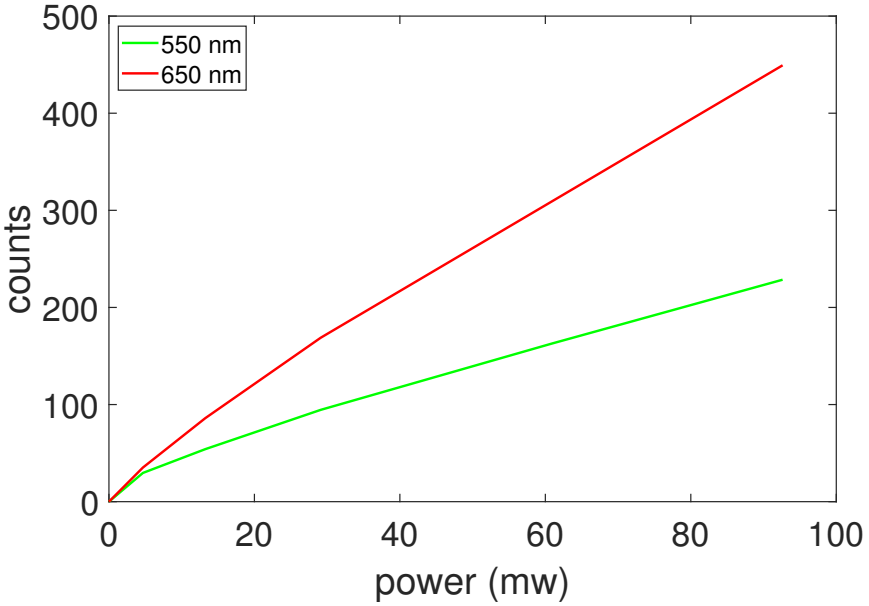

Figure S9: Upconversion emission of 650 nm and 550 nm when varying the incident power for 100 nm × 100 nm aperture.

F. Emission ratio

Figure S10 shows the 650 nm to 550 nm emission ratio when varying the length of rectangular aperture from 100 nm to 226 nm in steps of 2 nm. The ratio between the 650 nm and 550 nm emission increases as the plasmonic enhancement increases. Figure S11 shows the 650 nm

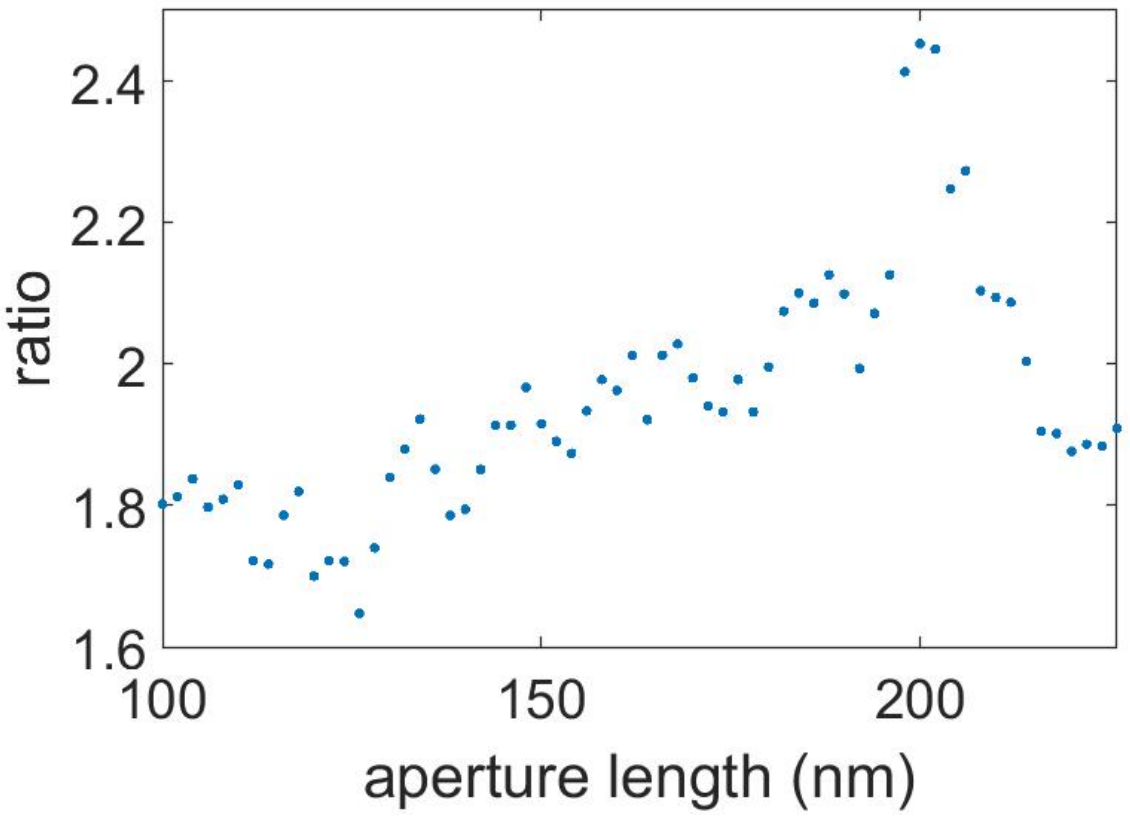

Figure S10: Upconversion ratio of 650 nm to 550 nm emission when varying the length of rectangular aperture from 100 nm to 226 nm.

to 550 nm emission ratio with varying incident power. As the pumping power at 980 nm increases, the 650 nm emission increases with respect to the 550 nm.

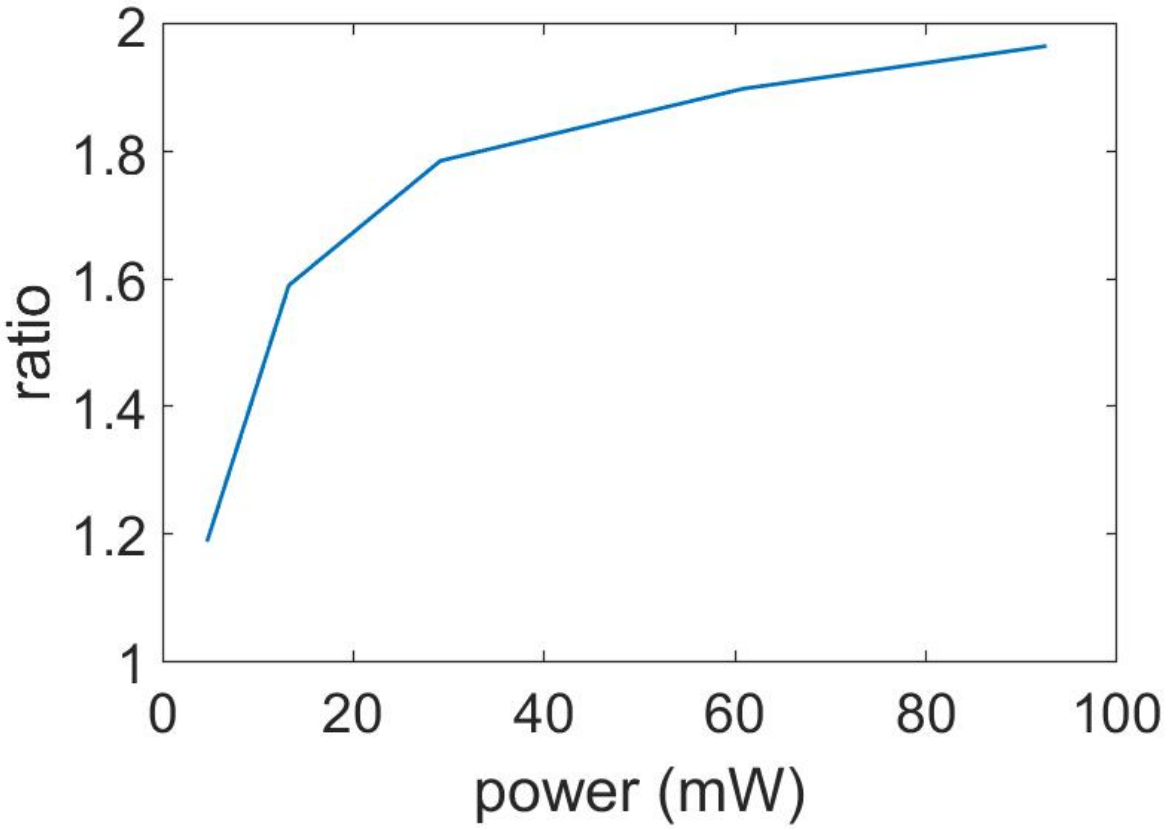

Figure S11: Upconversion ratio of 650 nm to 550 nm emission when varying the incident power for 100 nm × 100 nm aperture.

G. Polarization dependence

Fig. 3 shows the polarization dependence of upconversion emission of a trapped UCNC for 550 nm and 650 nm. Data obtained is for the 210 nm by 100 nm aperture, integrated over a period of 20 s with an incident power of 30 mW. The emission at 650 nm is polarized along the short axis of the aperture (the same polarization as the incident pump), and the 550 nm emission is along the short axis. The fit shows a degree of polarization of 0.72 for 550 nm and 0.7 for 650 nm.

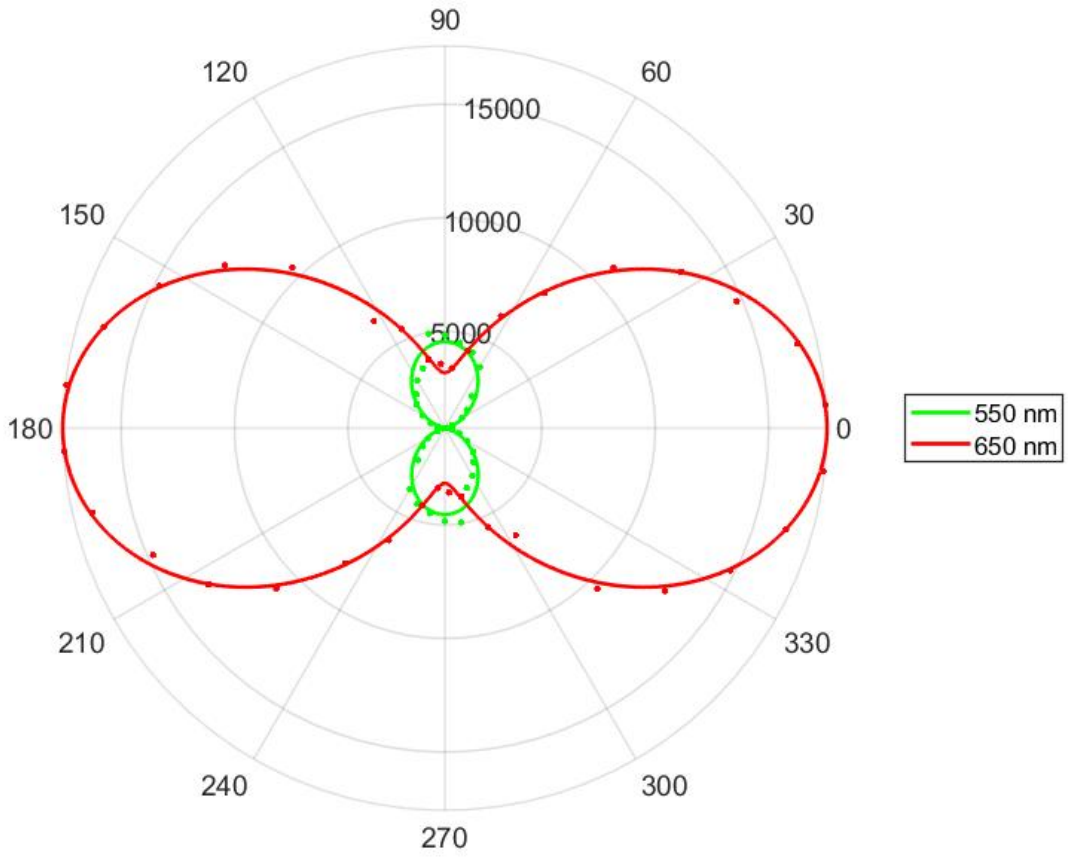

Figure S12: Polarization dependence of upconversion emission at 550 nm and 650 nm (counts). This data is for a single upconverting nanocrystal (26 nm diameter) trapped in a rectangular aperture.

References

(1) Sobolev, B. P.; Mineev, D.; Pashutin, V. Low-temperature hexagonal modification of $NaYF_4$ having the gagarinite structure. Doklady Akademii Nauk. 1963; pp 791–794.

(2) Piper, R. B.; Yoshida, M.; Farrell, D. J.; Khoury, T.; Crossley, M. J.; Schmidt, T. W.; Haque, S. A.; Ekins-Daukes, N. Kinetic insight into bimolecular upconversion: experiment and simulation. *Rsc Advances* **2014**, *4*, 8059–8063.