Amplified Luminescence in Organo-Curium Nanocrystal Hybrids

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Electronic Supplementary Information

S1. Methods

Nanoparticle Synthesis & Ligand Modification.

Nanoparticles were synthesized according to a protocol modified from Wang et al.,[1] with changes made to account for the small quantities of curium used in these nanocrystal preparations. A dilute stock solution of $^{248}CmCl_3$ (prepared in standardized 1 M HCl with a 95.78% ^{248}Cm, 4.12% ^{246}Cm, 0.06% ^{245}Cm, 0.02% $^{244}Cm/^{247}Cm$ isotopic distribution by atom percentage) was reconstituted in pH 3.1 acetic acid as a 300 µM $Cm(CH_3COO)_3$ solution. Due to the limited $^{248}Cm^{3+}$ quantity, reaction conditions as specified by Wang et al. were scaled down accordingly. Briefly, nanoparticles were grown through the addition of 100 µl of 200 mM $Gd(CH_3COO)_3 \cdot xH_2O$ (Sigma-Aldrich), and 50 µl of the dilute curium acetate stock to a stirring solution of 400 µl 1-oleic acid (Alfa Aesar) and 600 µl 1-octadecene (90%, Sigma-Aldrich) in a 20 ml Schlenk tube uniformly heated to 150 °C for 1 hour on a sand-filled heating mantle (prior to synthesis, the Schlenk tube was cleaned in aqua regia followed by rinsing in milliQ water). After heating, the reaction was allowed to cool to room temperature, with the thermally-equilibrated solution being rapidly injected with a precipitant consisting of 50 µl NaOH and 165 µl of ammonium fluoride. The reaction vessel was promptly sealed on a vacuum line and heated to 100 °C, at which point a vacuum was pulled over the flask, at this temperature, for 10 minutes. Following this, the temperature was raised to 280 °C and held there for 1.5 hours. The resulting mixture was again passively cooled to room temperature, and the ambient-temperature vessel was injected with 400 µl ethanol. Following transfer of the reaction solution to 2-ml Eppendorf tubes, the solutions were pelleted by centrifugation at 13,000 rpm for 5 minutes. Following solvent removal, the pellets were resuspended in 400 µl ethanol/methanol using sonication. This process was repeated a total of three times before a final resuspension and storage of the particles in 400 µl cyclohexane. Ligand modification was achieved by precipitating the particles through addition of 400 µl ethanol, followed by centrifugation at 13,000 rpm and removing the solvent via micropipette. 800 µl of 7.5 mM 3,4,3-LI(1,2-HOPO) (Ash Stevens, Inc., prepared as described in the literature[3]) in pH 6.0 50 mM Hepes buffer was added. The tube was covered in foil and incubated on a shaker at 60 °C overnight at room temperature to allow for 343 binding to the nanoparticles. Following ligand incubation, samples were washed at least four times in ethanol using the sequence of centrifugation and resuspension via sonication described earlier.

Steady-State Photoluminescence.

Steady-state luminescence spectra were collected on a Jobin Yvon Horiba Fluorolog spectrophotometer. Luminescence spectra of nanoparticles were collected using a 357-nm excitation wavelength sourced from a xenon arc lamp, 1 nm excitation / 3 nm emission slit settings

and 1.0 s integration times averaged over three scans. Excitation (action) spectra were collected by monitoring the $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition at 598 nm using 1 nm slits for excitation and 3 nm slits for emission monochromators and 1.0 s integration times. Nanoparticle samples were prepared as dilute solutions in 400 µl ethanol to ensure stability of the suspension over the course of data collection (A_{500} ~ 0.3; 0.1 mg ml^{-1}). Determination of the triplet state of 3,4,3-LI(1,2-HOPO) bound to $NaGdF_4$ nanoparticles via cryogenic luminescence measurements has been reported elsewhere.[2]

Time-Resolved Photoluminescence.

Curium luminescence lifetimes were determined using the Fluorolog system in time-resolved (MCS lifetime) mode. Excitation parameters were as follows: 350 nm excitation, 14 nm excitation bandpass; 598 nm observation, 4 nm emission bandpass; 10 µs $channel^{-1}$ and 1000 channels $sweep^{-1}$ (10.0 ms observation window). Decay parameters were resolved through multi-exponential fitting in MATLAB. 3,4,3 phosphorescence lifetimes were determined in an earlier study.[2]

Quantum Yields.

Quantum yields were determined according to the same protocols already detailed in our past work.[2] Briefly, this was accomplished using an integrated sphere according to the methodology of de Mello et. al[33]. In these experiments, a neutral density filter was placed between the sphere's entry port and the PMT detector when measuring the excitation beam signals. As a result, this modifies de Mello's equation for quantum yield calculation to:

$$\Phi = f_{exc}\left[\frac{P_c - (1 - A)\,P_b}{L_a A}\right] \quad ;$$

$$A = 1 - \frac{L_c}{L_b} \quad .$$

$P_{b,c}$ are the integrated emission spectra acquired under the respective conditions of indirect and direct excitation in the sphere. $L_{a,b,c}$ represent the filtered, integrated excitation beam as measured for the respective cases of no sample, indirect sample excitation and direct sample excitation. The factor f_{exc} represents the fraction of excitation light transmitted by the filter. The filter's light transmission at 355 nm (0.160) was determined through measurement of the lamp excitation beam at 355 nm and taking the ratio of the filtered/unfiltered integrated light intensity at this wavelength.

Cm nanoparticle emission spectra were collected using 1 nm slits for both excitation and emission, under 355 nm sample excitation and a 365-650 nm observation window at 1 nm spectral resolution. The spectra for quantum yield determinations were generated using 4.0 s integration times.

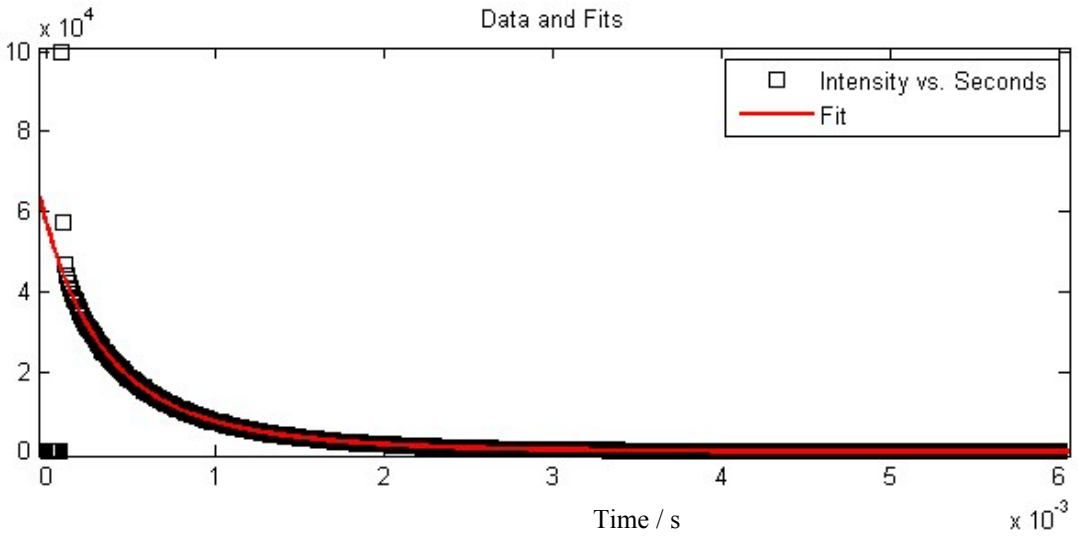
Quantum yield luminescence spectra were corrected through the subtraction of residual solvent autoluminescence and a response adjustment for any wavelength-dependent light transmission bias of the sphere.

Transmission Electron Microscopy.

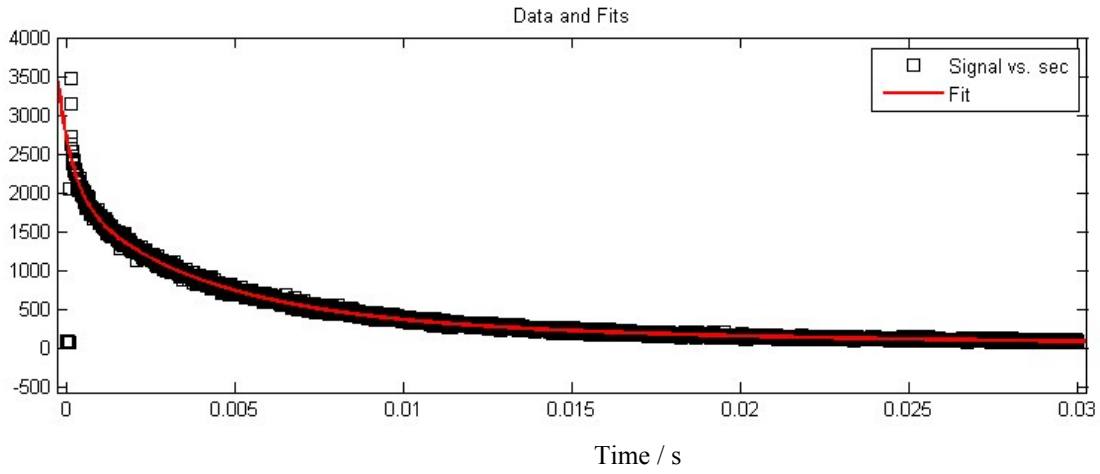
Morphology, crystallography and chemical composition of the samples was investigated using transmission electron microscopy (TEM). Samples were dropcast onto a Cu TEM-grid, and then analyzed using the TitanX TEM/STEM which is a FEI Titan 80-300 (the TitanX). The accelerating voltage was 60 kV, exposure times were kept low to prevent beam damage, and images were taken before and after every lengthy acquisition. The microscope is equipped with a windowless Bruker SuperX energy-dispersive X-ray spectroscopy (EDS) detector, which was used to measure the chemical composition. High-resolution TEM (HRTEM) images were acquired with a Gatan Ultrascan 1000 CCD camera, high-angle annular dark field scanning TEM (HAADF-STEM) images with a Fischione detector.

S2. Time-Resolved Luminescence

Cm^{3+} emission



3,4,3 ligand triplet (Quenched/Unquenched) emission (from Ref. 2)



S3. Transient Luminescence Analysis & Energy Transfer Calculations

Note: donor data from ref. 2:

NaGdCmF4-3,4,3	Rates (k_n)	Normalized Coefficients (c_n)	Mean Decay Rate (s-1)	Mean Lifetime / ms
Decay phase 1	2205.00	0.29	647.00	0.00125901
Decay phase 2	252.90	0.55	138.90	
Decay phase 3	53.27	0.16	8.38	
			794.27	
NaGdF4-3,4,3 (donor)	**Rates (k_n)**	**Normalized Coefficients (c_n)**	**Mean Decay Rate (s-1)**	**Mean Lifetime / ms**
Decay phase 1	1513.33	0.32	488.94	0.001606523
Decay phase 2	238.63	0.54	129.79	
Decay phase 3	28.03	0.13	3.73	
			622.46	

Energy transfer efficiency:

1 – (donor-acceptor lifetime / donor-only lifetime) = 1 – (1.259 ms / 1.606 ms) = **0.216**

S4. Nanoparticle Spectra

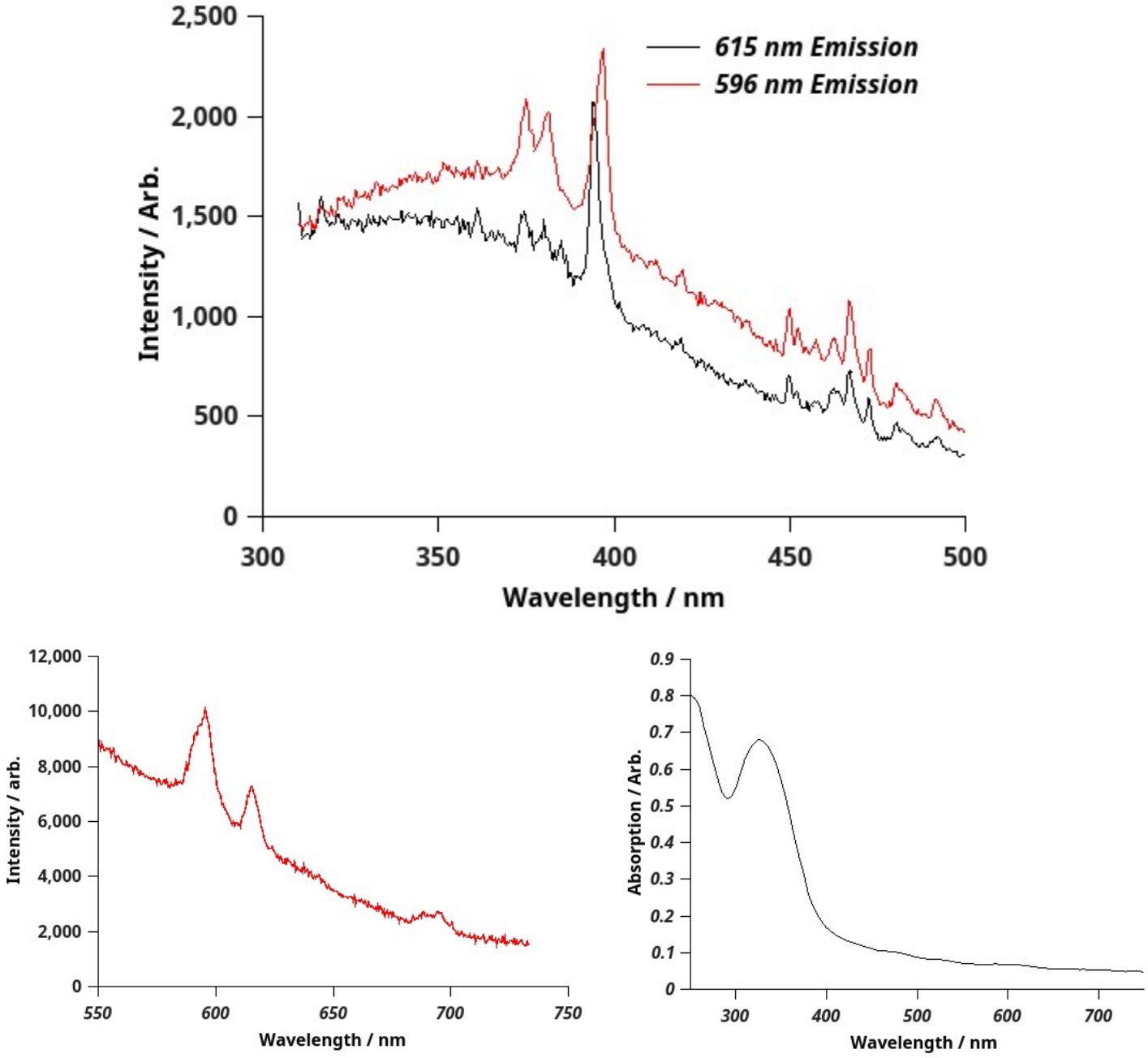


Figure S4. Top: Excitation spectra of $NaGdF_4$:Eu^{3+}, Cm^{3+} nanoparticles, monitoring 615 nm Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ and 596 nm $^6D_{7/2} \rightarrow {}^8S_{7/2}$ Cm^{3+} emission. In the case of Eu^{3+} emission at 615 nm, absorption peaks from Cm^{3+} are readily apparent in the excitation spectrum, indicating the presence of direct energy transfer between Eu^{3+} and Cm^{3+} ions.
Bottom, Left: Emission spectrum of $NaGdF_4$:Eu^{3+}, Cm^{3+} nanoparticles.
Bottom, Right: Absorption spectrum of 3,4,3-$NaGdF_4$:Cm^{3+} nanoparticles. The broad peak between 300 and 400 nm represents the sum of the 3,4,3 ligand absorption and nanoparticle Rayleigh scatter.

S5. Nanoparticle Washes – Removal of Excess Ligand.

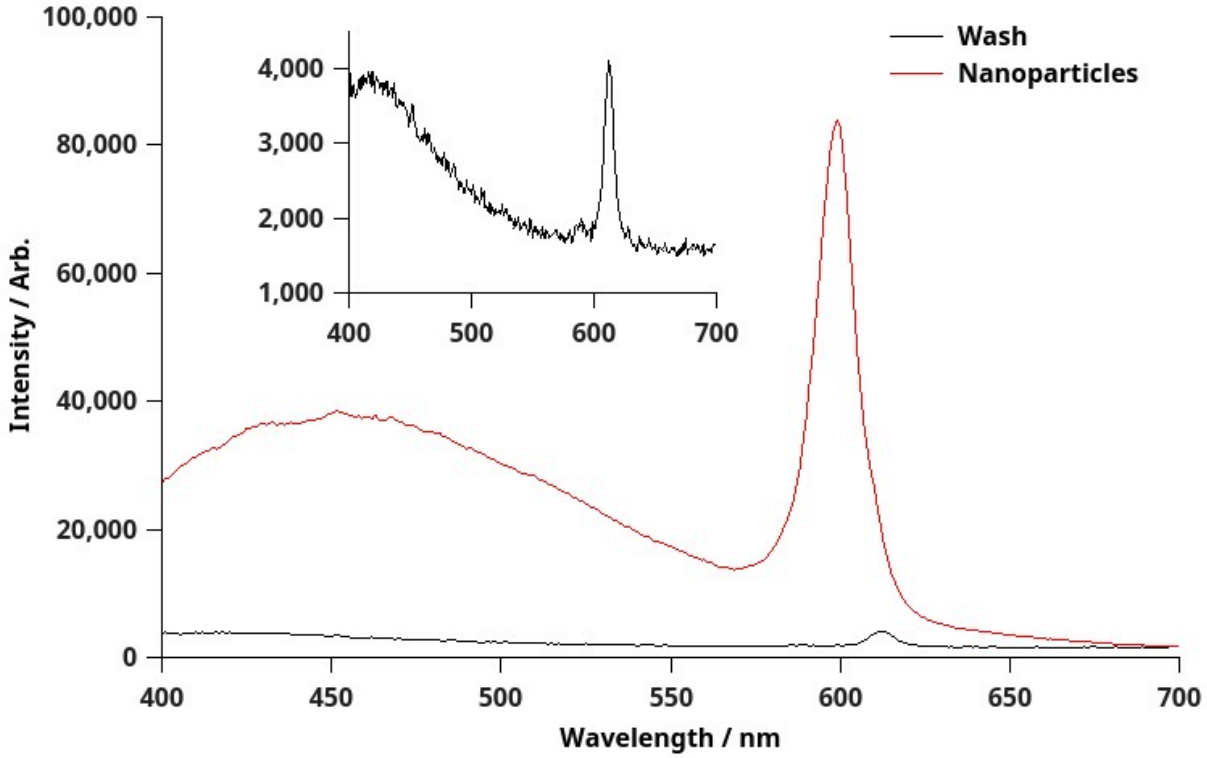


Figure S5. Comparison between luminescence of 3,4,3-modified nanoparticles and supernatant wash. Magnified view of emission of the third wash is shown as an inset. Nanoparticle samples show a significantly higher emission intensity than the supernatant after the third wash. The broad emission is ligand luminescence, with the sharp peak at 598 nm arising from sensitized curium emission. Luminescence emission in the wash is shifted by 12 nm relative to the nanoparticle emission, consistent with reports of the 3,4,3-Cm^{3+} molecular complex showing sensitized emission at 610 nm.

1. Wang, F., et al., *Nature protocols* **2014,** *9* (7), 1634.
2. Agbo, P., et al., *ACS Photonics* **2016,** *3* (4), 547-552.
3. Abergel, R. J., et al., *Health Phys.* **2010**, *99*, 401-407.