Supporting Information

Excitation Modulation of Upconversion Nanoparticles for Switch-like Control of Ultraviolet Luminescence

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1. Materials and Methods of Synthesis

All lanthanides were in the form of the 99.9% pure lanthanide oxides (Sigma-Aldrich, St. Louis, MO, USA). UNPs were prepared in two different methods. The first method was a previously reported hydrothermal synthetic method.[1] The second synthesis was a previously reported thermolytic decomposition.[2] A range of hydrothermal syntheses were performed with yttrium doped out from 0 to 99.5% ytterbium and 0.5% thulium. These syntheses included original hydrothermal formation along with the secondary heating to 220°C in a PTFE pressure vessel. The thermolytic synthesis was performed using 30% ytterbium, 0.5% thulium doping. Thermolytic decomposition UNPs were suspended in chloroform at a concentration of 3.9 mg mL^{-1}. Hydrothermal UNPs were dispersed in deionized water at a concentration of 5 mg mL^{-1}. For lipid coated UNPs, lipids were dissolved in choloroform to form the 89:10:1 mixture of DPPC, DSPE(carboxy)PEG1K, and DSPE(methoxy)2K respectively. Lipids were added in a 1:10 mass ratio to UNPs obtained by thermolytic synthesis, sonicated then dried. The dried UNPs and lipid mixture was resuspended in PBS forming a spontaneous lipid coating.

2. Characterization Methods

For acquisition of luminescence emission spectra, 2 mL of UNPs in a standard 1 cm path-length quartz cuvette were placed into a Fluorolog (Horiba Y-J, Edison, New Jersey, USA). The excitation light is provided perpendicular to the collection through the side port of the sample compartment by an ILX Lightwave (Newport, Bozeman, MT, USA) with a 2 W 980nm diode. Using a fixed 10% duty cycle and current the sample is excited with a range of pulse widths, from 10 µs to 2 ms. Spectra were collected with a 5 nm width on the monochromators, double pass collection, and 10-second integration from 300 nm to 900 nm. Luminescnce lifetimes were acquired from the same sample by placing it in a mount and exciting with a 980 nm, 20 Hz pulse, 4 ns pulse width beam from a tunable OPO pumped by Q-switched Nd:YAG laser (Ekspla, Vilnius, Lithuania). Emission was captured by a photon counting avalanche diode (PerkinElmer, Vaudreuil, Quebec, Canada) and counted using a multi-channel scaler (Picoquant, Berlin, Germany). Lifetime data was analyzed using tail fitting in the FluoFit software by PicoQuant. Particle sizing was performed by dynamic light scattering on the ZS-90 Zetasizer (Malvern, Worcestershire, United Kingdom), using 1 mL of dispersed UNPs loaded into a quartz cuvette. Particles were also characterized using TEM and XRD To prepare for TEM, UNPs were dispersed in chloroform then added dropwise to copper 300 mesh grids (Electron Microscopy Sciences, Hatfield, PA, USA) as the dispersant evaporated. The UNP obtained by thermolytic method are 36 nm in diameter sized by electron microscopy using a Tecnai Spirit (FEI, Hillsboro, OR, USA). Similar preparation was done for XRD utilizing a glass substrate rather than copper grid.

3. UNP to DPA energy transfer

After initial collections of UNPs, 4.2 mg of DPA (Sigma-Aldrich, St. Louis, MO, USA) is added to a 2mL aliquot of the UNP suspension resulting in a 6.35 mM solution. Excitation was provided with the same 980nm diode excitation regimens in the absence of other light. Finally, the sample is measured with using the Fluorolog excitation source set at 372 nm to measure DPA fluorescence emission to observe any matrix changes from a standard DPA emission spectrum.

To determine adsorption of DPA to UNP, upconverting nanoparticles were first dispersed with DPA in chloroform. The nanoparticles were then separated from the supernatant by centrifugation, and the pellet was re-dispersed in equivalent volume. The sample was excited using 2 ms pulse width, 10% duty cycle 980 nm laser light and fluorescence of DPA was measured at 432 nm. This is fluorescence of energy acceptor in the energy transfer pair, attributed to DPA adsorbed to UNPs. This result was compared to fluorescence of energy acceptor in the energy transfer pair in freely dispersed sample (without the centrifugation step), attributed to freely diffusing DPA. The adsorbed fluorescence intensity is an order of magnitude less than the free dispersed, indicating negligible contribution of adsorbed DPA. This signal can be due to DPA adsorption to silica and residual supernatant.

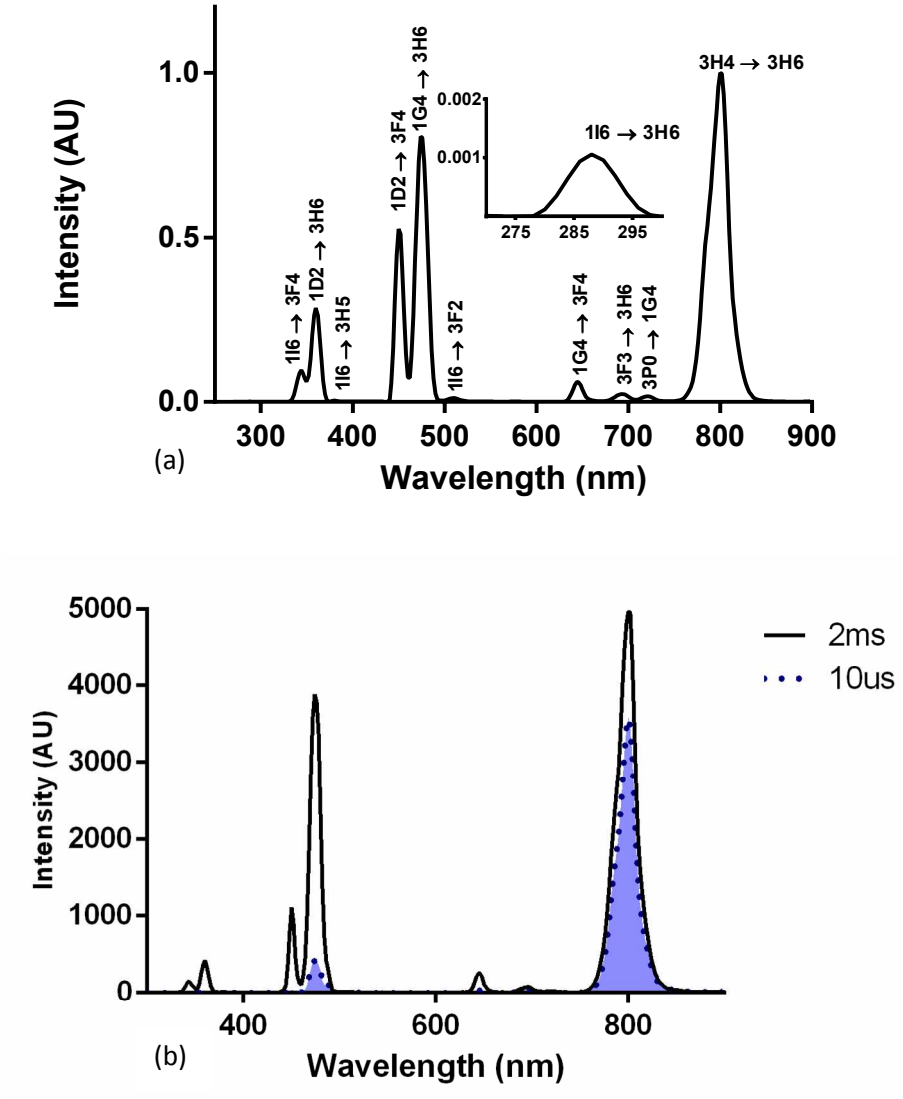


Figure S1. (a) Luminescence spectrum of thermolytic decomposition UNPs in chloroform excited with 2 ms pulse width 980 nm diode laser. (b) Luminescence spectra of lipid coated thermolytic decomposition UNPs in 1x PBS excited with 2 ms and 10 µs pulse widths using 980 nm diode laser.

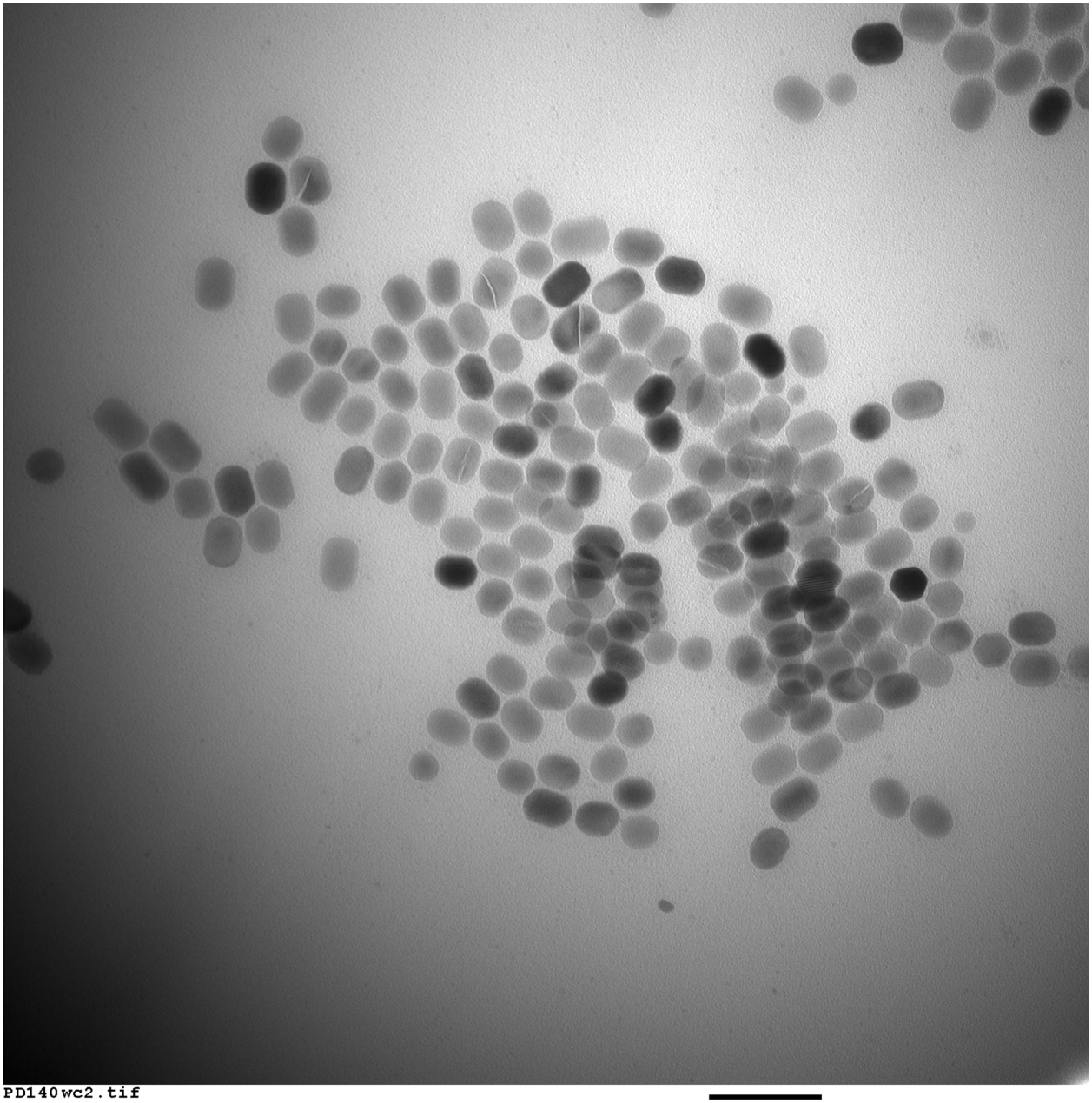


Figure S2. TEM image of thermolytic synthesis particles at 105000x.

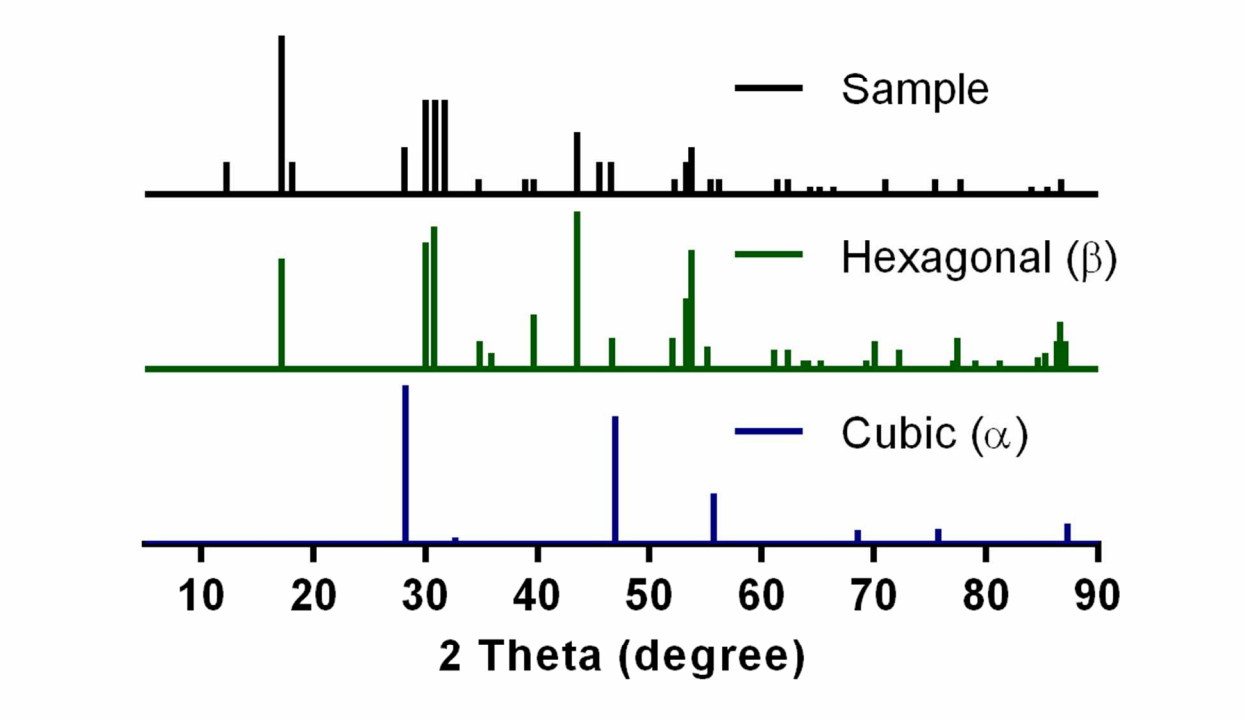


Figure S3. XRD diagram of thermolytic synthesis sample (black) as compared to reference hexagonal (00-016-0334) (green) and reference cubic (01-077-2042) (blue)

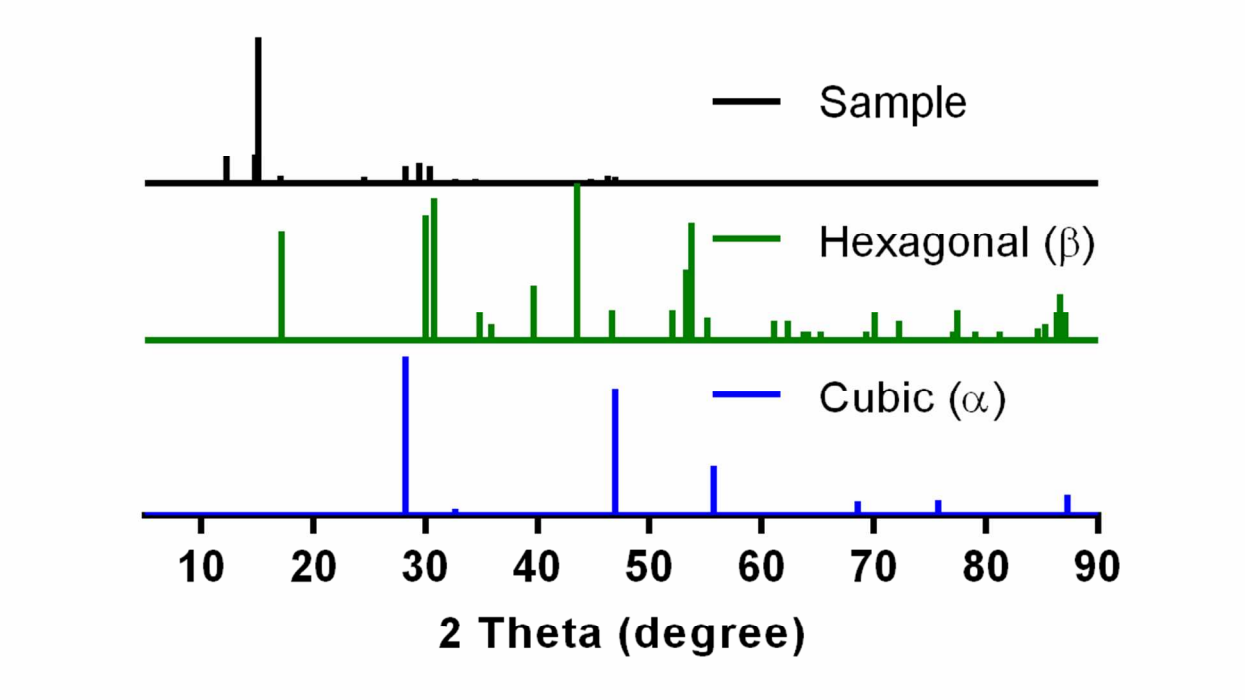


Figure S4. XRD diagram of hydrothermal synthesis sample (black) as compared to reference hexagonal (00-016-0334) (green) and reference cubic (01-077-2042) (blue).

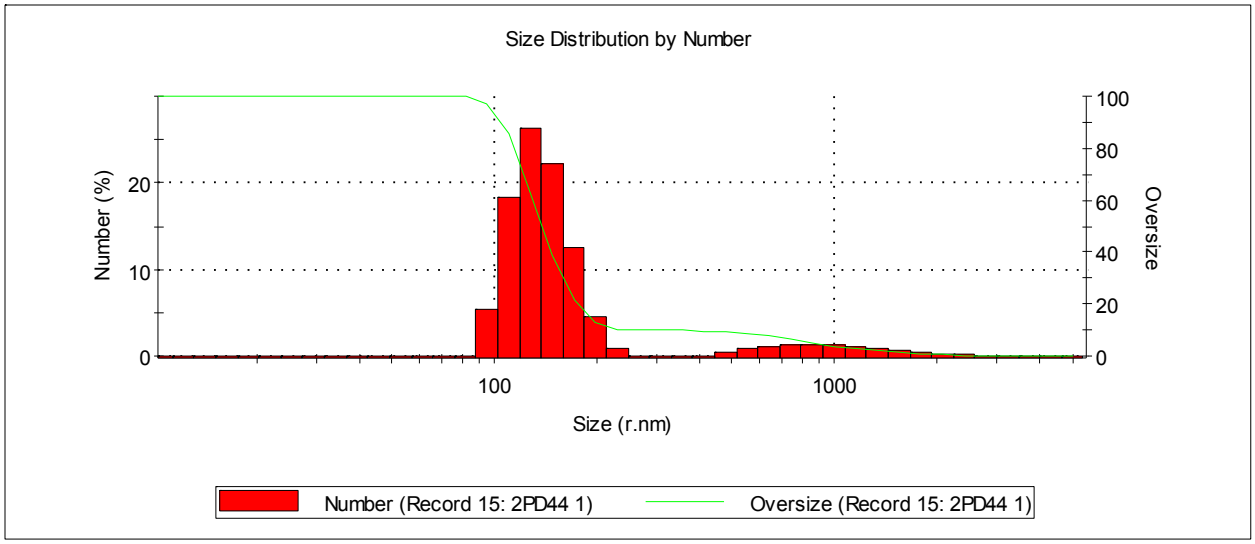
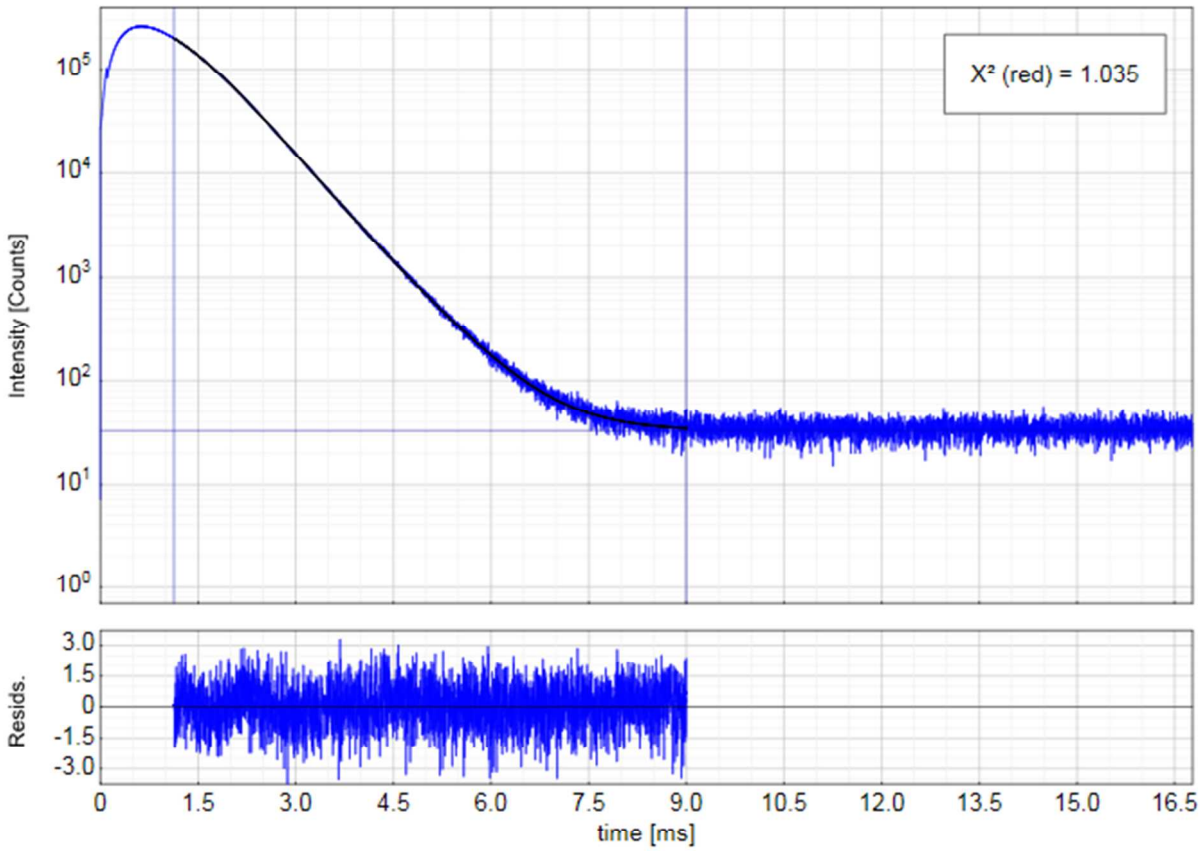


Figure S5. Histogram size distribution of hydrothermal synthesis UNPs showing particles and their aggregates.



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	144990	-260	+260	Fitting
τ_1 [ms]	0.69665	-0.00085	+0.00085	Fitting
A_2 [Cnts]	450400	-360	+360	Fitting
τ_2 [ms]	0.45734	-0.00037	+0.00037	Fitting
A_3 [Cnts]	-512880	-440	+440	Fitting
τ_3 [ms]	0.34432	-0.00033	+0.00033	Fitting
A_4 [Cnts]	118490	-540	+540	Fitting
τ_4 [ms]	0.2465	-0.0014	+0.0014	Fitting
Bkgr. $_{Dec}$ [Cnts]	32.8	-1.9	+1.9	Fitting

Average Lifetime:

$\tau_{Av.1}$=0.69525 ms (intensity weighted)

$\tau_{Av.2}$=0.79406 ms (amplitude weighted)

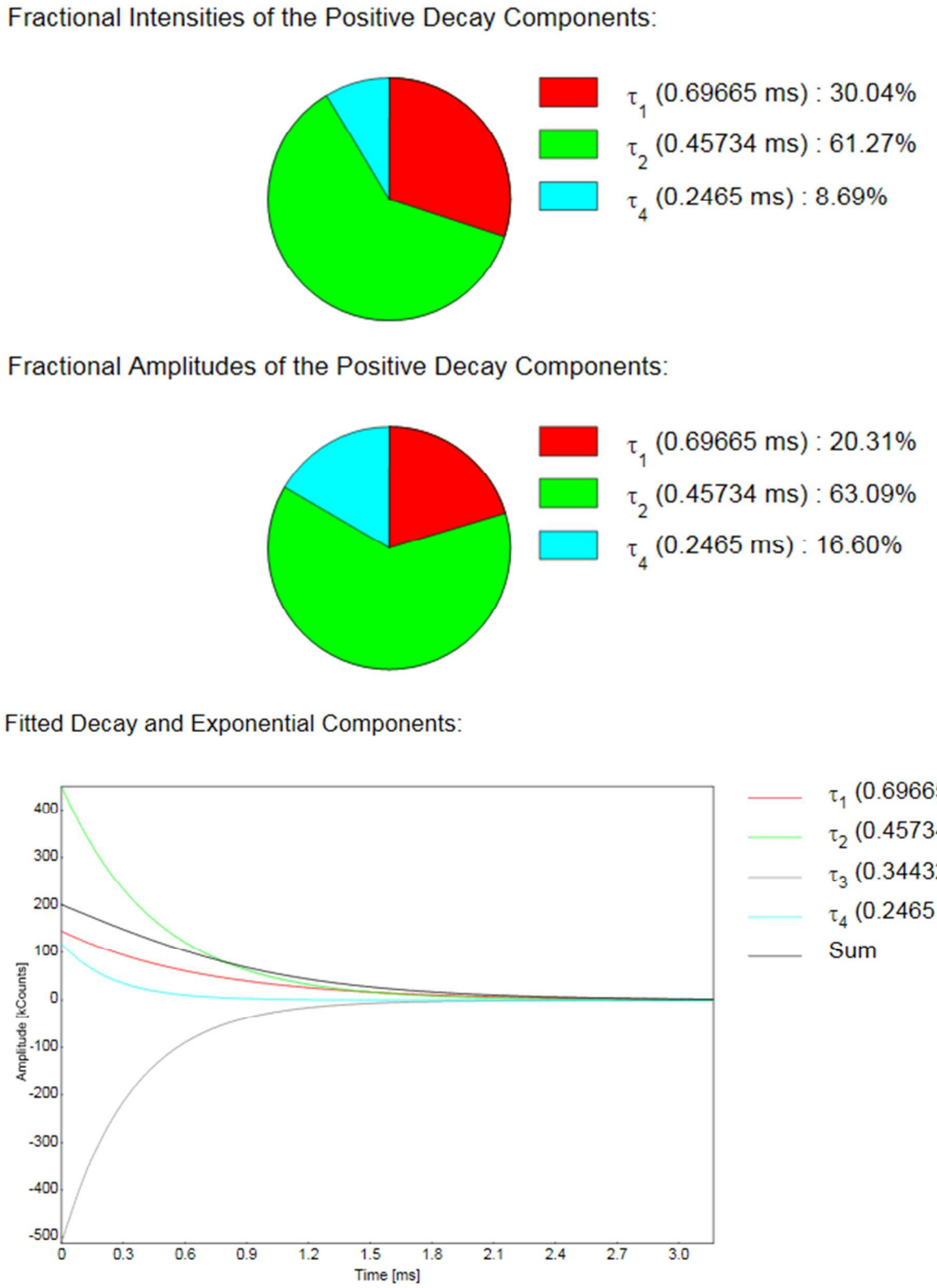
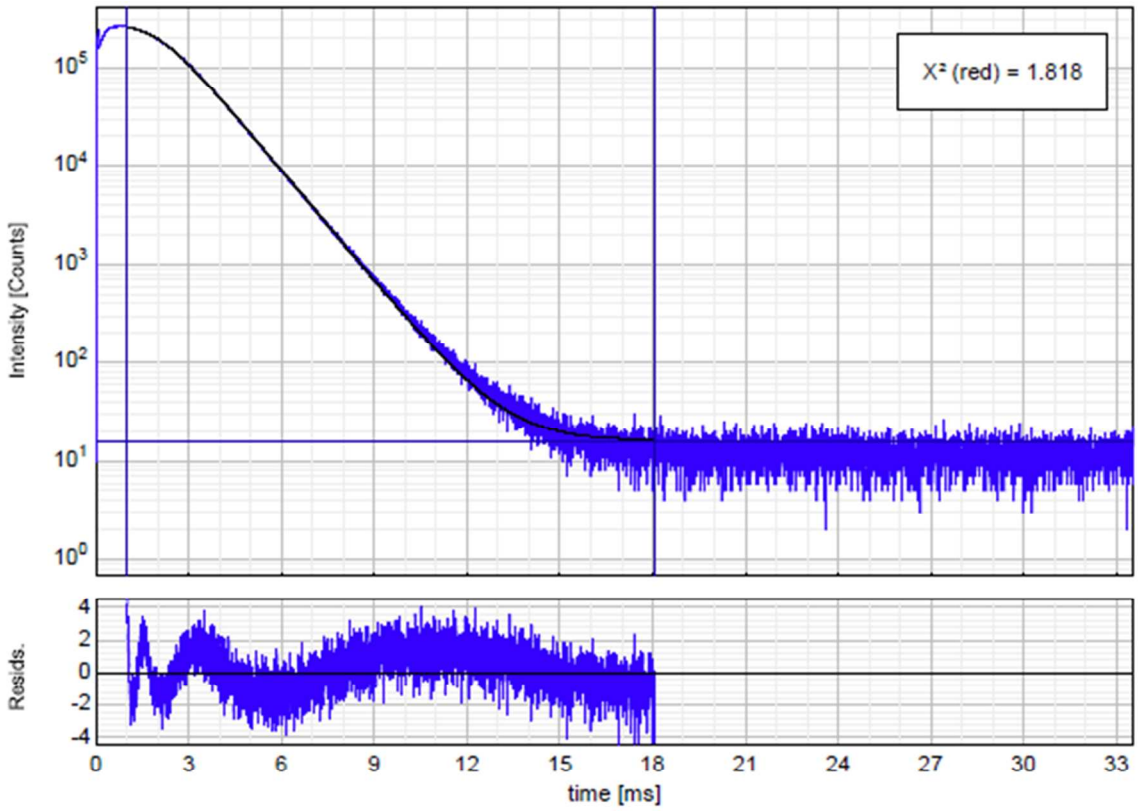


Figure S6. Lifetime data and tailfit analysis for the blue (450nm and 475nm) emission region of the thermolytical synthesis UNPs.



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

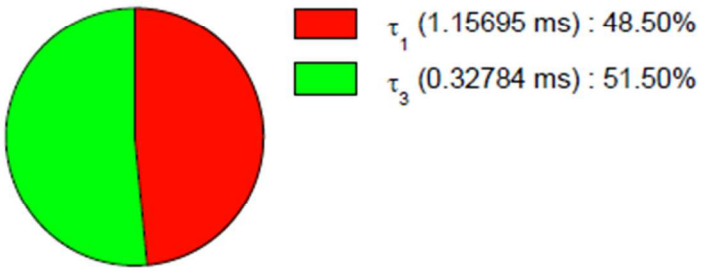
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	671520	-520	+520	Fitting
τ_1 [ms]	1.15695	-0.00083	+0.00083	Fitting
A_2 [Cnts]	-2015240	-950	+950	Fitting
τ_2 [ms]	0.42233	-0.00027	+0.00027	Fitting
A_3 [Cnts]	2516200	-1100	+1100	Fitting
τ_3 [ms]	0.32784	-0.00019	+0.00019	Fitting
A_4 [Cnts]	-916200	-1200	+1200	Fitting
τ_4 [ms]	0.26196	-0.00047	+0.00047	Fitting
Bkgr. Dec [Cnts]	16.0	-1.6	+1.6	Fitting

Average Lifetime:

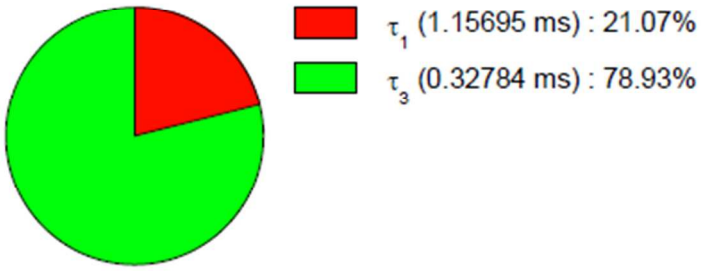
$\tau_{Av.1}$=1.46264 ms (intensity weighted)

$\tau_{Av.2}$=1.99328 ms (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:



Fitted Decay and Exponential Components:

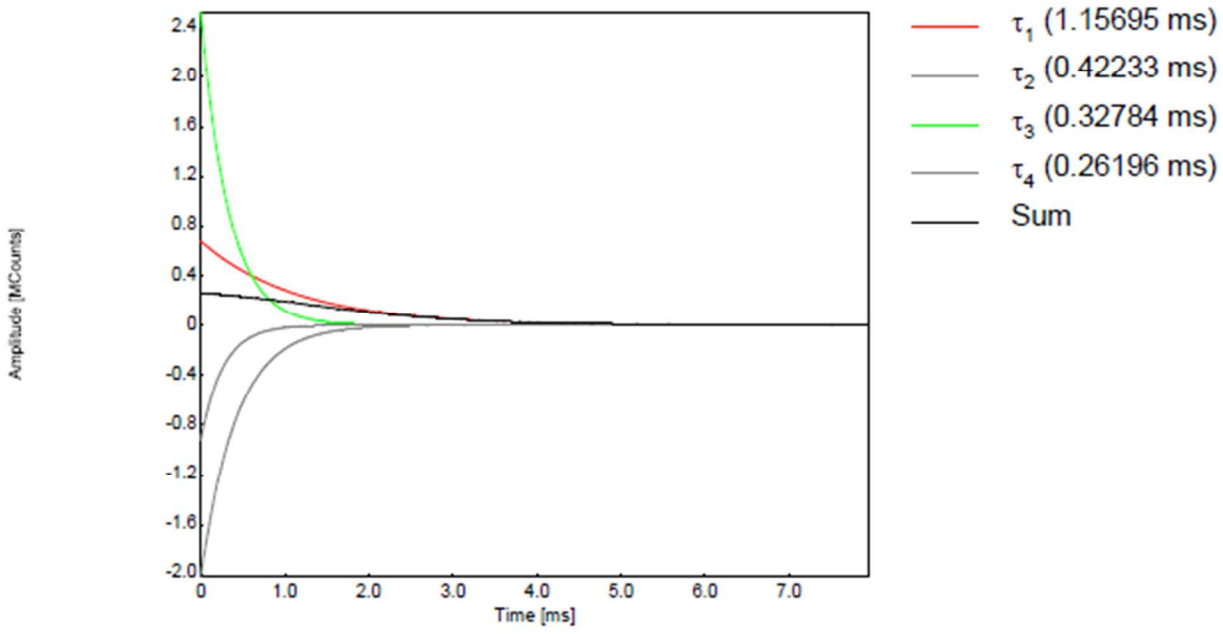
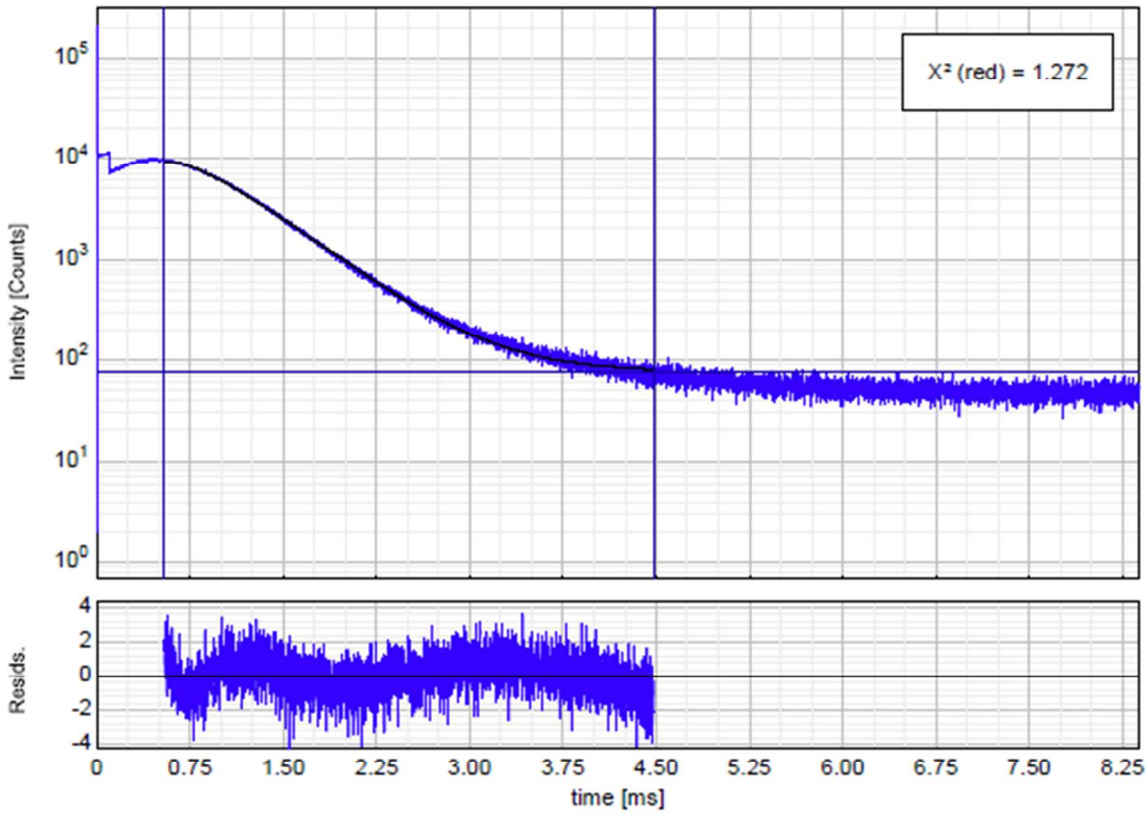


Figure S7. Lifetime data and tailfit analysis for the NIR (800nm) emission region of the thermolytical synthesis UNPs.



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	20877	-62	+62	Fitting
τ_1 [ms]	0.4667	-0.0012	+0.0012	Fitting
A_2 [Cnts]	-11518	-92	+92	Fitting
τ_2 [ms]	0.2525	-0.0024	+0.0024	Fitting
Bkgr. Dec [Cnts]	76.2	-2.7	+2.7	Fitting

Average Lifetime:

$\tau_{Av.1}$=0.5578 ms (intensity weighted)

$\tau_{Av.2}$=0.7304 ms (amplitude weighted)

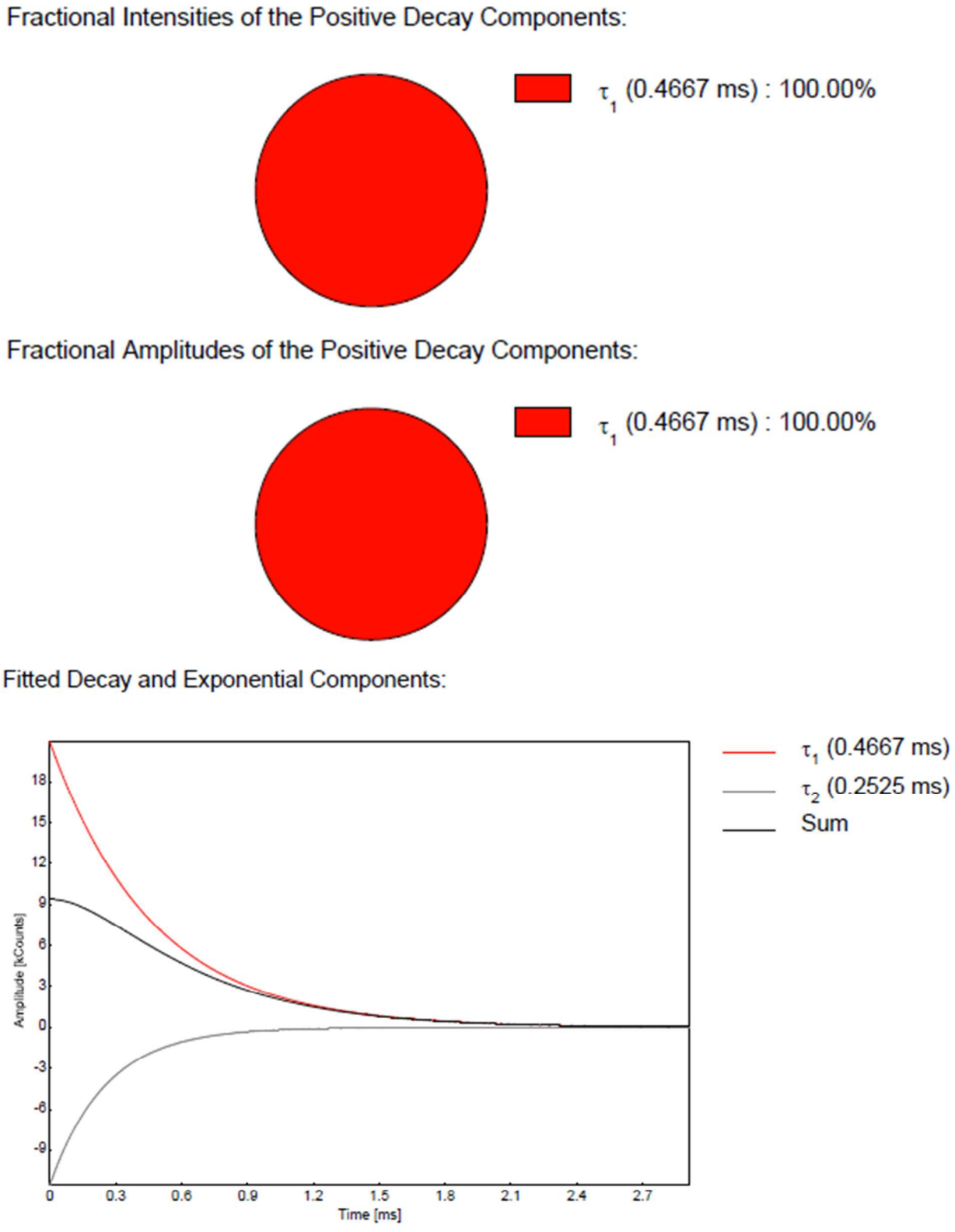


Figure S8. Lifetime data and tailfit analysis for the UV (345nm, 360nm) emission region of the thermolytical synthesis UNPs.

References:

(1) Tang, C.; Wu, Q.; Zhuang, J.; Yang, X.; Wang, J.; Wu, M.; Ozin, G. a. *CrystEngComm* **2014**, *16* (29), 6526.

(2) Yan, B.; Boyer, J. C.; Branda, N. R.; Zhao, Y. *J. Am. Chem. Soc.* **2011**, *133* (49), 19714.