Electronic Supplementary Material (ESI) for Nanoscale.
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Energy transfer in diiodoBODIPY-grafted upconversion nanohybrids

Supporting Information

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1. Experimental Section

Materials

All chemicals used for the UCNP synthesis (lanthanide chlorides ($YCl_3{\cdot}6H_2O$, $YbCl_3{\cdot}6H_2O$ and $ErCl_3{\cdot}6H_2O$ (>99.9%, all of them)), 1-octadecene (95%), oleic acid (99.9%), NaOH and NH_4F (99.99%)) were purchased from Sigma-Aldrich and used without previous purification. HS-PEG-NH_2 was purchased from Rapp-Polymere (3.0 KDa).

Equipment

UV-Vis measurements. UV-Vis spectra were recorded using a quartz cuvette (1x1x4 cm) in a SECOMAN Uvi Light XT-5 spectrometer provided with Lab power junior software 3.05 version.

Steady-state upconversion emission measurements. Upconversion emission spectra were collected by excitation at 975 nm using a CW 975 nm diode laser (Thorlabs L975P1WJ) with a 2-nm slit width and 4 nm/s speed scan at 293K as excitation source coupled to the SLM AmingoBowmann series 2 (AB2) fluorimeter (Microbeam, S.A.).

Time-resolved upconversion emission measurements. Fluorescence decay curves were recorded with a FLS980 spectrofluorometer from Edinburg Scientific with a 8W quasi-CW 975 nm laser diode coupled to fiber. A low pass dichroic filter was used to quench 9705 nm laser radiation and let pass the whole visible spectrum towards emission monochromator. The LD was triggered by the FLS980 system, and multi-scaling software from Edinburg Scientific was used for decays collection. All the measurements were carried out at room temperature.

Centrifugation. Centrifugation was carried out in an Eppendorf Centrifuge 5804 R.

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) images were obtained using a Jeol 1010 microscope operating at 100 kV equipped with a AMT RX80 (8Mpx) digital camera. High resolution transmission electron microscopy (HRTEM) images were recorded using a TECNAI G2 F20 with a field of emission transmission of 200 kV with 0.24 nm (Point resolution). It is equipped with a camera CCD GATAN and "Digital Micrograph" Software of image acquisition. For the preparation of the UCNP samples, 10 mL of a 0.05 mg/mL solution of the UCNPs was left to dry under vacuum at room temperature on a formvar/carbon film supported on a 300 mesh copper grid.

X-Ray Difraction (XRD). XRD pattern was obtained using a powder diffractometer D5005 model Bruker brand with a 0-20 configuration, Cu anode X-ray tube, secondary monochromator of diffracted beam, scintillation detector, automatic slits and rotating sample holder (15-120 rpm), with automatic charger of 40 specimen containers.

Syntheses of UCNPs and nanohybrids

Oleate-capped upconversion nanoparticles

$NaYF_4$: Yb^{3+}, Er^{3+} nanoparticles were synthesized following a described protocol with some modifications.[1] 0.8 mmol $YCl_3{\cdot}6H_2O$, 0.18 mmol $YbCl_3{\cdot}6H_2O$ and 0.02 mmol $ErCl_3{\cdot}6H_2O$ were mixed with 12 mL oleic acid and 15 mL octadecene in a 50 mL round-bottom flask under stirring. The mixture was heated to 160 ºC until dissolution of salts. Then, solution was cooled at 110 ºC and a mixture of NaOH (2.5 mmol), NH_4F (4.0 mmol) and methanol (10 mL) was slowly added to allow the formation of the nanoparticles precursors. Methanol was evaporated at 100 ºC during 30 minutes under N_2 flow. After that, solution was heated at 305ºC and kept at this temperature for 1 hour, under vigorous stirring and N2 atmosphere. Finally, solution was cooled at room temperature and nanoparticles were precipitated by centrifugation at 10000 rpm, 10 minutes. Precipitated was washed 3 times with a 43.5:40.5:16 v/v hexane-acetone-methanol solution. Nanoparticles were dried at vacuum for 24 h.

PEG-coated up-conversion nanoparticles: UCNP@PEG

These nanoparticles were prepared following a previously method described by our group.[2] 10 mg of oleate-capped nanoparticles were dispersed by sonication (15 min) in degassed chloroform (5 mL). Then, 100 mg of HS-PEG-NH_2 were added. This mixture was kept in dark, under strong stirring and nitrogen atmosphere at 60 ºC overnight. Chloroform was evaporated in vacuum and 5 mL of MiliQ water were added and sonicated for 15 minutes. Nanoparticles were recovered by centrifugation at 10000 rpm, 10 minutes, 25º. Then, 5 cycles of sonication/centrifugation with a total of 50 mL of acetonitrile were carried out in order to remove the oleate and PEG excess. UCNP@PEG were resuspended in 1 mL of MilliQ water and stored at +4ºC.

UCNP–IBDP@PEG

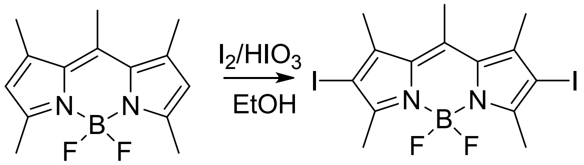
UCNP-IBDP@PEG were synthesized following a protocol developed in our group.[3] 500 mL of a dispersion of UCNP@PEG (10 mg·mL^{-1}) in MiliQ water was sonicated for 15 minutes and a solution of 3-(2’,6’-diiodo-1’,3’,5’,7’-tetramethyl-4’,4’-difluoro-4’-bora-3’a,4’a-diaza-s-indacen-8’yl)propanoic acid[4] (IBDP, 2.5 mg; UCNP–IBDP@PEG 1 mg per 0.5 mg ratio) in TEA (0.5 mg mL^{-1}) was added. This mixture was stirred at room temperature for 24 h. After that, nanoparticles were separated by centrifugation (10000 rpm, 10 min, 25ºC) and purified by 5 cycles of sonication for 15 minutes with acetonitrile and centrifugation for 10 minutes at 10000 rpm. Nanohybrids were resuspended in MilliQ water.

UCNP-IBDP

UCNP-IBDP were synthesized analogously to UCNP-2IBDP@PEG. 5 mg of oleate-capped UCNP, 2.5 mg of IBDP and 3 mL of TEA buffer (pH = 7.5) were sonicated for 15 minutes. Then, the mixture was stirred at room temperature for 24 h in an orbital shaker (350 ppm). Nanoparticles were precipitated by centrifugation (10000 rpm, 10 min, 25ºC) and redispersed by sonication in acetonitrile (5 mL) followed by centrifugation in order to remove IBDP excess. 5 cycles more of sonication/centrifugation were carried out. Finally, UCNP-IBDP nanohybrid was resuspended in toluene.

Syntheses of IBDPnc

4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diiodo-4-bora-3a,4a-diaza-s-indacene.



In this work, the iodation was performed with iodine and iodic acid in methanol at room temperature with a quantitative yield from 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene. The characterisation of the purified product matches perfectly well with that described by Bonardi et al.[5]

2. Characterization

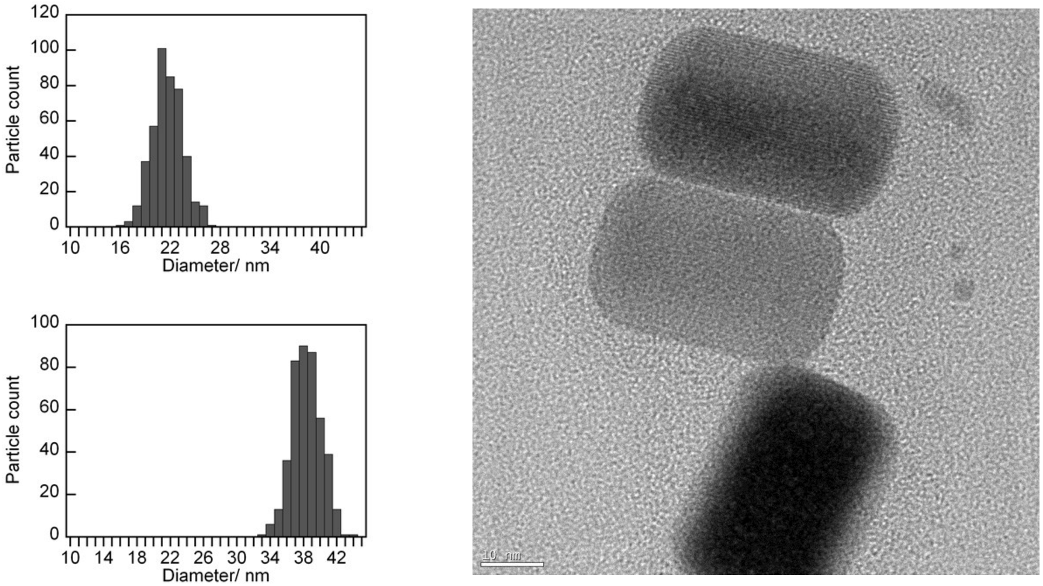
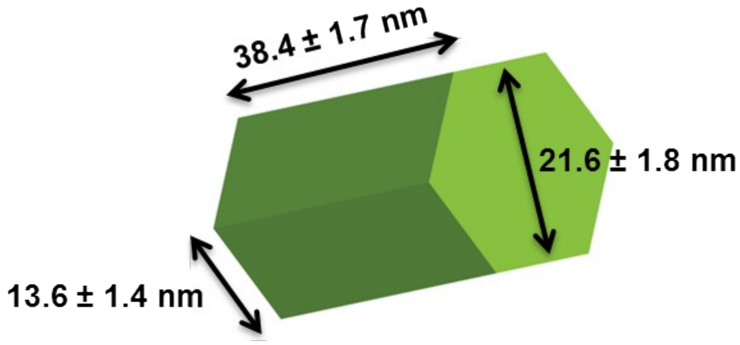


Figure S1. Histogram and HRTEM image and histograms of the oleate-capped UCNPs**.** Scale bar: 10 nm



Cartoon S1. Size of the core of UCNP@OA nanoparticles.

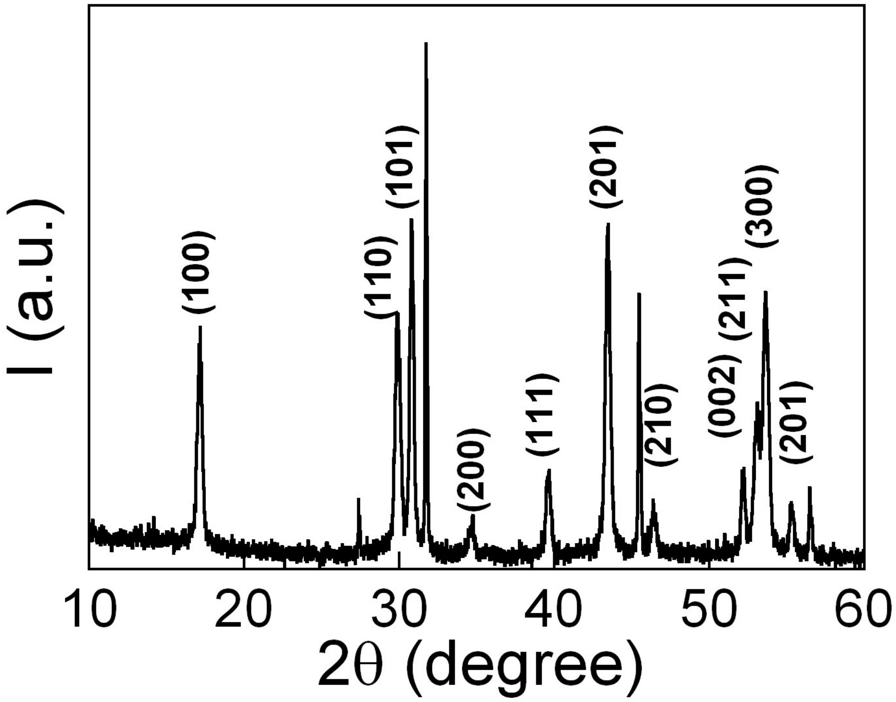


Figure S2. XRD spectrum of the initial oleate-capped UCNPs. The extra diffraction peaks in spectrum are due to NaCl (DB card number 01-070-2509 Halite, syn; 2: 27.33, 31.64, 45.39, 56.41).

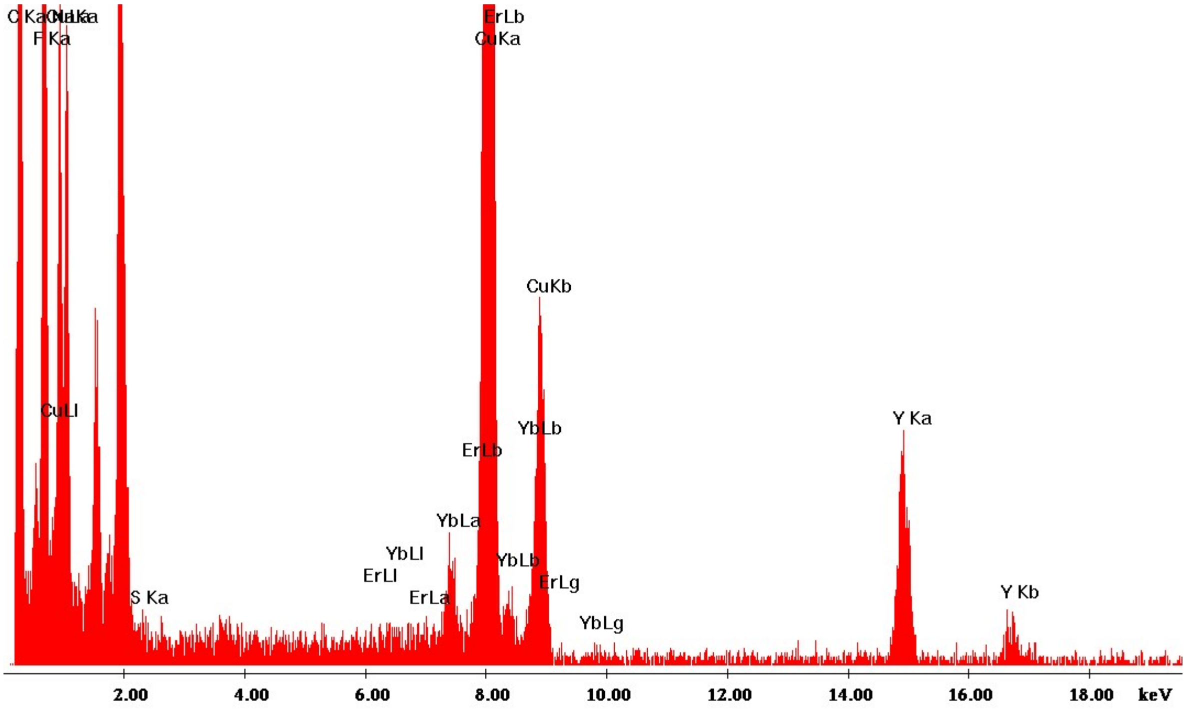


Figure S3. EDAX analysis of the initial UCNP@OA: $NaYF_4$,Yb^{3+} (16%), Er^{3+} (4%).

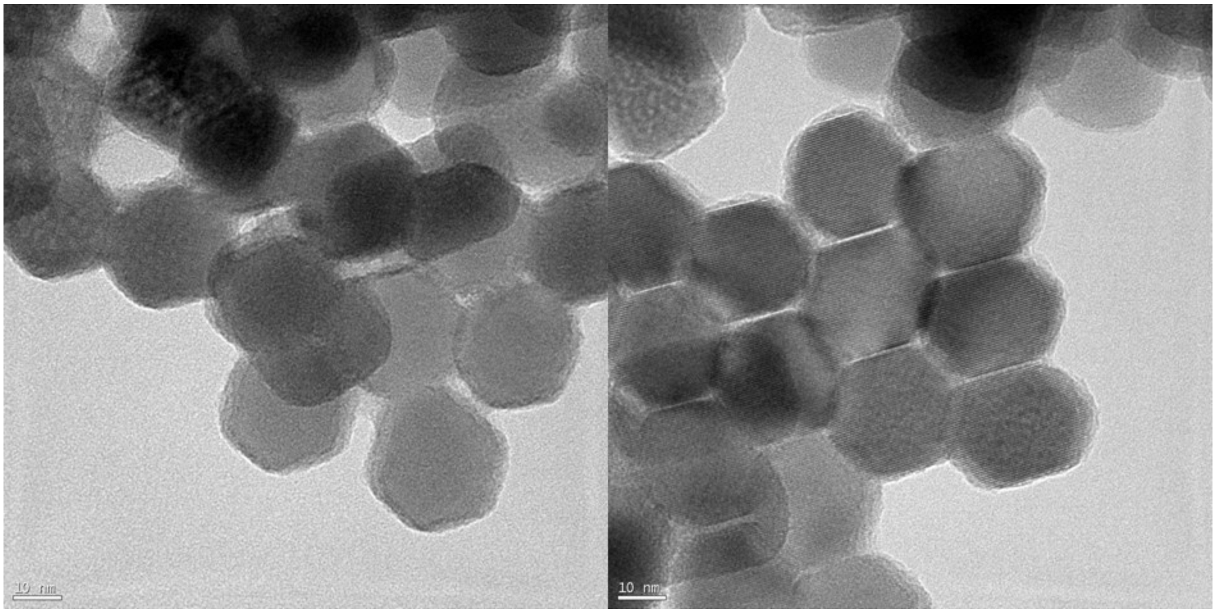


Figure S4. HRTEM images of UCNP@PEG nanohybrids. Scale bar: 10 nm

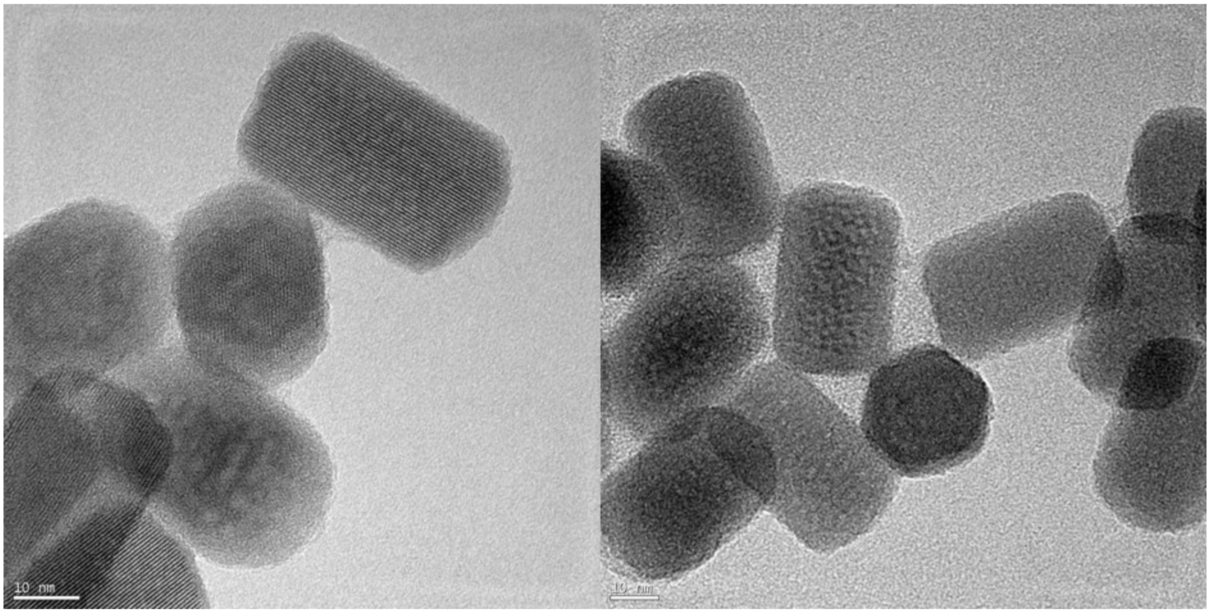


Figure S5. HRTEM images of UCNP-IBDP@PEG nanohybrids. Scale bar: 10 nm.

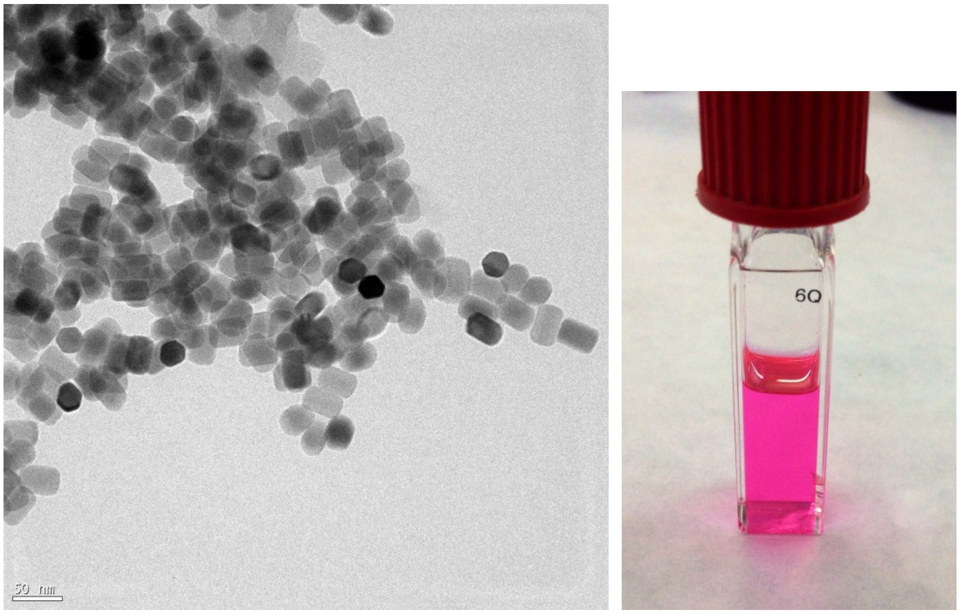


Figure S6. (Left) HRTEM image of UCNP-IBDP@OA nanohybrids. Scale bar: 50 nm. (Right) image of UCNP-IBDP@OA nanohybrid in toluene.

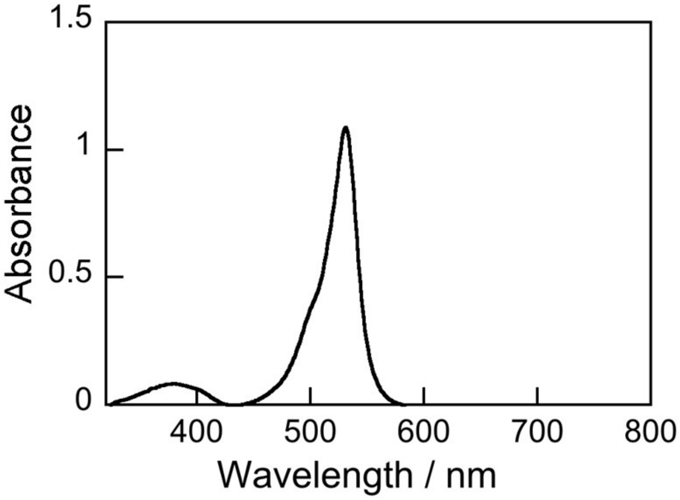


Figure S7. Absorption spectrum of IBDP in toluene. ($\varepsilon = 2.6\text{x}10^6$ M^{-1} cm^{-1}).

The area under the curve for each emission band is plotted versus the excitation power. See example below for naked UCNPs.

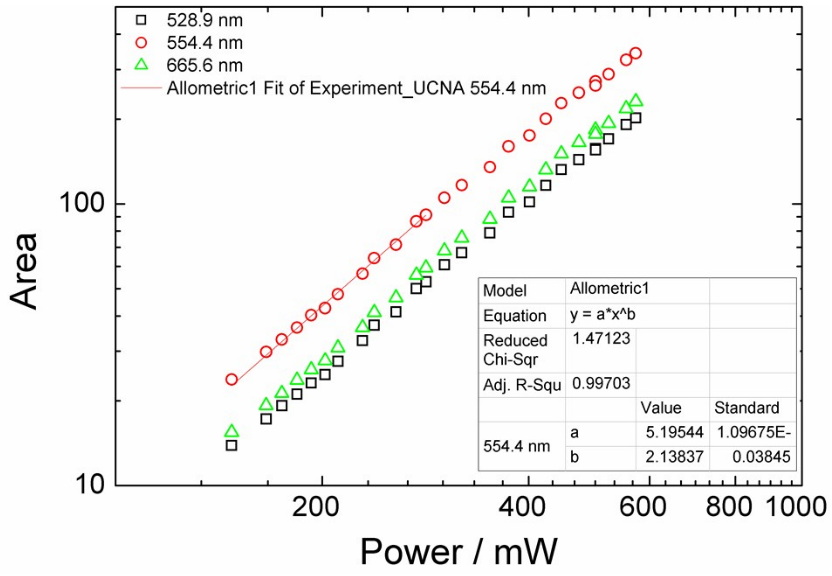


Figure S8. Double logarithmic plots of the integrated intensities of the upconversion emissions obtained under 975 nm CW laser excitation.

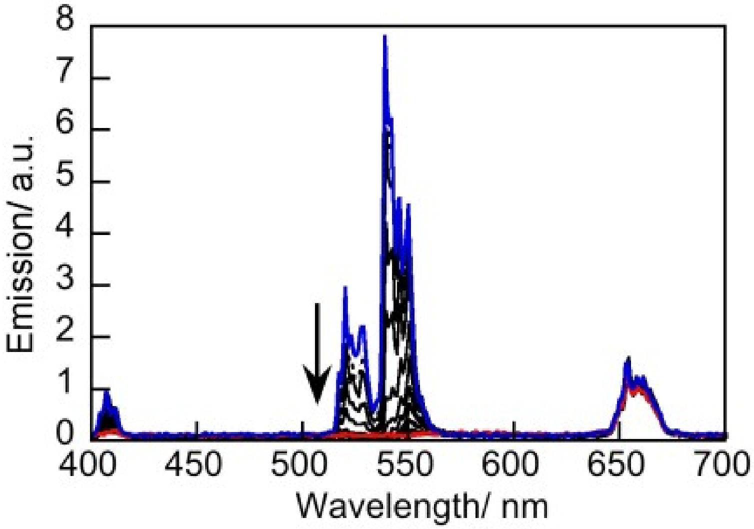


Figure S9. Emission spectra (λ_{exc}=975 nm) of UCNP@OA (1 mg in 1 mL toluene) upon incremental additions of a toluene solution of an IBDP lacking the carboxylic group (IBDPnc). Blue line: emission spectrum of UCNP@OA. Red line: emission spectrum of the final solution with an IBDPnc concentration of 0.45 mM.

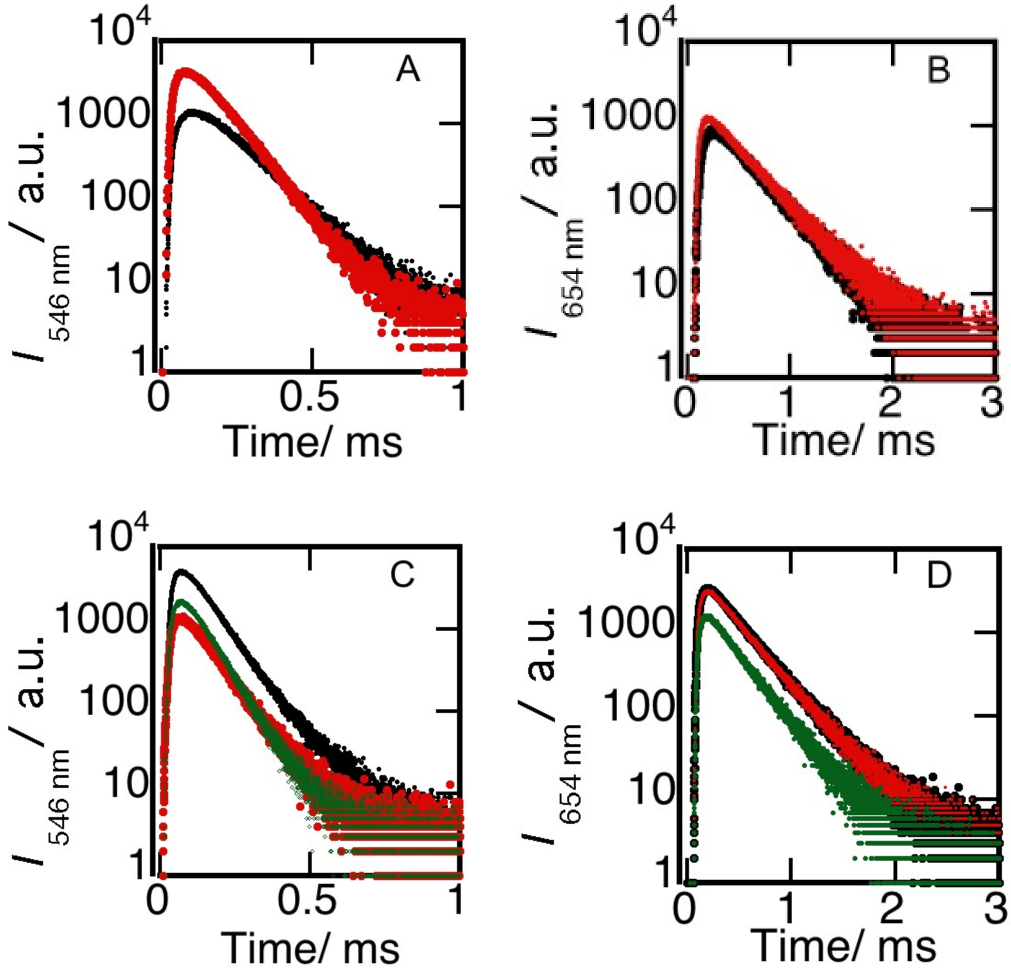
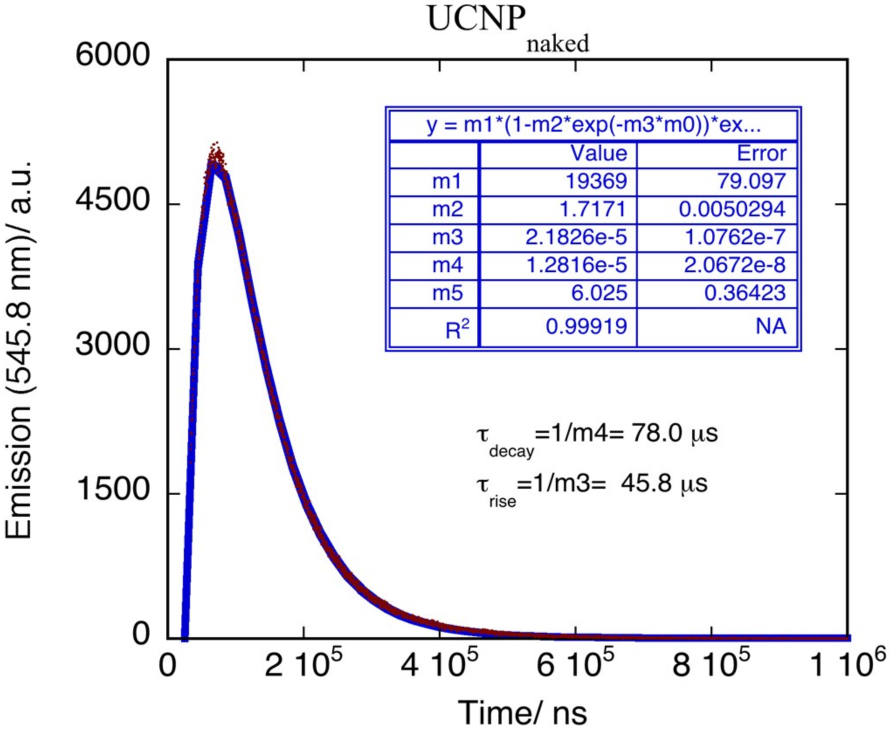


Figure S10. Kinetic time profiles of UCNP@OA (black trace) and UCNP-IBDP@OA (red trace) in toluene at A) 546 nm, B) 654 nm; and UCNP$_{\text{naked}}$ (black trace), UCNP@PEG (red trace), and UCNP-IBDP@PEG (green trace) in water at C) 546 nm, D) 654 nm.

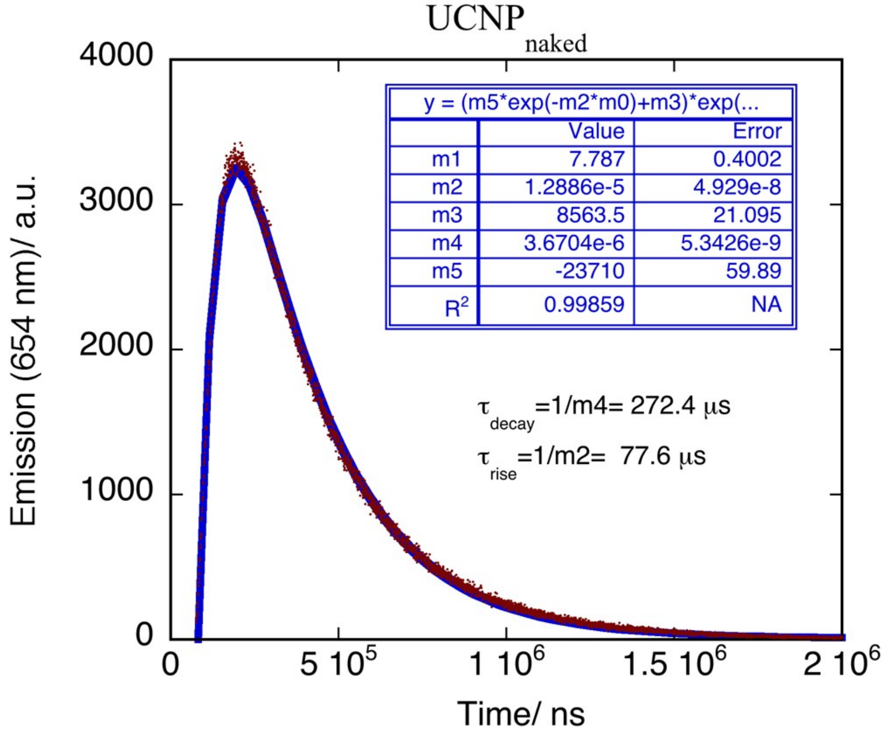
The rise and decay lifetimes (τ_{rise} and τ_{decay}, respectively) were determined by fitting the data to the following equation:

$$y = A_1 (1 - A_2 \exp^{-A_3 t}) \cdot \exp^{-A_4 t} + A_5$$

Time-resolved experiments in water (selected kinetics).



	Value	Error
m1	19369	79.097
m2	1.7171	0.0050294
m3	2.1826e-5	1.0762e-7
m4	1.2816e-5	2.0672e-8
m5	6.025	0.36423
R^2	0.99919	NA



	Value	Error
m1	7.787	0.4002
m2	1.2886e-5	4.929e-8
m3	8563.5	21.095
m4	3.6704e-6	5.3426e-9
m5	-23710	59.89
R^2	0.99859	NA

Figure S11. Kinetic time profiles of UCNP$_{naked}$ at 546 nm and 654 nm in water.

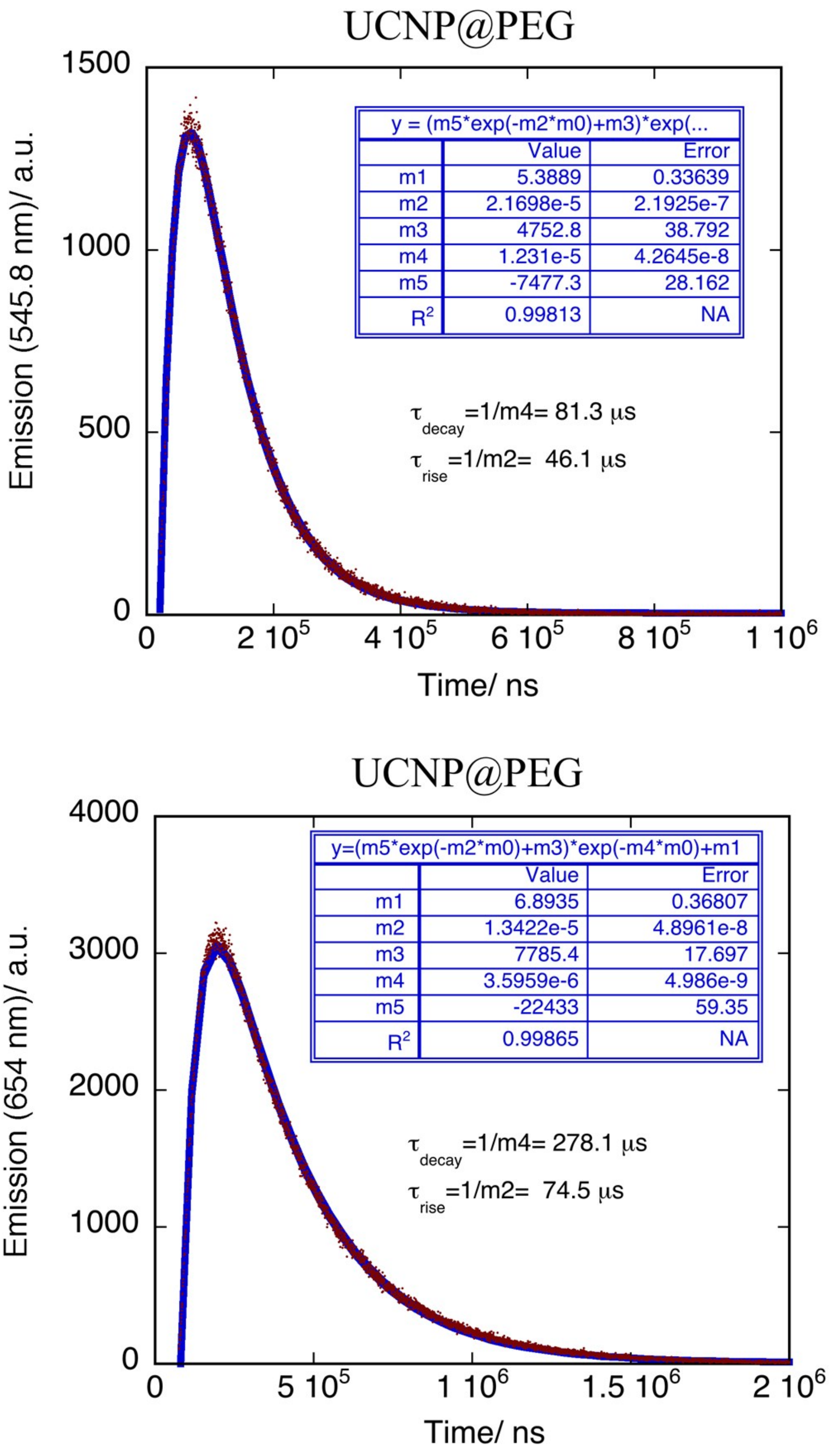
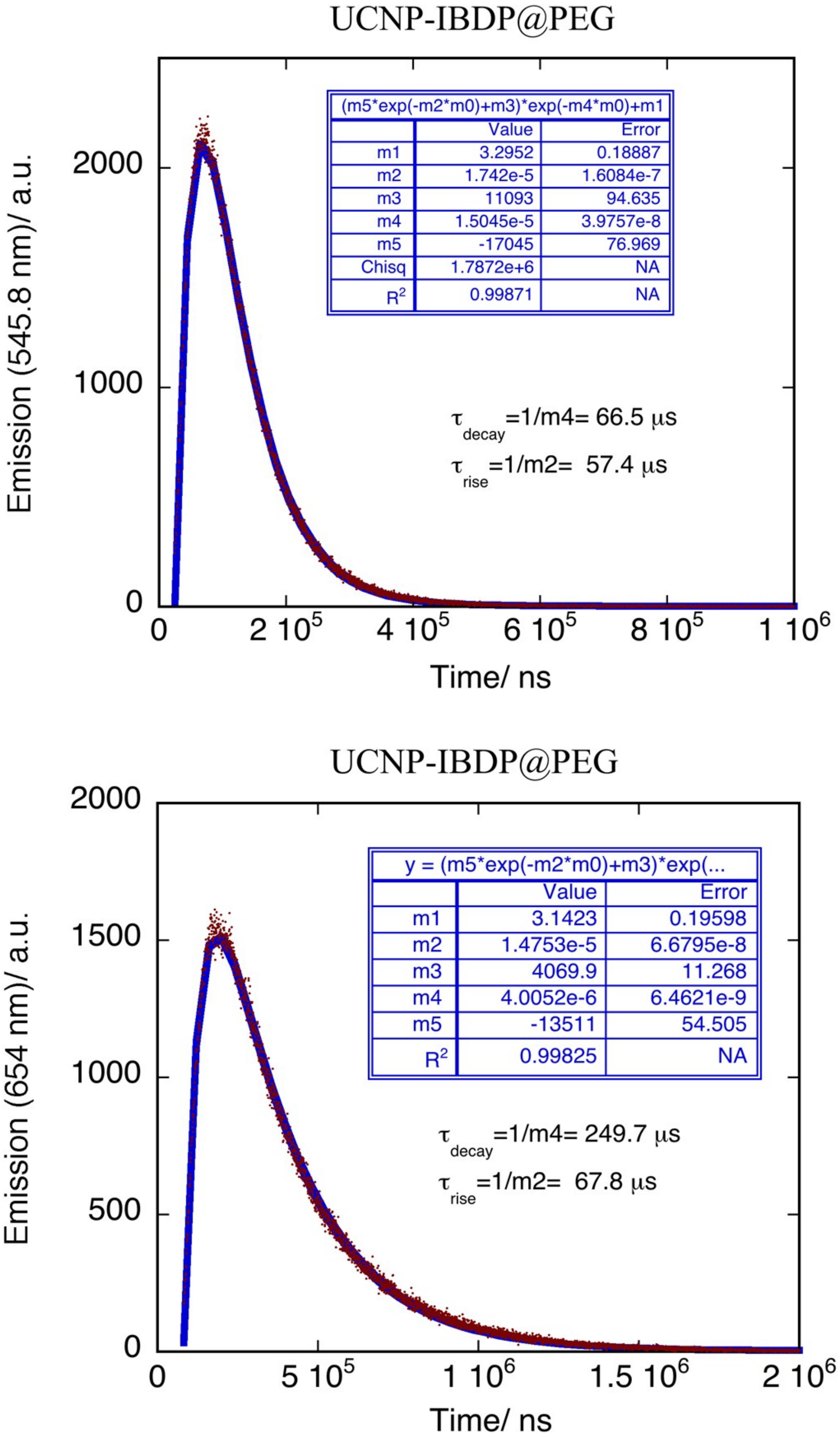


Figure S12. Kinetic time profiles of UCNP@PEG at 546 nm and 654 nm in water.



UCNP-IBDP@PEG

(m5*exp(-m2*m0)+m3)*exp(-m4*m0)+m1		
	Value	Error
m1	3.2952	0.18887
m2	1.742e-5	1.6084e-7
m3	11093	94.635
m4	1.5045e-5	3.9757e-8
m5	-17045	76.969
Chisq	1.7872e+6	NA
R^2	0.99871	NA

τ_{decay}=1/m4= 66.5 μs

τ_{rise}=1/m2= 57.4 μs

UCNP-IBDP@PEG

y = (m5*exp(-m2*m0)+m3)*exp(...		
	Value	Error
m1	3.1423	0.19598
m2	1.4753e-5	6.6795e-8
m3	4069.9	11.268
m4	4.0052e-6	6.4621e-9
m5	-13511	54.505
R^2	0.99825	NA

τ_{decay}=1/m4= 249.7 μs

τ_{rise}=1/m2= 67.8 μs

Figure S13. Kinetic time profiles of UCNP-IBDP@PEG at 546 nm and 654 nm in water.

Time-resolved experiments in toluene

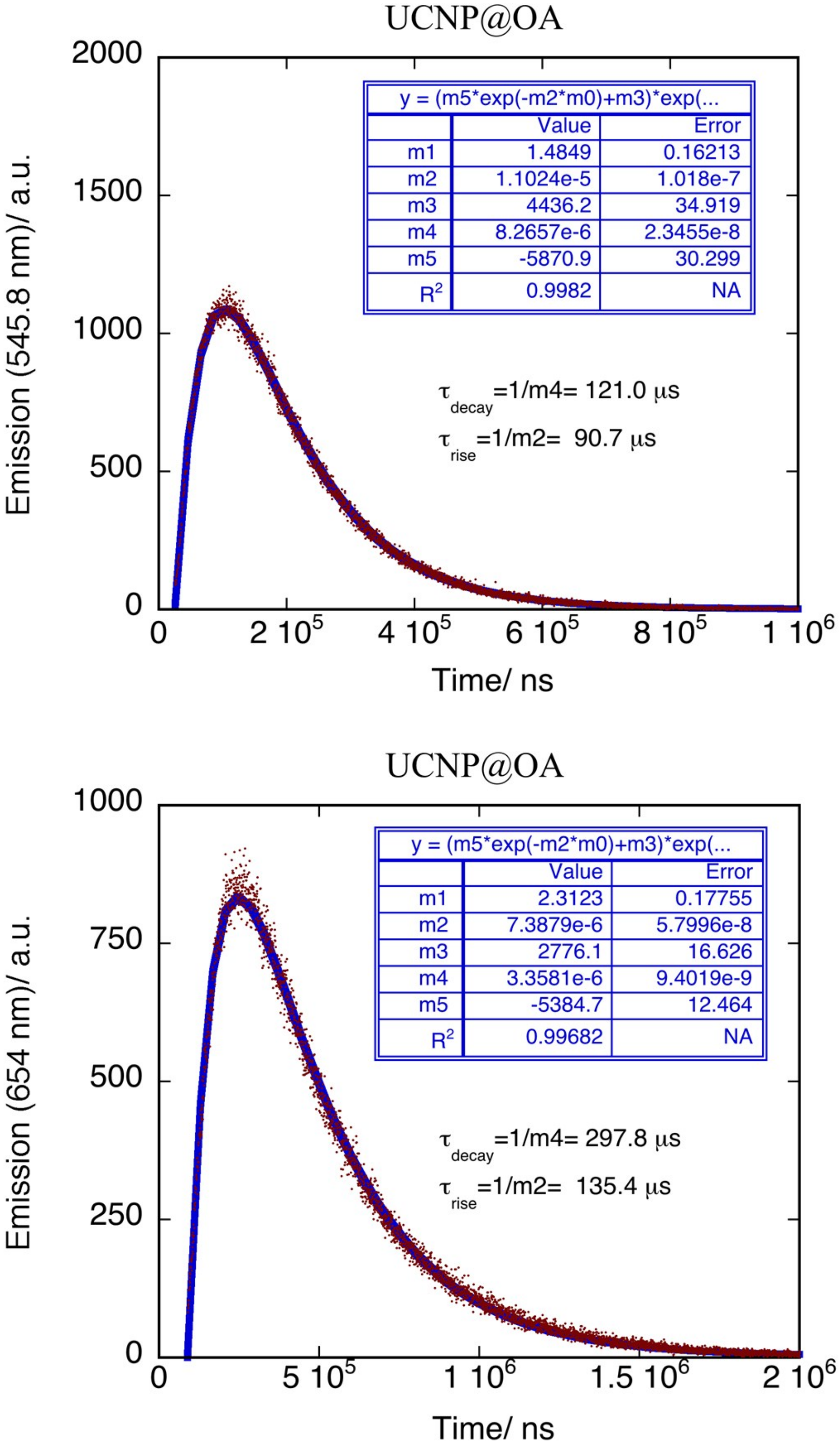
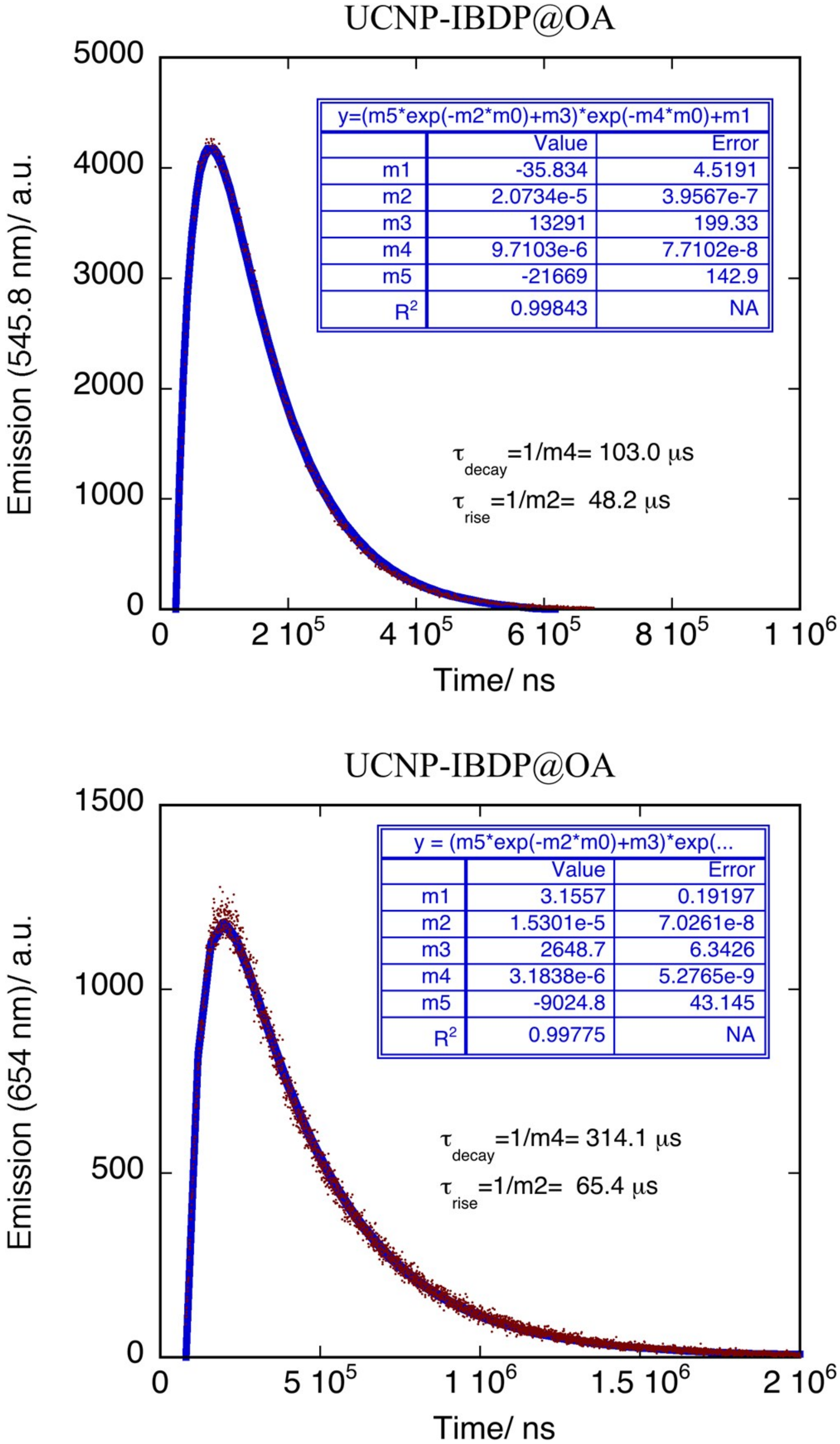


Figure S14. Kinetic time profiles of UCNP@OA at 546 nm and 654 nm in toluene.



y=(m5*exp(-m2*m0)+m3)*exp(-m4*m0)+m1

	Value	Error
m1	-35.834	4.5191
m2	2.0734e-5	3.9567e-7
m3	13291	199.33
m4	9.7103e-6	7.7102e-8
m5	-21669	142.9
R^2	0.99843	NA

y = (m5*exp(-m2*m0)+m3)*exp(...

	Value	Error
m1	3.1557	0.19197
m2	1.5301e-5	7.0261e-8
m3	2648.7	6.3426
m4	3.1838e-6	5.2765e-9
m5	-9024.8	43.145
R^2	0.99775	NA

Figure S15. Kinetic time profiles of UCNP-IBDP@OA at 546 nm and 654 nm in toluene.

Experiments in toluene.

- Intermolecular quenching

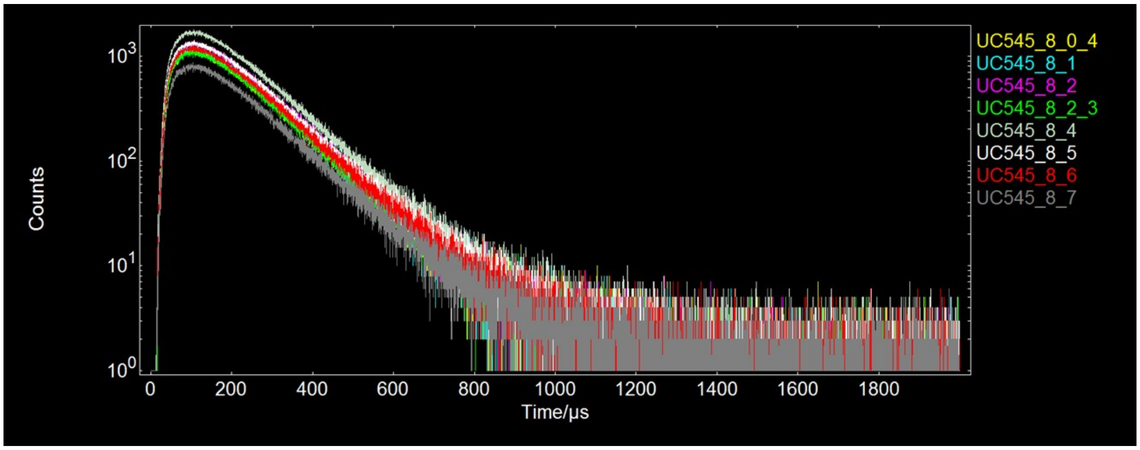
To a solution of UC@oleate in toluene (1 mg/ml) increasing amounts of IBDP were added (stock=0.016 M). Quartz cuvettes 1x1cm. IBDP has low fluorescence (Φ_F=0.02 in methanol).

Concentrations added:

V_{add}	V_{total}	[IBDP]/ mM	Sample name
0	0	0	**UC_545_8_0**
2	2	0.016	**UC_545_8_1**
3	5	0.039	**UC_545_8_2**
5	10	0.078	**UC_545_8_3**
10	20	0.16	**UC_545_8_4**
30	70	0.54	**UC_545_8_6**
50	120	0.93	**UC_545_8_7**

Please note that the TOD of the following kinetics cannot be compared since the measurements conditions were optimized for each sample.

1 Kinetics at 545.8 nm UC@OA + IBDP



Yb^{3+}-IBDP complexes

7 mg of $YbCl_3 \cdot 6H_2O$ were dissolved in a mixture of 1.2 mL of OA and 1.5 mL of ODE at 160ºC. This solution was cooled at room temperature. 700 µL of this solution was mixed with a solution of IBDP in toluene (6 mg/mL). For the 1:1 complex with 450 µL and for 1:2 complex with 890 µL. Then, toluene was added until a volume of 2 mL. Solutions were sonicated for 10 minutes.

Yb^{3+}-IBDP complexes

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References

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