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Supporting Information

for

Upconversion nanoparticles with a strong acid-resistant capping

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Materials. 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 used for the synthesis of UCNPs. 2-hydroxyethyl methacrylate and 2-acrylamido-2-methylpropanesulphonic acid (AMPS) and 2,2'-azobisisobutyronitrile (AIBN) were used for the polymerizations. All chemicals were purchased from Sigma-Aldrich and used as received without previous purification. Sodium carbonate (Na_2CO_3) was purchased form Merck and used as received.

Solvents used in this work are chloroform (Fischer), ethanol (Scharlau), dichloromethane (DCM; Scharlau), tetrahydrofuran (THF; Sigma-Aldrich), acetonitrile (ACN; Scharlau), n-propanol (Sigma-Aldrich) and diethyl ether (Scharlau) were used as received.

Synthesis of oleate-capped UCNPs. $NaYF_4$:Yb (18%), Er (2.0%) nanoparticles were synthesized following a previously reported protocol with some modifications.[1] Basically, $YCl_3 \cdot 6H_2O$ (0.8 mmol), $YbCl_3 \cdot 6H_2O$ (0.18 mmol), and $ErCl_3 \cdot 6H_2O$ (0.02 mmol) were mixed with 12 mL oleic acid and 15 mL octadecene (ODE) in a 50 mL round-bottom Pyrex flask under continuous stirring. The mixture was heated to 160ºC until complete dissolution of all the reagents and then it was cooled down to *ca.* 110°C. A 10 mL methanol solution containing NaOH (2.5 mmol) and NH_4F (4.0 mmol) was slowly added into the flask and the solution was stirred while being slowly heated to remove methanol, degassed at 100ºC for 30 min and heated to 305°C under argon flux during one hour. Then, the solution was cooled at room temperature and the UCNPs were precipitated by centrifugation (10000 rpm, 10 min, 25°C). Later on, the oleate-capped UCNPs were washed three times with a (43.5:40.5:16 v/v/v) hexane/acetone/methanol solution.

Methods. ^{1}H-NMR spectra were registered at room temperature in a Bruker AVANCE DRX 300 spectrometer. Deuterated chloroform or deuterated water were used as solvents. Chemical shifts are reported in parts per million (δ, ppm) using the peak of the solvent as internal reference. The following abbreviations are used to describe signals: s (singlet), d (doublet), t (triplet), q (quartet), m (complex multiplet).

Attenuated Total Reflectance (ATR) spectra were recorded using a FT-IR spectrometer Thermo Nicolete Nexus, with ATR module Smart Orbit™. The spectra were recorded in a wavenumber range of 4000-500 cm^{-1}.

The absorption measurements were carried out in a SECOMAN UVI Light UV-Visible spectrophotometer.

The pH measurements were registered with a pH-Meter GLP 21+ (Crison).

Upconversion emission spectra were collected by excitation of the samples with a CW 975 nm diode laser (Thorlabs L975P1WJ) with an excitation density of 249.4 mW/cm^2 and coupled to the SLM Amingo Bowmann series 2 (AB2) fluorimeter (Microbeam, S.A.).A front face set up has been used to avoid scattering in the colloidal dispersions when coated with polymers. The emission spectra have been recorded under the same conditions (laser power, slits (2nm), speed scan, etc.).

Transmission electron microscopy (TEM) images were taken using a Jeol 1010 microscope operating at 100 kV equipped with a charge-coupled device (CCD) camera. High resolution TEM (HRTEM) was carried out by using a Field Emission Gun (FEG) TECNAI G_2F20 microscope operated at 200 kV equipped with a charged coupled device (CCD) GATAN and "Digital Micrograph" Software of image acquisition and treatment. The TEM samples were prepared by dropping sample solutions onto a 300-mesh carbon coated copper grid (3 mm in diameter) followed by the evaporation of the solvent.

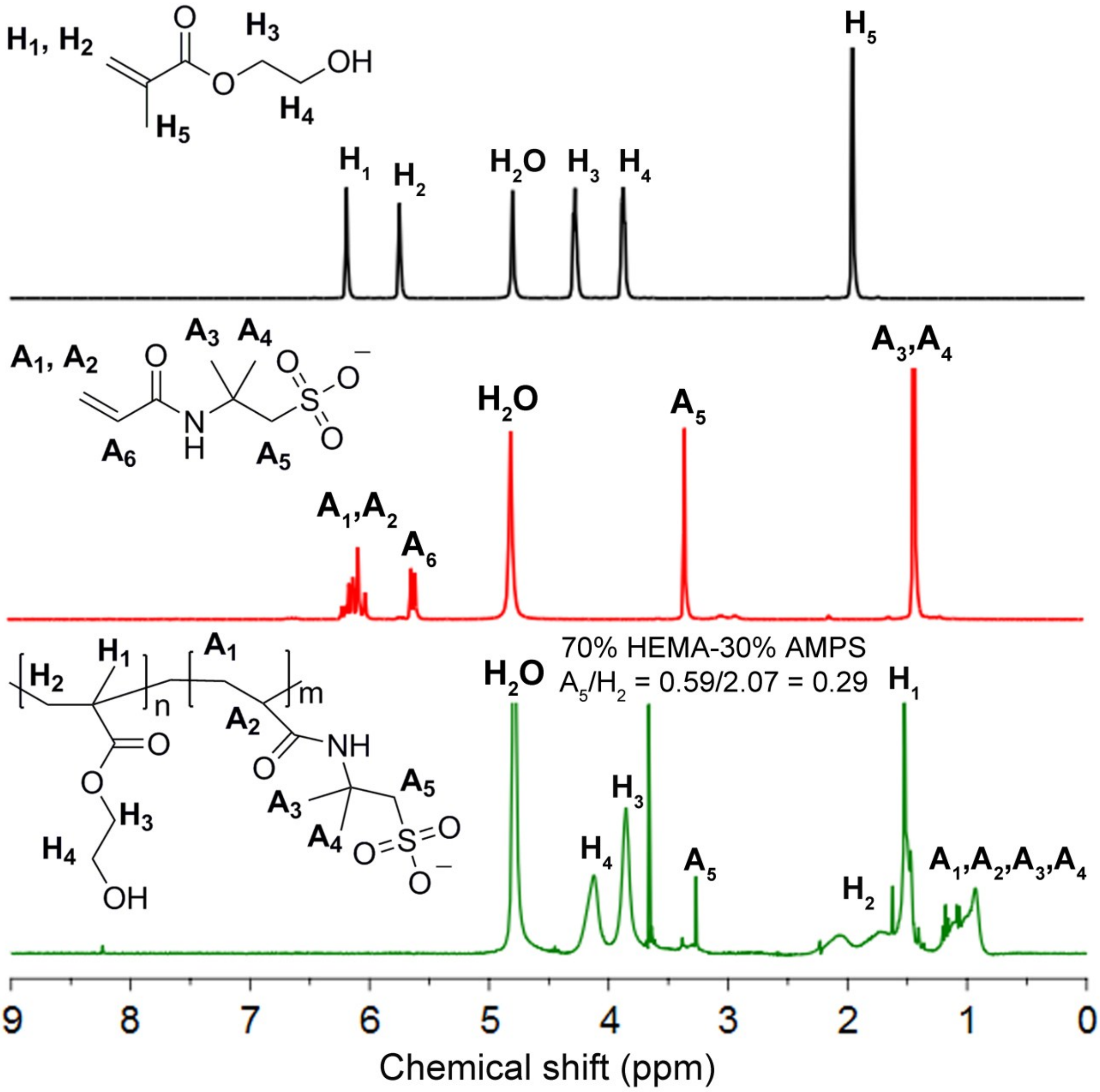
The ligand contents in the copolymer-capped UCNPs and the thermal behavior of the copolymer were evaluated by thermogravimetric analysis (TGA). The thermogram curves were recorded on a Perkin-Elmer TGA-7 model, at a heating rate of 10°C/min, under nitrogen.

The average molecular number (Mn), molecular weight (Mw) and polydispersity (Mw/Mn) of the copolymer were determined by size exclusion chromatography (SEC) system equipped with a Waters 1515 Isocratic HPLC Pump with a Waters 2414 refractive index detector and provided with two columns Styragel HR3 and HR5 from Waters, using DMF (1 % wt. LiBr) as eluent at 30 °C and a flow rate of 0,7 mL min^{-1}. Polystyrene (PS) standards were employed for the calibration.

XRD was carried out with a PANalytical Empyrean X-ray powder diffractometer Cu radiation Oxford Cryostream provided with hybrid monochromator (Cu K alpha 1), focussing mirror and PIXcel detector XRPD for capillary measurements.Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano Z spectrometer with a 10 mW HeNe laser at 633 nm. All measurements were performed at a scattering angle of 173°. All samples are measured at 1mg/mL concentration in water. Samples were kept in solution overnight before measurements in order to ensure pH equilibration (initial pH = 3.5).

References

(1) Zhenquan Li, Z., Y *Nanotechnology,* **2008**, *19*, 345606-345610.



	H_1	H_2	H_3	H_4	H_5	A_1	A_2	A_3	A_4	A_5	A_6
HEMA	1.00	1.00	2.02	1.99	2.94	--	--	--	--	--	--
AMPS	--	--	--	--	--	2.11		6.14		2.03	1.00
COP	3.28	2.07	2.00	2.20	--	2.39				0.59	--

Figure S1. Top: ^{1}H-NMR spectra of HEMA (black line), AMPS (red line) and COP (green line) in D_2O. Bottom: normalized integration values for HEMA, AMPS, and COP.

Table S1. Characterisation of Poly(HEMA-co-AMPS) copolymer (COP).

M_{nSEC}(g mol^{-1})	M_{wSEC}(g mol^{-1})	M_w/M_n	T_g (°C)
19763	21548	1.09	120-150

$M_{n\ SEC}$, average number (calculated by SEC), M_w/M_npolydispersity index and T_g, glass transition temperature.

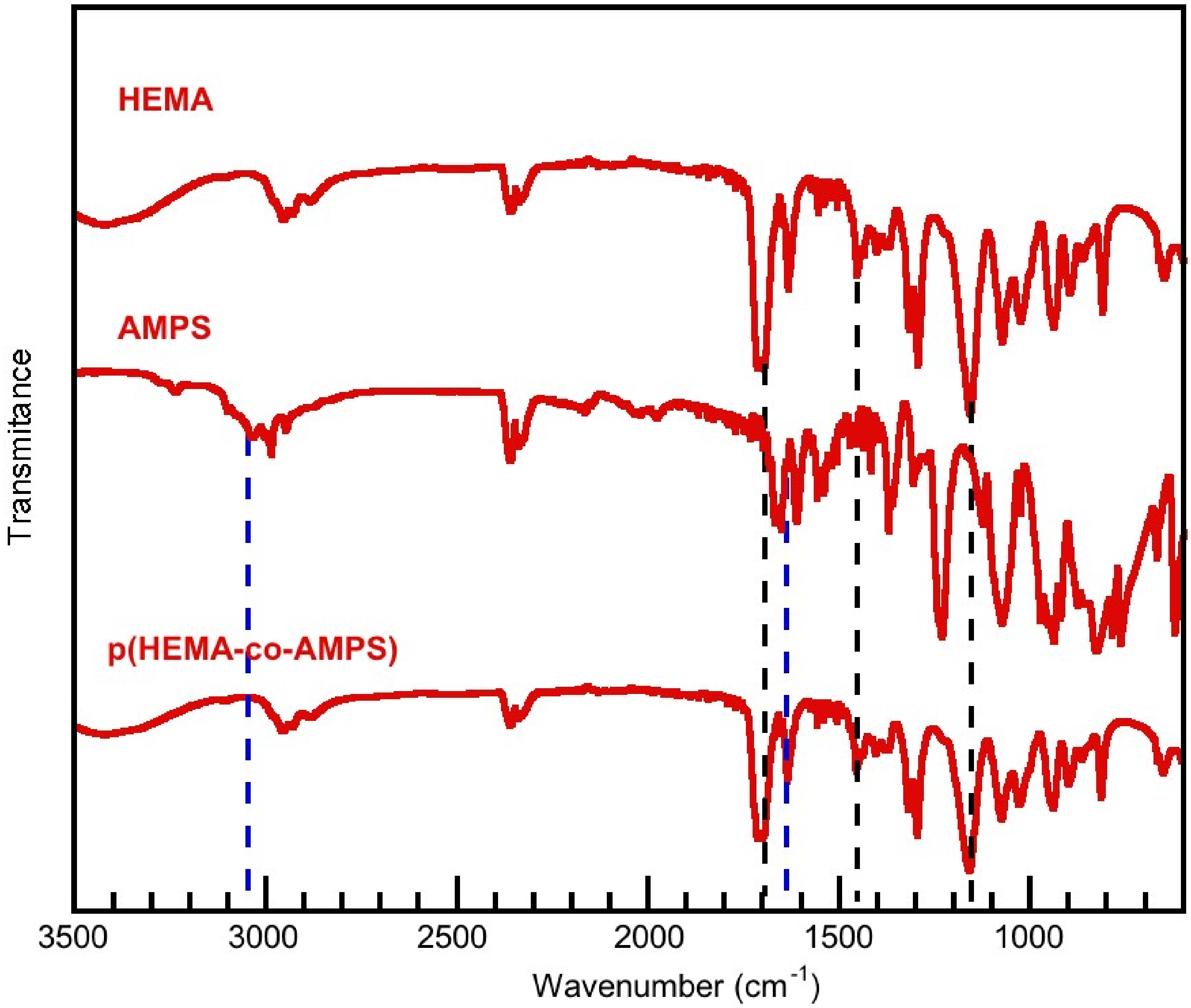


Figure S2. FTIR-ATR spectra of HEMA (top), AMPS (middle) and (HEMA-co-AMPS) copolymer, COP (bottom).

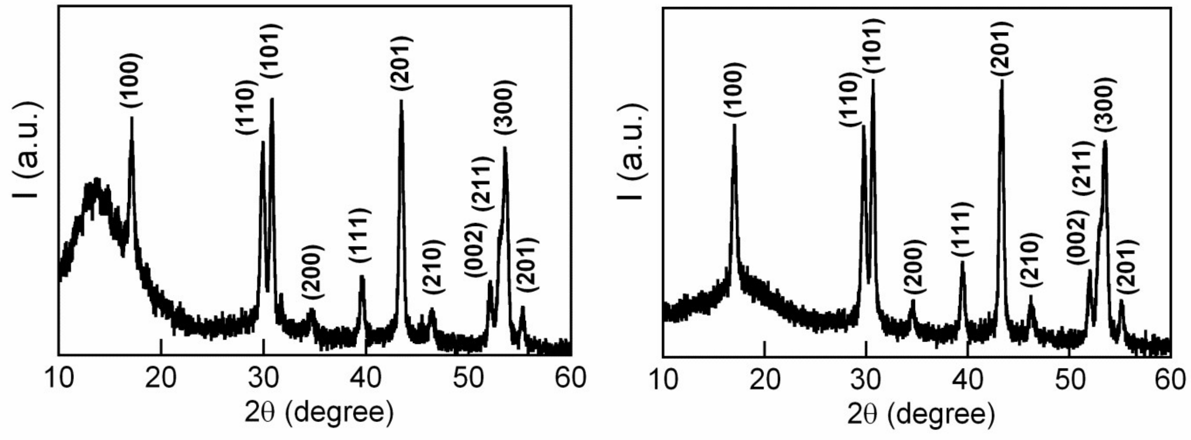


Figure S3. X-ray power diffraction of (XRD) spectrum of the UCNP@oleate(left) and UCNP@COP (right).(JCPDS standard card no. 28-1192).[1]

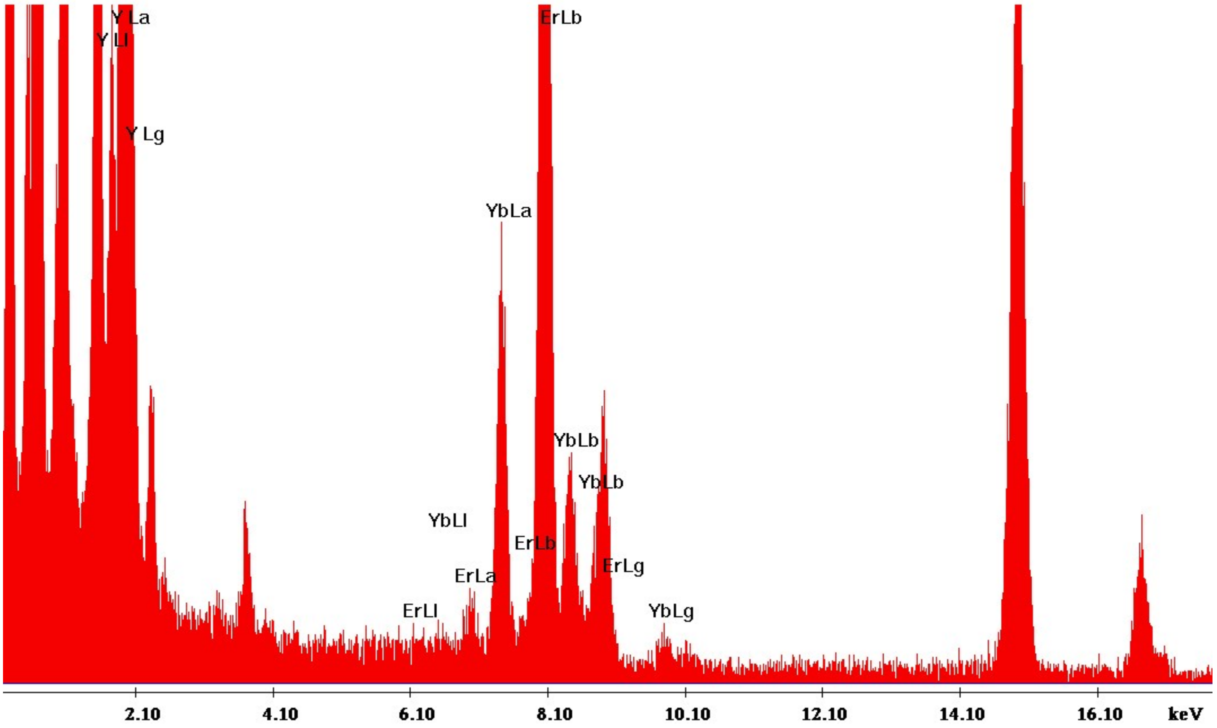


Figure S4. Energy-dispersive X-ray (EDX) of UCNP@oleate.

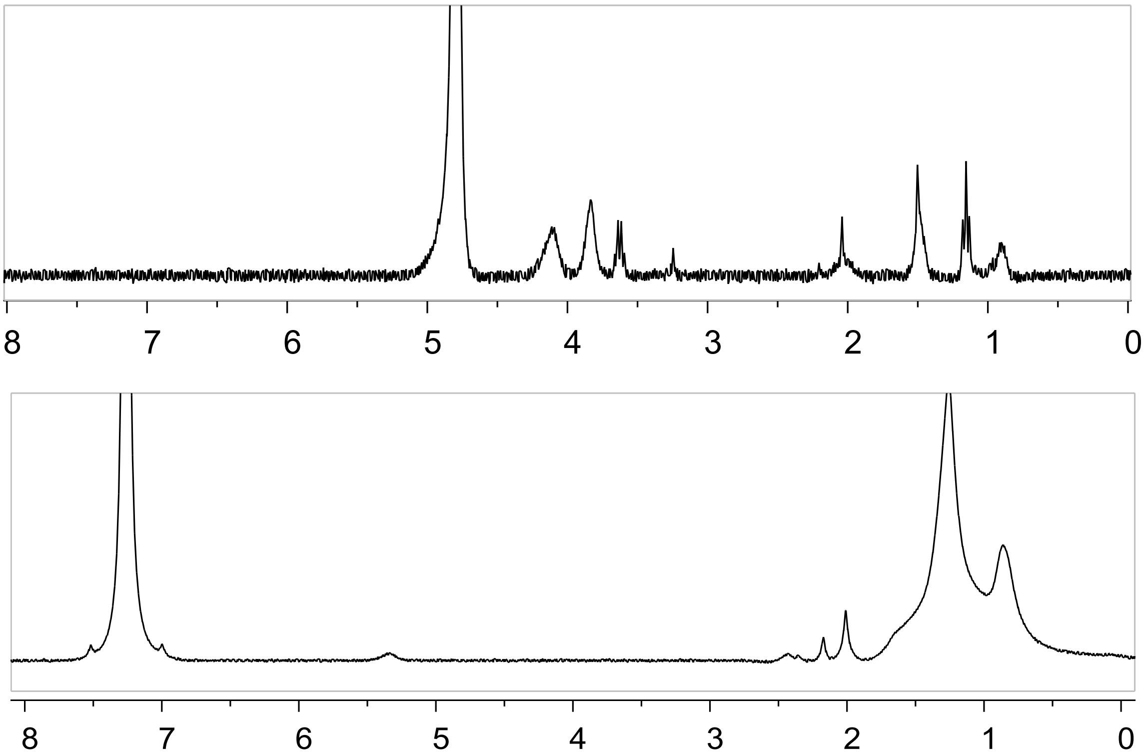


Figure S5.^{1}H-NMR spectra of (top) UCNP@COP (D_20) and (bottom) UCNP@oleate ($CDCl_3$).

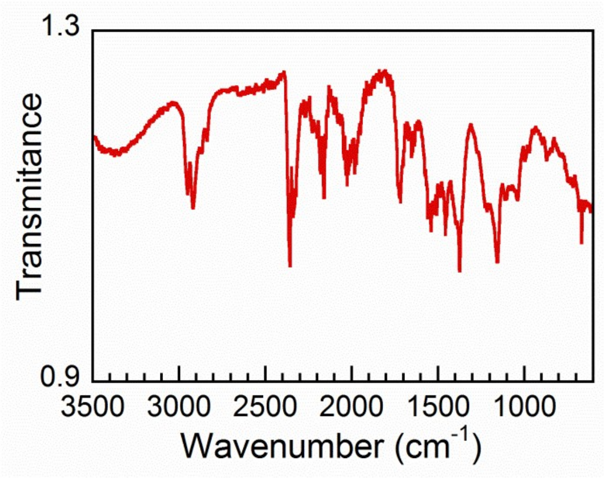


Figure S6. FTIR-ATR spectrum of the precipitate obtained by centrifugation (10000 rpm, 10 min) of a sample of UCNP@COP nanoparticles after being dispersed in water and kept at pH ca. 2 for 2h.

Table S2. Zeta potential and conductivity values of the precipitate re-dispersed in water (1 mg/mL, pH=8) and the supernatant obtained after centrifugation (10000 rpm, 10 min) of a sample of UCNP@COP nanoparticles dispersed in water and kept at pH ca. 2 for 2h.

Sample	**Zeta Potential** (mV)	**Conductivity** (ms·cm^{-1})
Precipitate*	-34.8 ± 1.2	0.0542 ± 0.0007
Supernatant	-3.4 ± 1.0	3.425 ± 0.195

*water colloidal solution

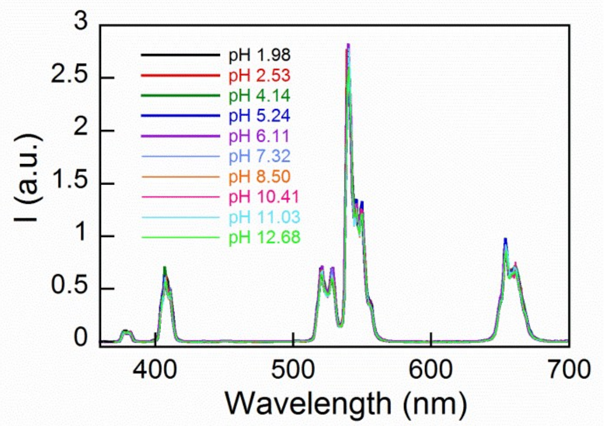


Figure S7. Emission spectra (λ_{exc} = 980 nm) of UCNP@COP (1 mg/mL in water) at different pHs.

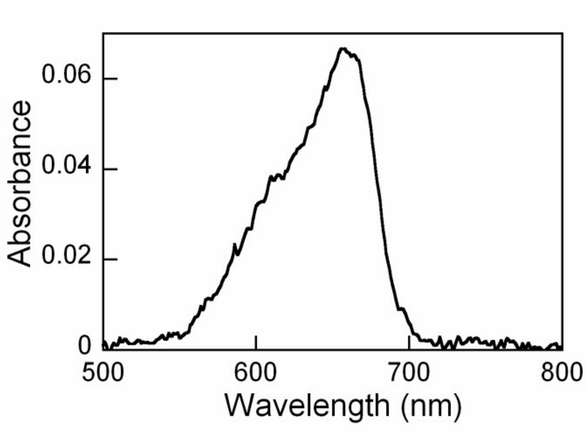


Figure S8. Absorption spectrum of MB in UCNP@COP@MB obtained after subtracting the spectrum of UCNP@COP@MB (2 mg/mL in water) and that of UCNP@COP.