

Supporting information

Investigating the growth of hyperbranched polymers by self-condensing vinyl RAFT copolymerization from the surface of upconversion nanoparticles

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β -NaYF₄:Yb³⁺, Er³⁺ nanocrystals (UCNP@OA)

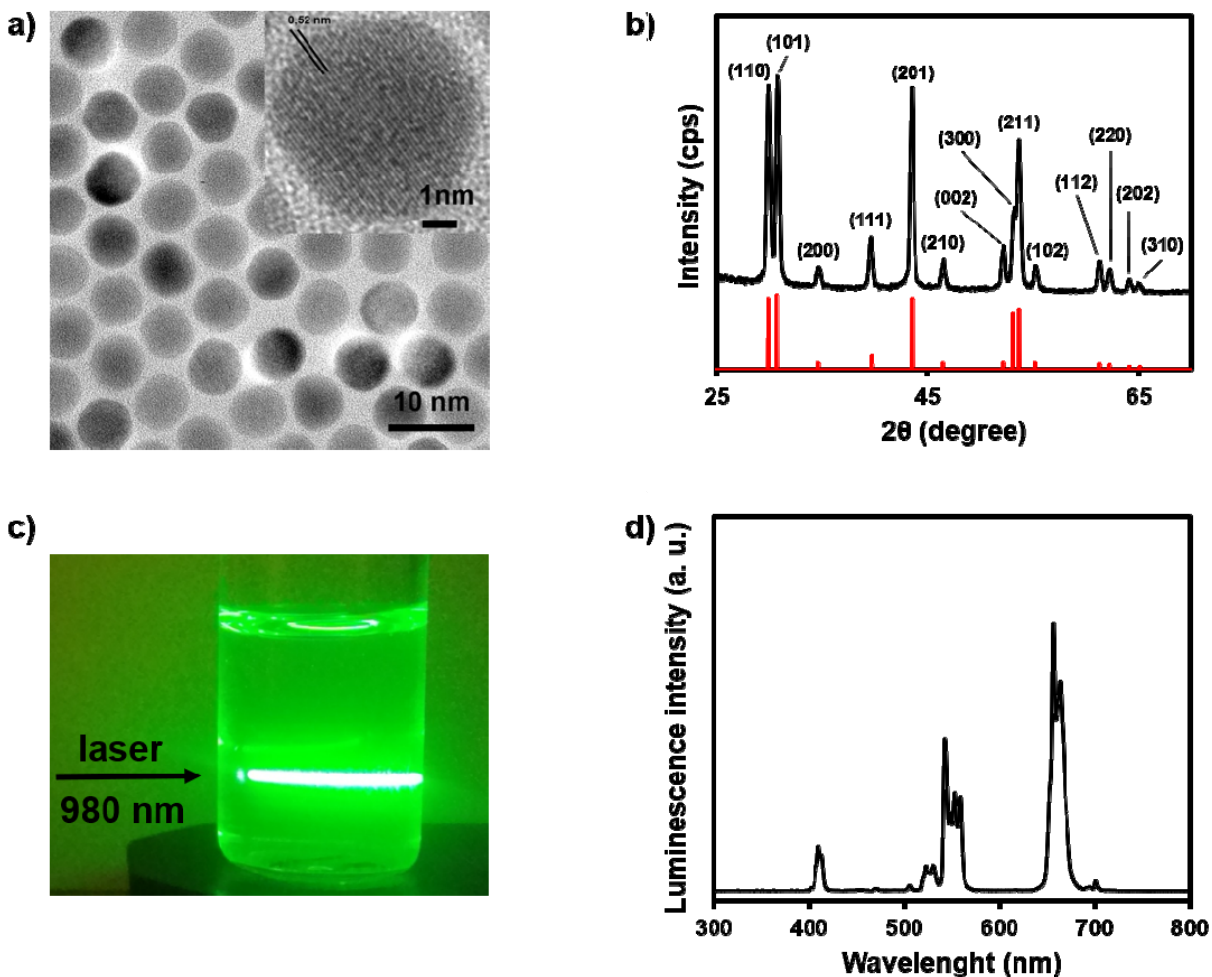


Figure S1. Characterization of UCNPs@OA: (a) TEM image with a zoom on a single nanoparticle in inset highlighting the lattice fringe, (b) X-ray diffractogram of the synthesized UCNPs@OA in black) and the standard pattern of β -NaYF₄ (JCPDS 06-0334) in red, (c) image of UCNPs@OA solution in cyclohexane excited at 980 nm and (d) upconversion emission spectrum (20 mg/mL).

Amine-functionalized upconversion nanoparticles (UCNP@NH₂)

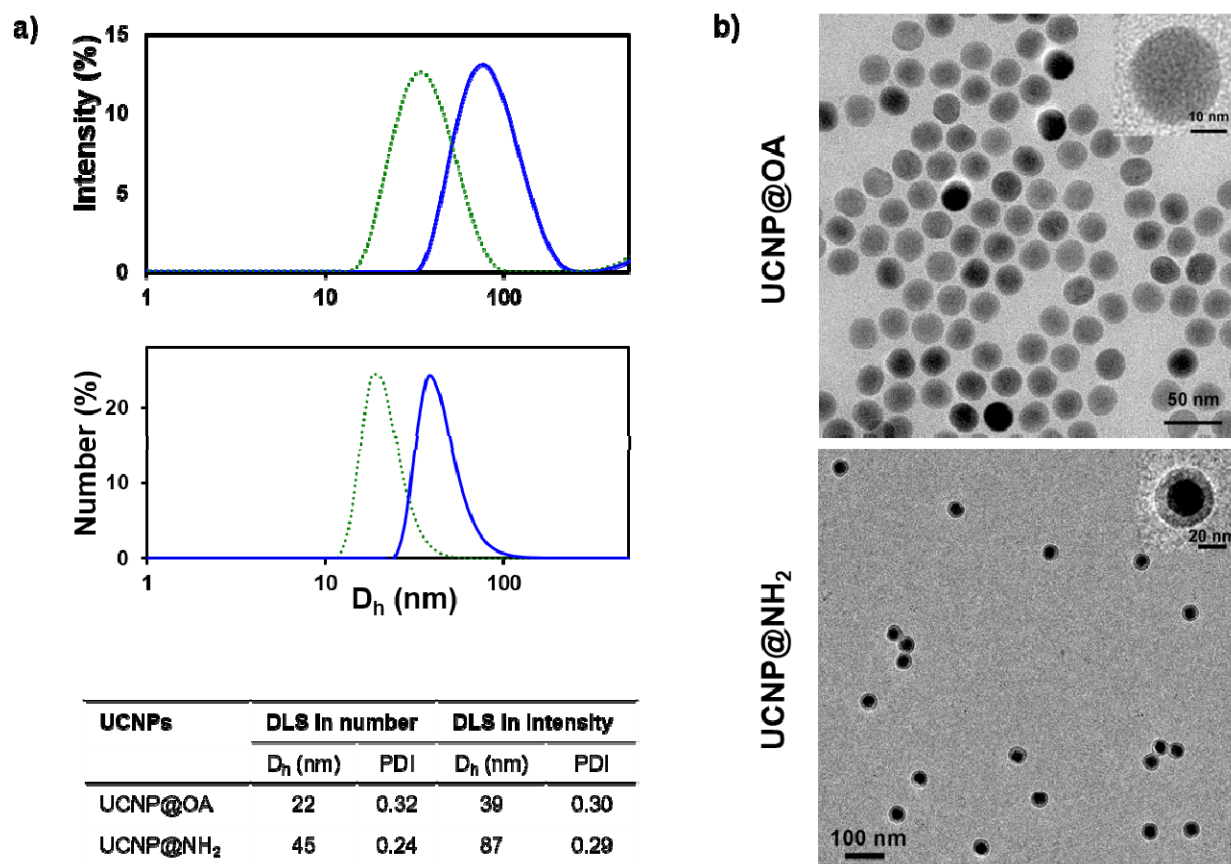


Figure S2. Size of UCNPs before (UCNP@OA) and after (UCNP@NH₂) their modification to create a silica shell with amine groups: (a) DLS measurements in intensity and number of the UCNPs dispersed in cyclohexane for UCNPs@OA (dashed green line) and ethanol for UCNPs@NH₂ (full blue line), and (b) HR-TEM (inset zoom of a single nanoparticle) of UCNPs.

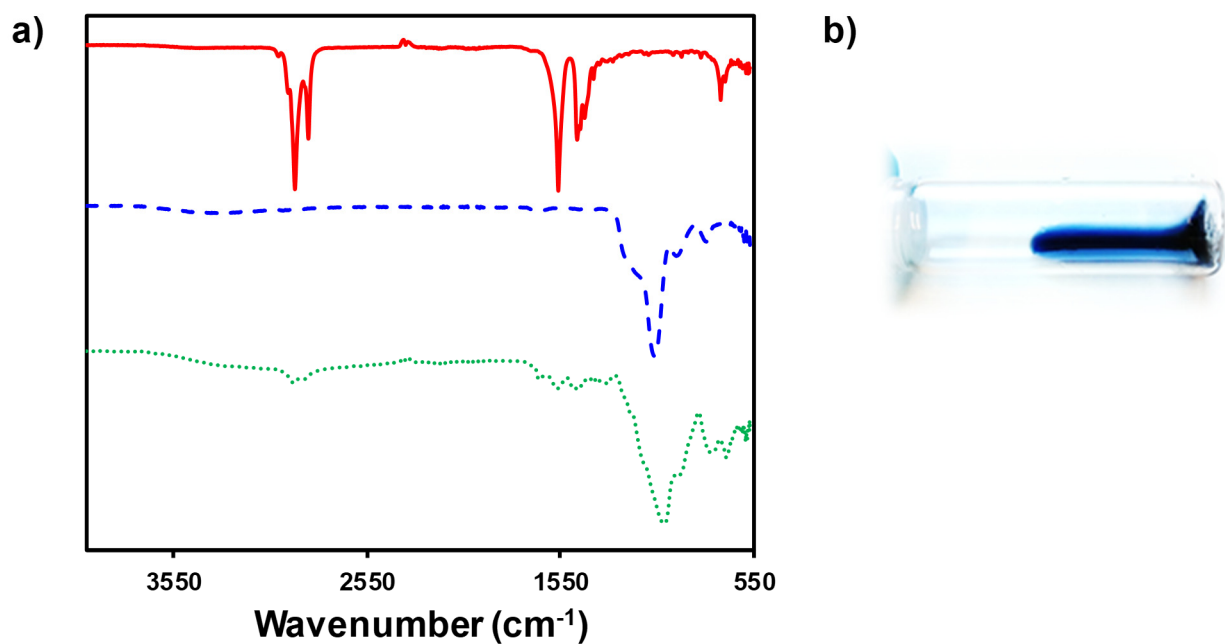


Figure S3. Identification of the amino groups at the surface of UCNPs: (a) IR spectra of UCNP@OA (solid red line), UCNP@SiO₂ (blue dashed line), and UCNP@NH₂ (green dotted line) and (b) Kaiser test of UCNP@NH₂.

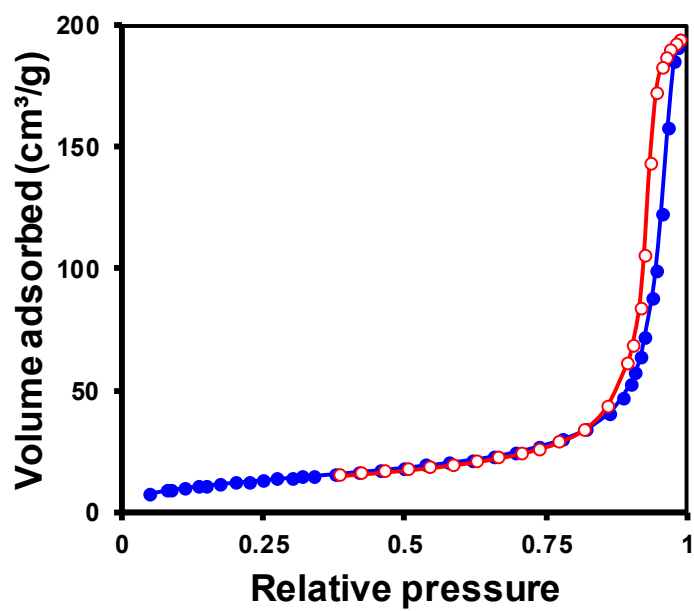


Figure S4. N₂ isotherms of adsorption (filled blue symbols) and desorption (open red symbols) for UCNP@NH₂.

CPABD-functionalized upconversion nanoparticles (UCNP@CPABD)

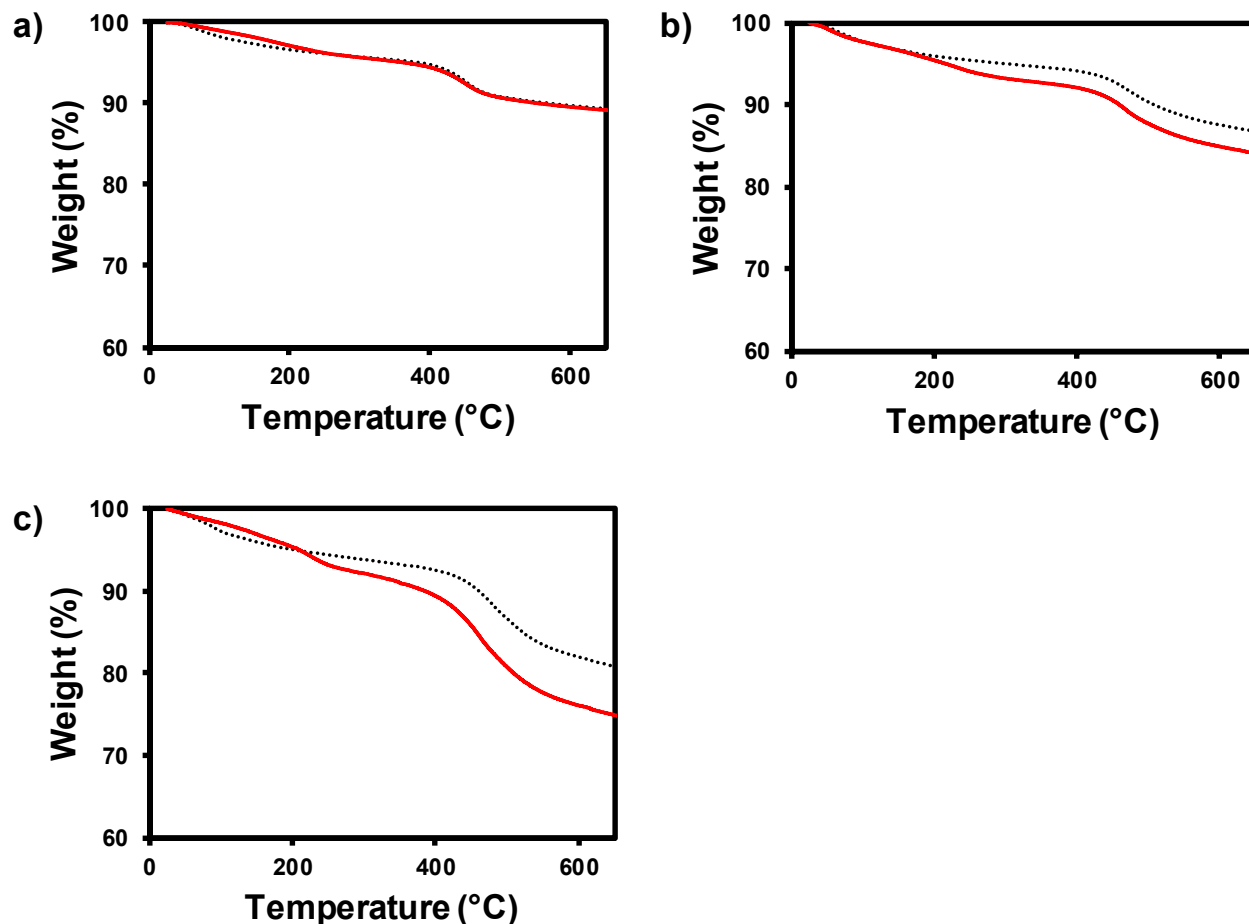


Figure S5. TGA thermograms of (a) UCNP@CPABD_{low}, (b) UCNP@CPABD_{medium}, and (c) UCNP@CPABD_{high} (solid red line) compared to UCNP@NH₂ (black dotted line) prepared with 7.5, 15 and 30 μL of APTS respectively for 80 mg of UCNP@OA.

Table S1. Quantification of CPABD grafting density on UCNPs by TGA

Samples	APTS (μL)	%wt	mmol of CPABD/g UCNP	Grafting density (CPABD/ nm^2)
UCNP@CPABD _{low}	7.5	1.2	0.044	0.60
UCNP@CPABD _{medium}	15	2.6	0.094	1.41
UCNP@CPABD _{high}	30	6.8	0.240	3.13

Polymerization of HPMA from UCNP@CPABD

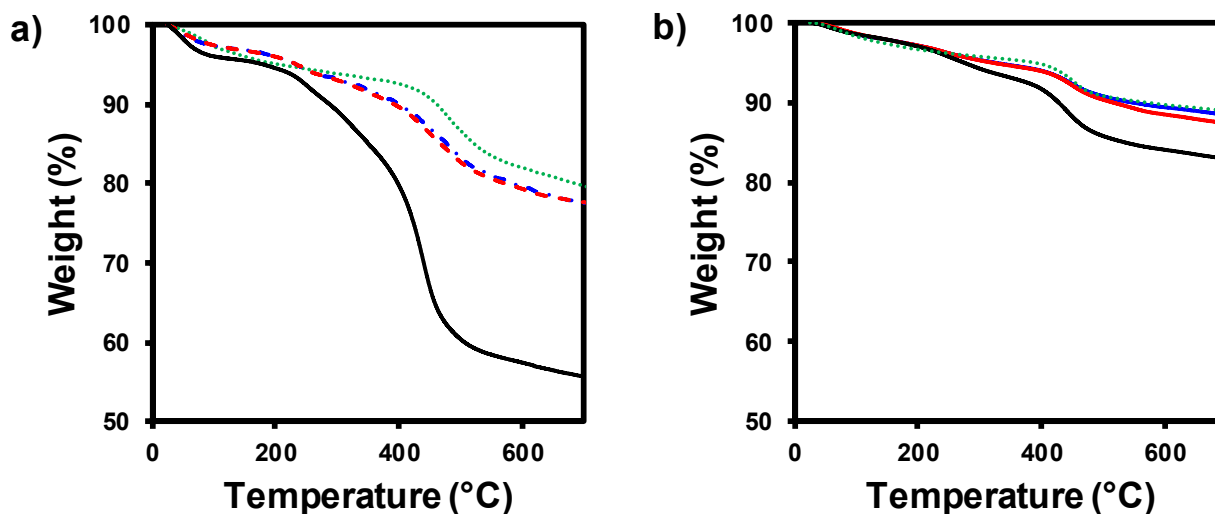


Figure S6. TGA thermograms of UCNP@polyHPMA for polymerizations conducted in MeOH (blue dashed line), DMF (red dashed line) and 1,4-dioxane (black solid line) using (a) UCNP@CPABD_{high} and (b) UCNP@CPABD_{low} relative to UCNP@CPABD (green dotted line).

Self-condensing vinyl copolymerization from UCNP@CPABD

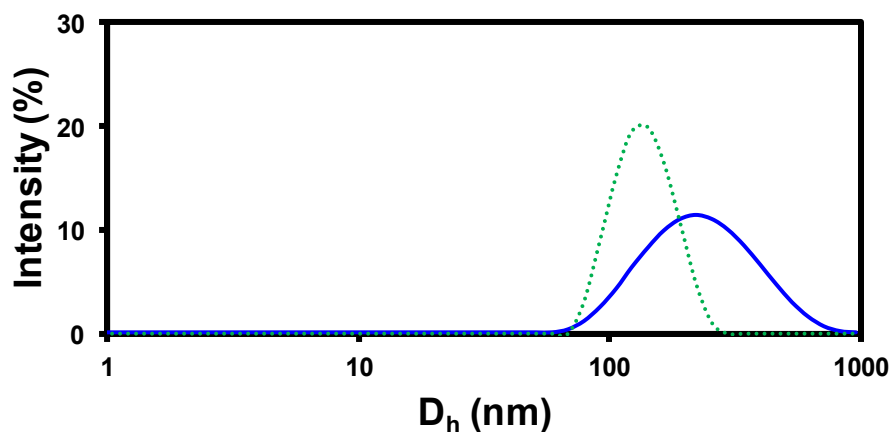
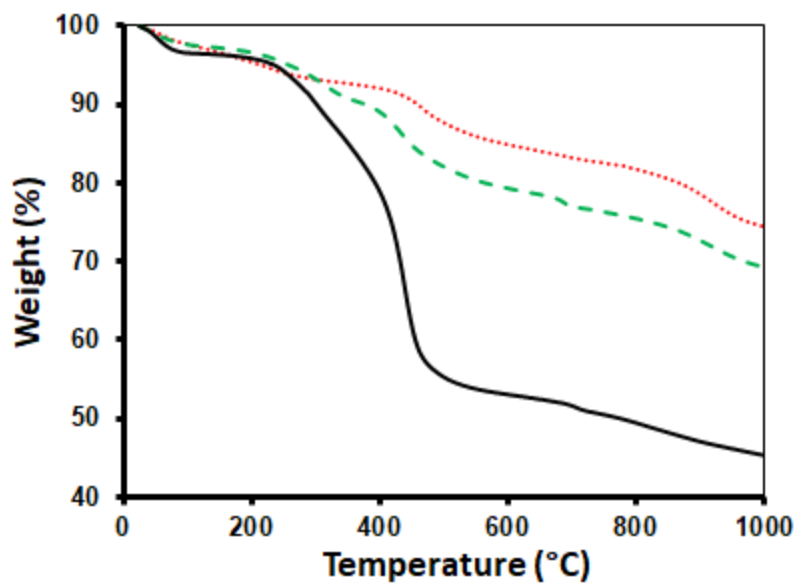
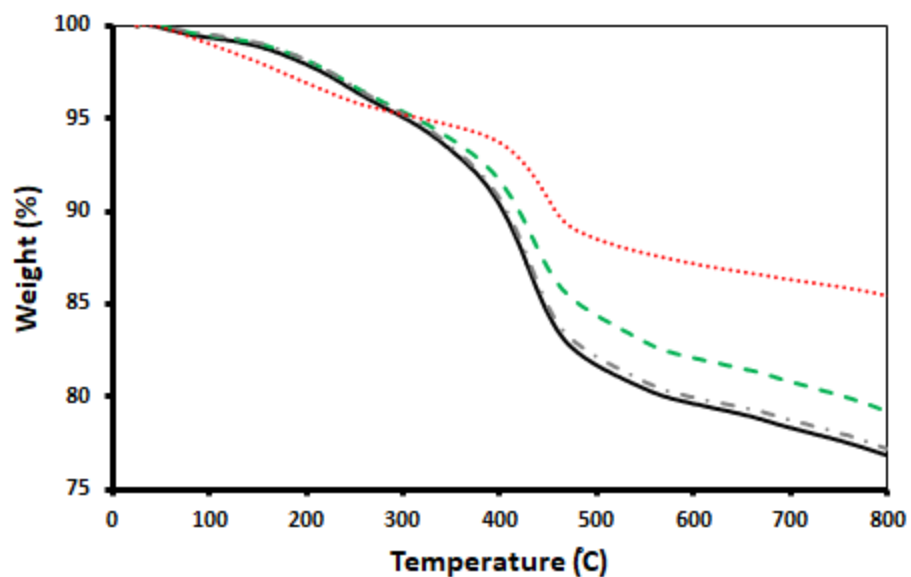


Figure S7. DLS in intensity of UCNP@polyHMPA (blue solid line) and UCNP@HBP (green dotted line) obtained from UCNP@CPABD_{high}.



UCNPs	Char (wt%)	Organic content in nanohybrid (wt%)
UCNP@CPABD	74	12
UCNP@HBP (3 mM of MA-CPABD)	45	44
UCNP@HBP (6 mM of MA-CPABD)	69	19

Figure S8. TGA thermograms of UCNP@CPABD_{medium} (red dotted line), UCNP@HBP using 3 mM of MA-CPABD (black solid line), and UCNP@HBP using 6 mM of MA-CPABD (green dashed line) from UCNP@CPABD_{medium}.



UCNPs	Char (wt%)	Organic content in nanohybrid (wt%)
UCNP@CPABD	85	11
UCNP@polyHPMA (3 mM of MA-CPABD)	77	20
UCNP@HBP (3 mM of MA-CPABD)	77	20
UCNP@HBP (6 mM of MA-CPABD)	79	18

Figure S9. TGA thermograms of UCNP@CPABD_{low} (red dotted line), UCNP@polyHPMA using 3 mM CPABD (dashdotted gray line), UCNP@HBP using 3 mM of MA-CPABD (black solid line), and UCNP@HBP using 6 mM of MA-CPABD (green dashed line) from UCNP@CPABD_{low}.

Luminescence properties

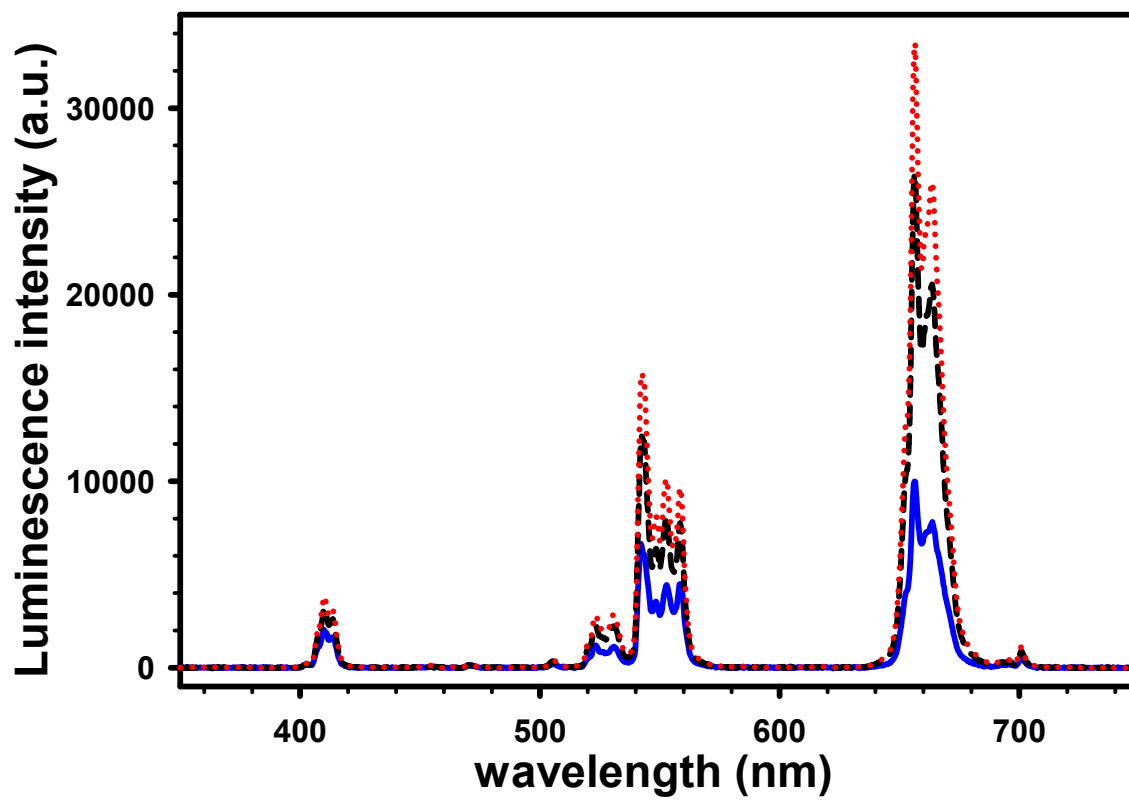


Figure S10. Luminescence spectra of UCNP@OA (blue solid line), UCNP@NH₂ (black dashed line) and UCNP@HBP (red dotted line).

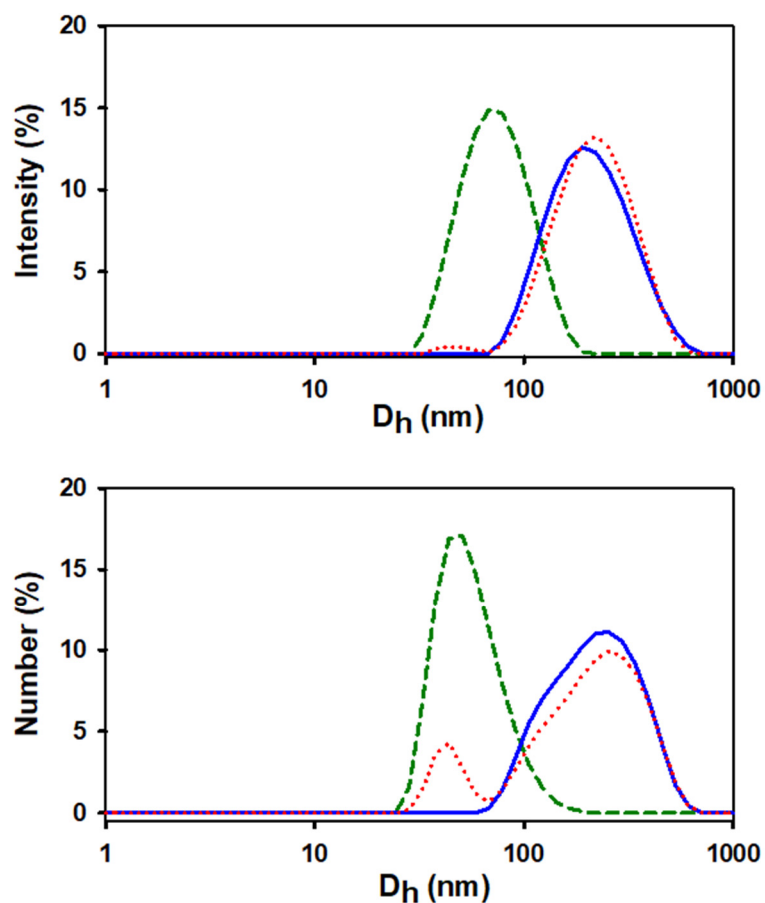


Figure S11. DLS measurements in intensity and number of the UCNP@OA dispersed in cyclohexane (dashed green line), UCNP@NH₂ in water (full blue line), and UCNP@HBP in water (dotted red line)

References

- (1) Li, Z.; Zhang, Y. An efficient and user-friendly method for the synthesis of hexagonal-phase NaYF₄:Yb, Er/Tm nanocrystals with controllable shape and upconversion fluorescence. *Nanotechnology* **2008**, *19*, 345606.
- (2) Kaiser, E.; Colescott, R. L.; Bossinger, C. D.; Cook, P. I. Color test for detection of free terminal amino groups in the solid-phase synthesis of peptides. *Anal. Biochem.* **1970**, *34*, 595–598.