

Supporting Information

Cucurbit[n]uril-capped upconversion nanoparticles as highly emissive scaffolds for energy acceptors

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Experimental Section

Materials and methods

Chemicals: The chemicals used for the UCNP synthesis were: lanthanide chlorides ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (>99.9%, all of them)), 1-octadecene (95%), oleic acid (99.9%), NaOH and NH_4F (99.99%). All these chemicals and Cucurbituril[n] were purchased from Sigma-Aldrich and used as received without previous purification. Pyronin Y was purchased from Acros Organics and purified by double recrystallization with ethanol.

Synthesis of Up-converting $\text{NaYF}_4:\text{Yb}^{3+}$, Er^3 Nanoparticles

$\text{NaYF}_4:\text{Yb,Er}$ nanoparticles were synthesized following a previously reported protocol with some modifications.¹ A mixture of 0.8 mmol $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 0.18 mmol $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 0.02 mmol $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mmol), 12 mL oleic acid and 15 mL octadecene (ODE) was heated to 160 °C in a 50 mL round-bottom Pyrex flask under continuous stirring. After dissolution of lanthanides chlorides (ca. 30 minutes), the mixture was cooled to 110 °C. Then, a 10 mL

methanol solution containing NaOH (2.5 mmol) and NH_4F (4.0 mmol) was slowly added into the flask. The mixture was degassed at 100 °C for 30 min under stirring and, finally, heated at 305 °C under N_2 flux during one hour. After that, the solution was cooled to room temperature and the nanoparticles were precipitated by centrifugation (10000 rpm, 10 min, 25 °C). Later on, the oleate-capped UCNPs were washed three times with (43.5:40.5:16 v/v) hexane/acetone/methanol solution.

Synthesis of uncapped $\text{NaYF}_4:\text{Yb}/\text{Er}$ up-converting nanoparticles: UCNPs

Uncapped $\text{NaYF}_4:\text{Yb},\text{Er}$ nanoparticles were synthesized following a previously described method.² 100 mg of oleate-capped UCNPs were dispersed in 10 mL of HCl aqueous solution at pH 4. The mixture was stirred for 2 h and the pH was maintained at 4 by addition of a HCl solution (0.1 M). After that, the oleic acid was removed by extraction with diethyl ether three times followed by the re-extraction with water of the combined ether phases. Then, the water phases were combined and re-extracted with diethyl ether. Uncapped UCNPs were recuperated from water phase by precipitation with acetone and subsequent centrifugation (10000 rpm, 15 min, 25°C). The precipitated was washed three times with acetone and re-precipitated by centrifugation. Finally, UCNPs were dispersed in Milli Q water.

Synthesis of $\text{CB}[n]$ -coated $\text{NaYF}_4:\text{Yb}/\text{Er}$ up-converting nanoparticles: $\text{UCNP}@ \text{CB}[n]$

Briefly, 0.01 mmol of $\text{CB}[n]$ were added to 30 mg of UCNPs. Then 15 mL of MilliQ water were added and the mixture was sonicated for 15 minutes. The solution was stirred during 24 h in an orbital shaker at 350 ppm and kept in the dark. In order to remove the $\text{CB}[n]$ excess, 5 cycles of centrifugation at 10000 rpm x 10 minutes with a total of 30 mL of water and 45 mL of acetonitrile were carried out. The $\text{UC}@ \text{CB}[n]$ were resuspended in MilliQ water.

Molecular modeling

Molecular modeling was performed on a PC using the molecular mechanics program MM2 from ChemBio3D Ultra 14.0.

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.

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.). The density power was 249.4 mW/cm².

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) images were obtained using a Jeol 1010 microscope operating at 100 kV equipped with a charge-coupled device (CCD) camera. For the preparation of the UCNP samples, 10 μ L of a 0.5 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. High resolution transmission electron microscopy (HRTEM) images were recorded using a TECNAI G2 F20 microscope operating at 200 kV (point resolution of 0.24 nm) and equipped with a CCD GATAN camera.

Infrared spectra measurements (FTIR)

All FTIR spectra were performed using a FTIR Thermo Nicolete Nexus spectrophotometer at room temperature.

Centrifugation

Centrifugation was carried out in an Eppendorf Centrifuge 5804 R.

Nuclear magnetic resonance measurements (NMR)

¹H-NMR (D₂O) spectra were recorded on an AVANCE 400 MHz Bruker spectrometer at room temperature. NMR data are reported in ppm.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was made using a Model Mettler Toledo TGA/SDTA 851e that operates in the range 25-1100°C with a sensibility of 0.1 micrograms.

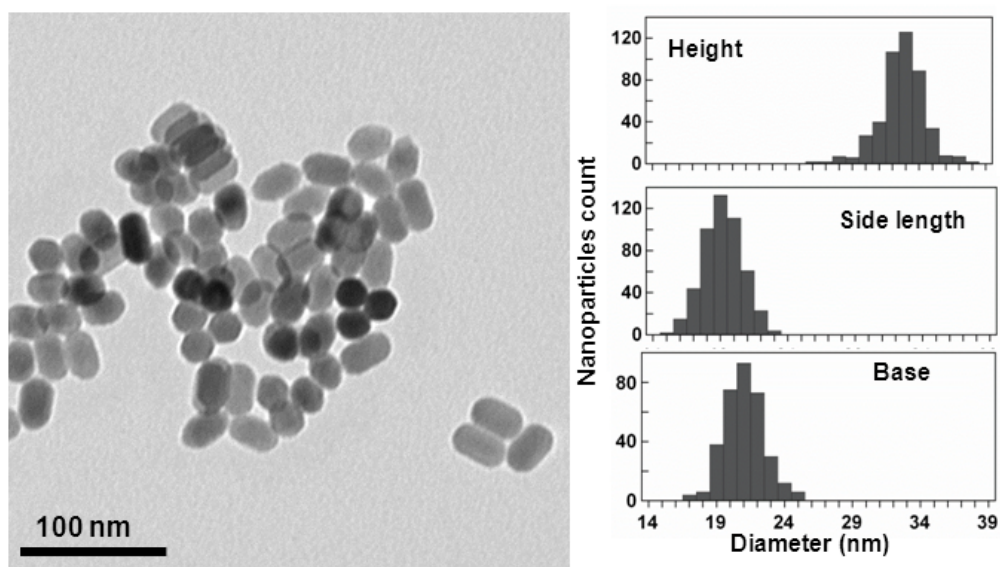


Figure S1. HRTEM image and histograms of the naked UCNPs.

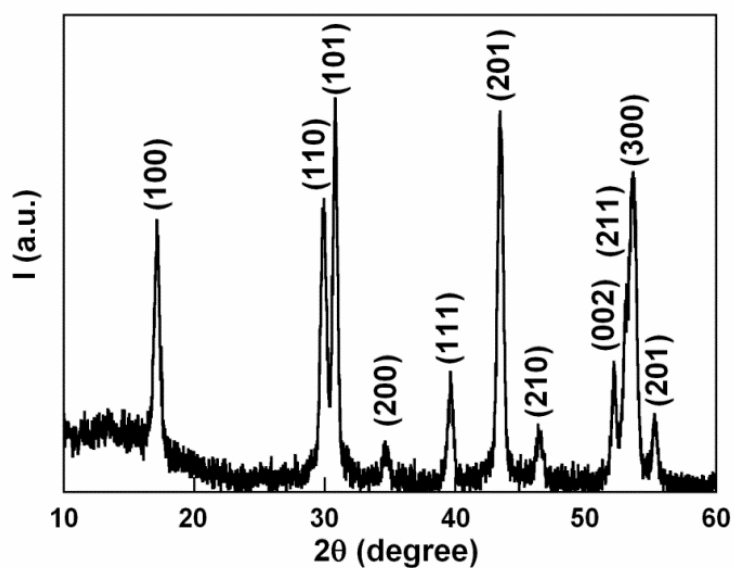


Figure S2. XRD spectrum of the naked UCNPs.

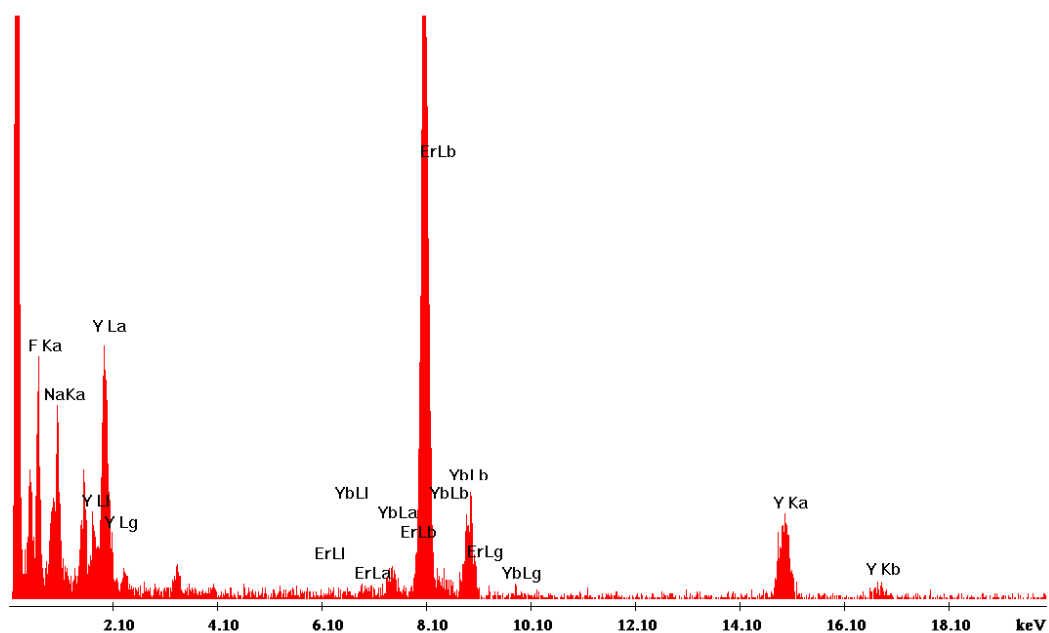


Figure S3. EDX spectrum of NaYF₄(80%):Yb³⁺(18%),Er³⁺(2%).

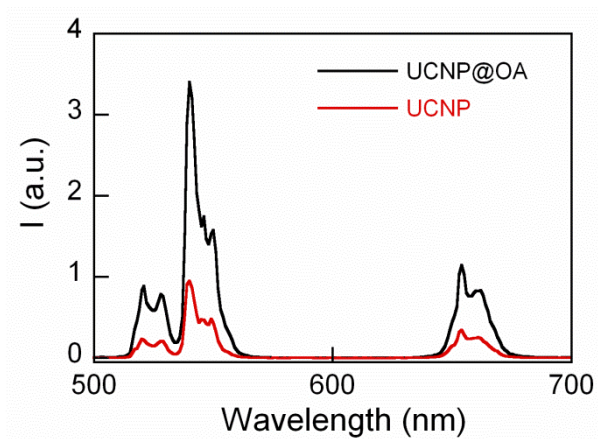


Figure S4. Emission spectrum at $\lambda_{\text{ex}}=980$ nm of oleate-capped UCNPs (UCNP@oleate, black line) in chloroform compared with that of the naked UCNPs (red line) in MilliQ water at the same concentration.

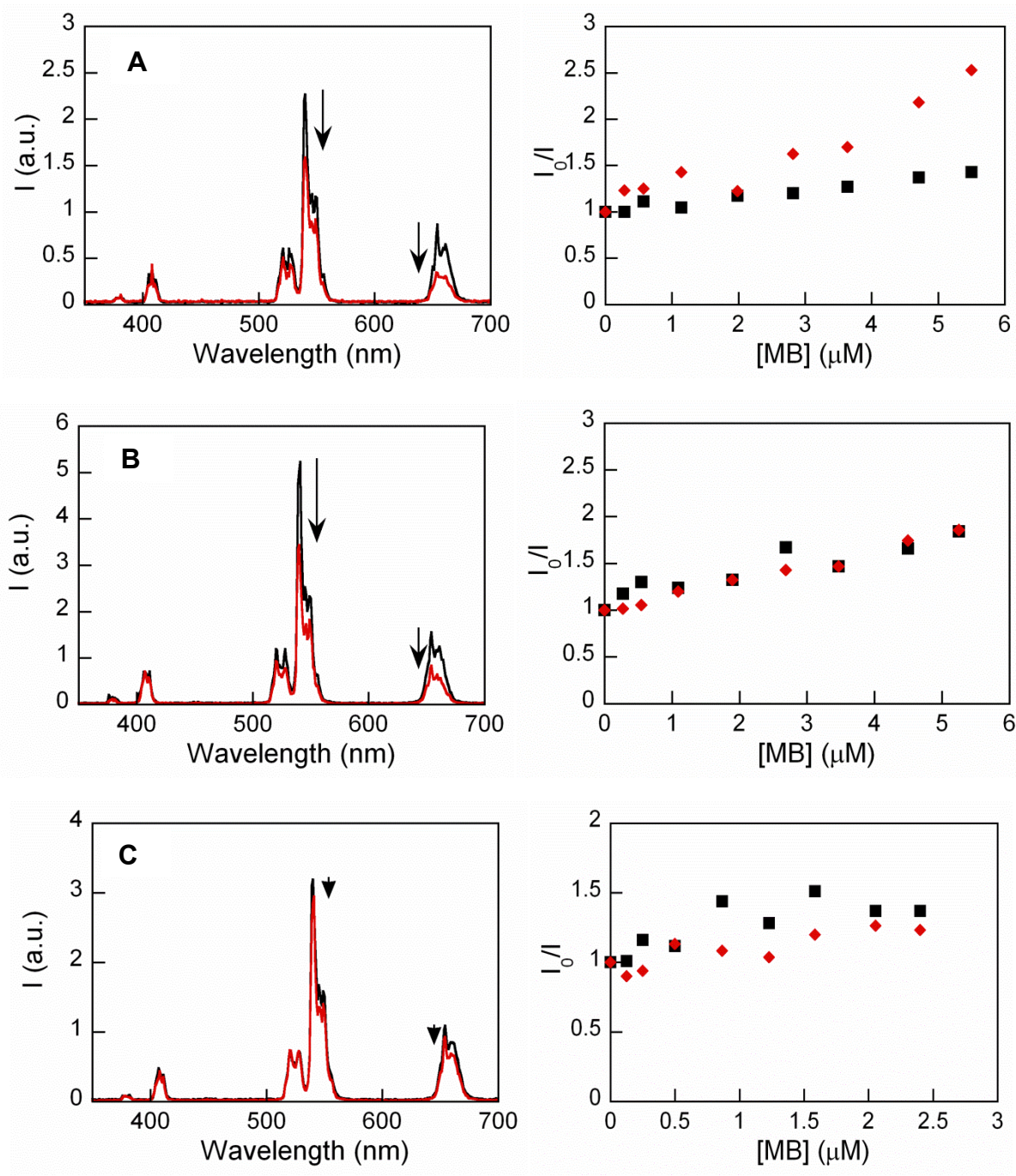


Figure S5. Left: Emission spectra at $\lambda_{\text{ex}}=980$ nm of A) UCNP@CB[6], B) UCNP@CB[7] and C) UCNP@CB[8] before and after addition of MB (concentration similar to that of the CB). **Right:** change in the emission intensity of UCNP@CB[n] at 540 and 654 nm after addition of increasing MB concentrations.

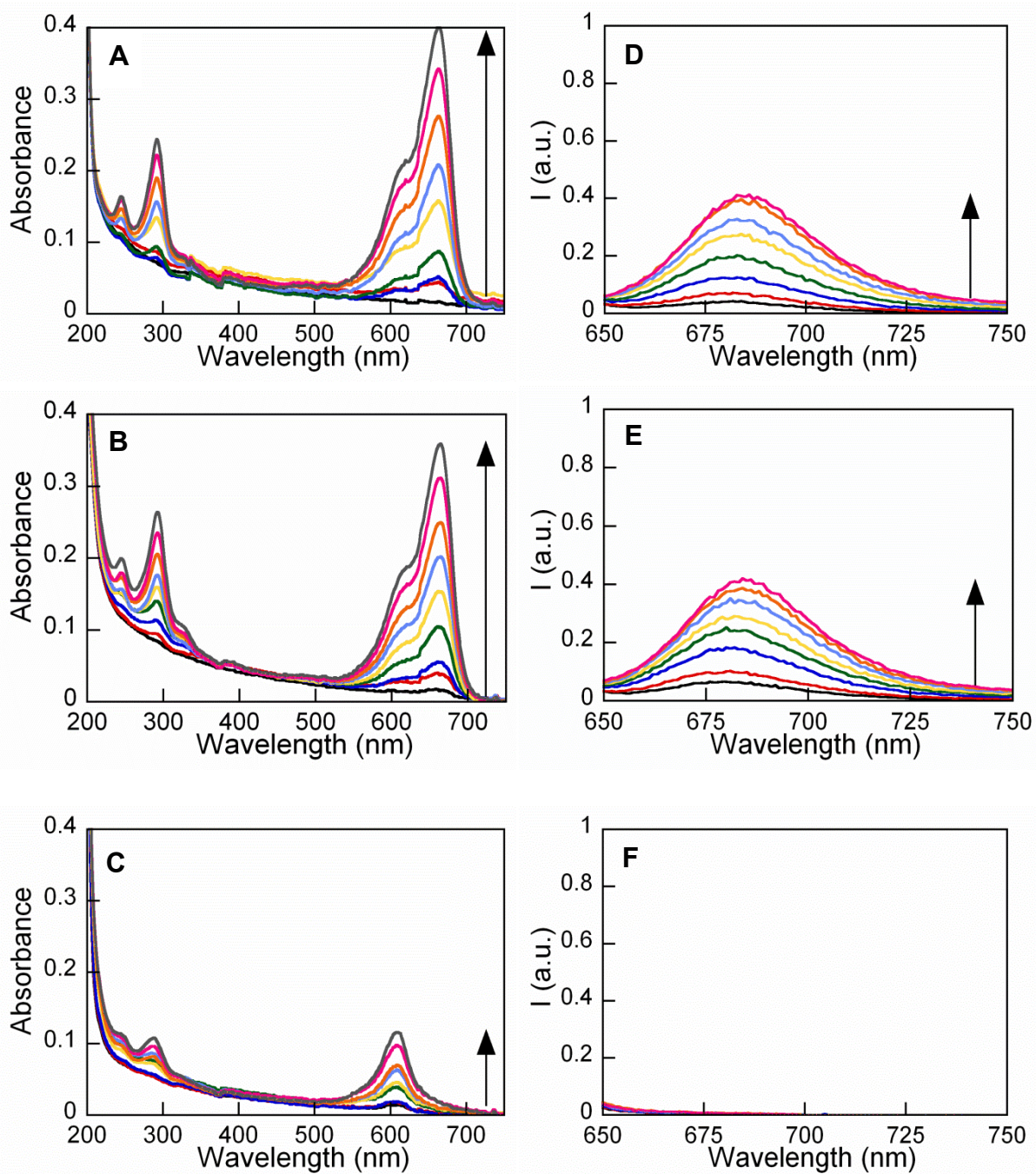


Figure S6. Absorption spectra of A) UCNP@CB[6], B) UCNP@CB[7] C) UCNP@CB[8] and emission spectra ($\lambda_{\text{ex}} = 640$ nm) of D)UCNP@CB[6], E) UCNP@CB[7] and F) UCNP@CB[8] after increasing additions of methylene blue. All samples were measured in milliQ water.

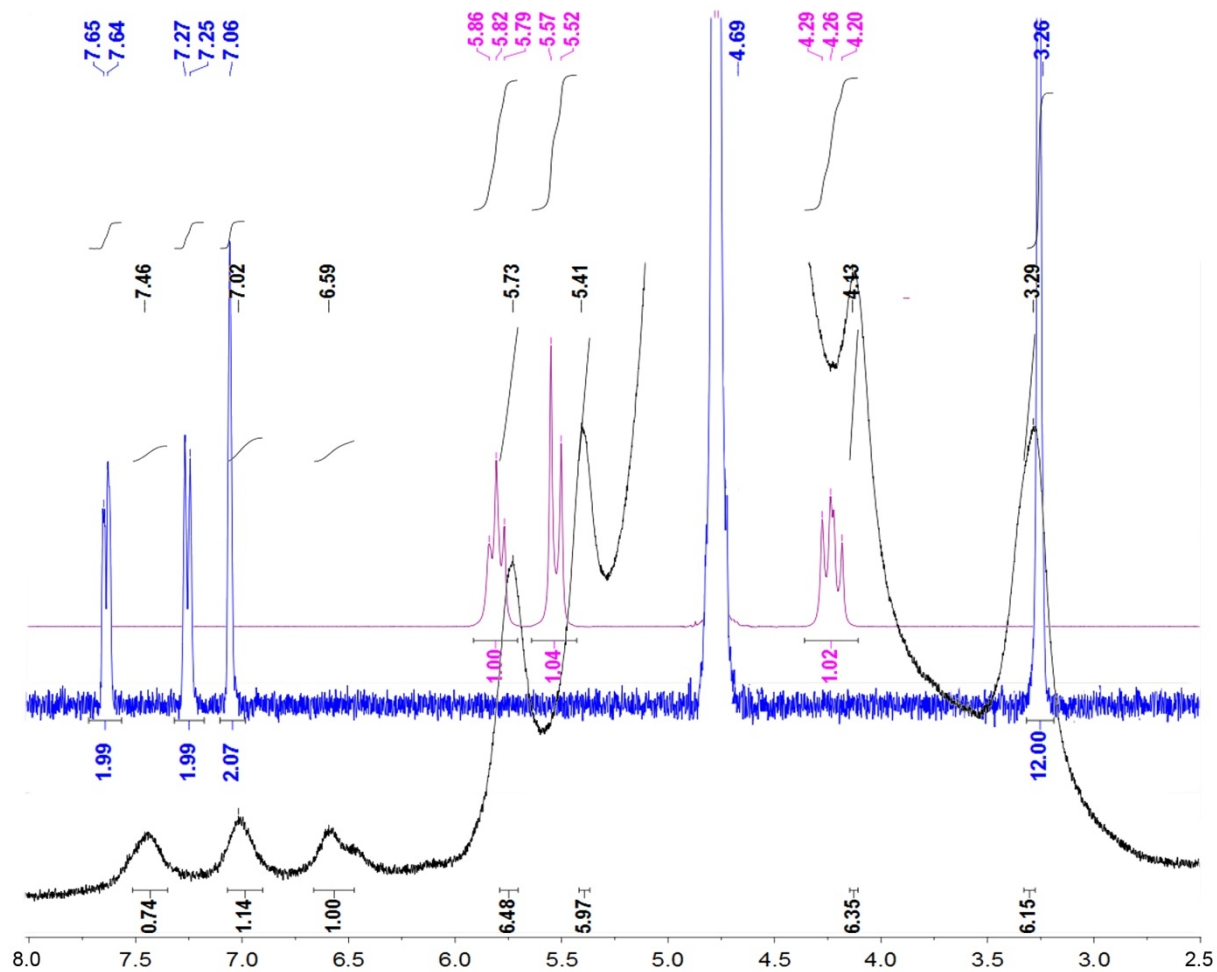


Figure S7. $^1\text{H-NMR}$ of CB[7] (purple line), MB (blue line) and UC@CB[7]@MB (black line).

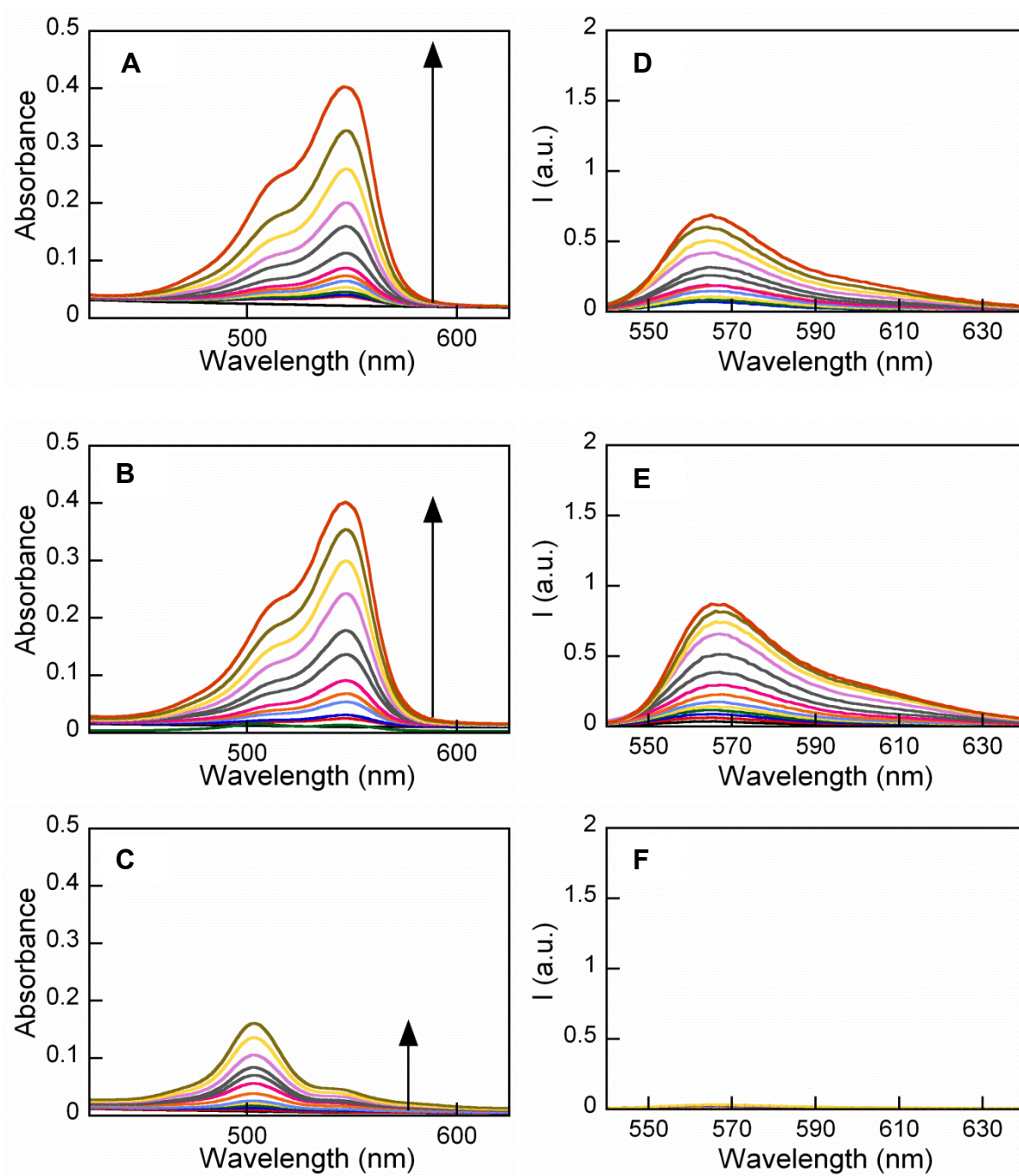


Figure S8. Absorption spectra of A) UCNP@CB[6], B) UCNP@CB[7], and C) UCNP@CB[8]; D) emission spectra ($\lambda_{\text{ex}}=545$ nm) of UCNP@CB[6], E) UCNP@CB[7] and F) UCNP@CB[8] after increasing pyronin Y concentrations. All samples were measured in milliQ water.

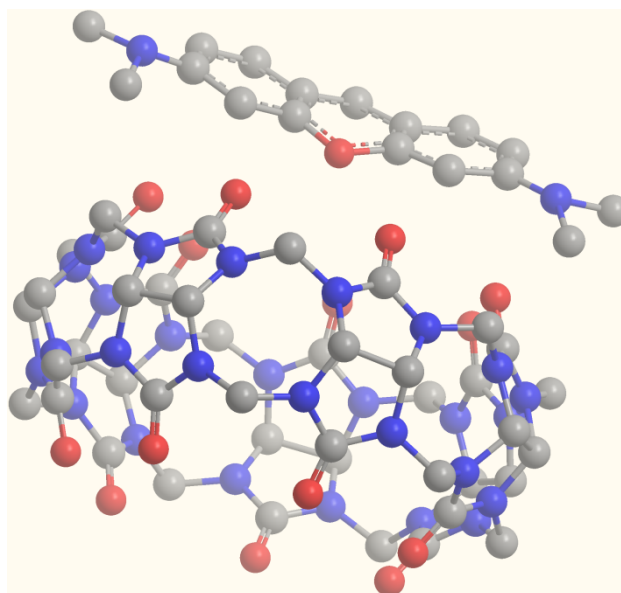


Figure S9. Proposed interaction between PYY and CB[7].

References:

1. Z. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606-345610.
2. N. Bogdan, F. Vetrone, G. A. Ozin and J. A. Capobianco, *Nano Lett.*, 2011, **11**, 835-840.