Supporting Information

Luminescent Nanoparticles with Lanthanide-Containing Poly(ethylene glycol)-Poly(ε-caprolactone) Block Copolymers

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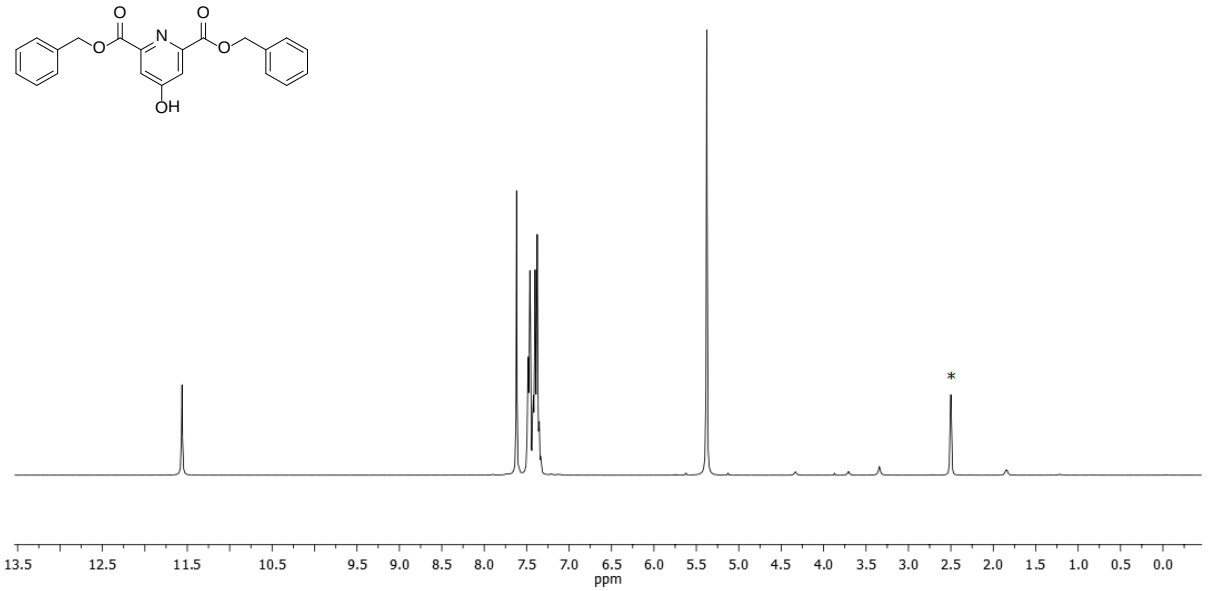

Figure S1. ^{1}H NMR spectrum of 4-hydroxypyridine-2,6-dicarboxylic acid dibenzyl ester, **2**. ^{1}H NMR (300 MHz, DMSO-*d6*) δ 11.56 (s, 1H, PyrO*H*), 7.79–7.08 (m, 12H, Ar*H*, Pyr*H*), 5.38 (s, 4H, CH_2Ph).

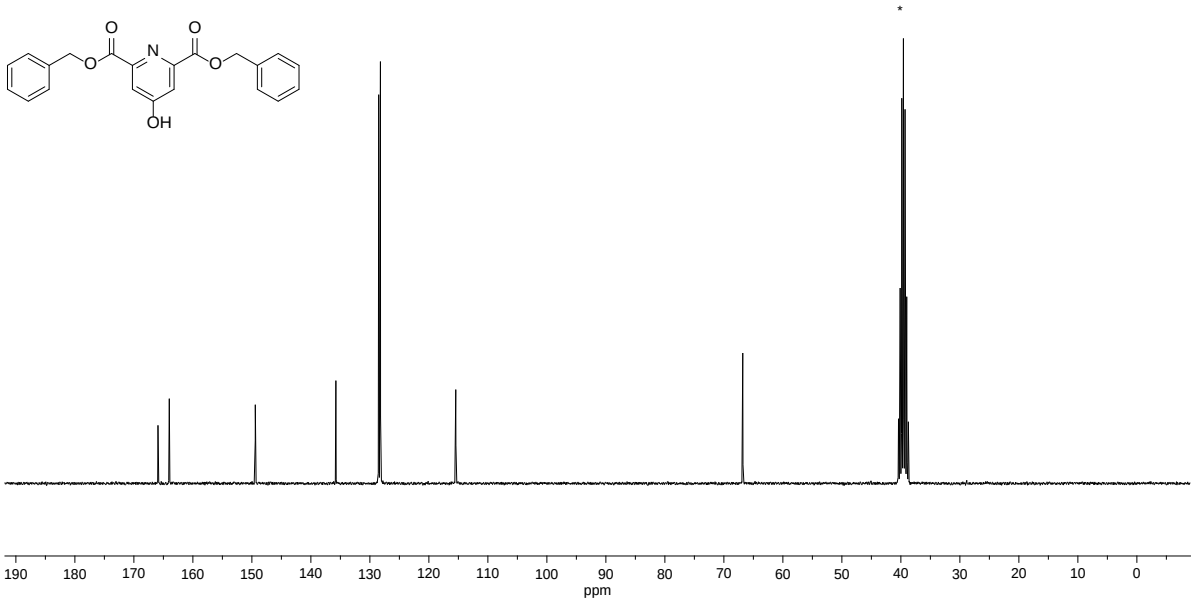

Figure S2. ^{13}C NMR spectrum of 4-hydroxypyridine-2,6-dicarboxylic acid dibenzyl ester, **2**. ^{13}C NMR (75 MHz, DMSO-*d6*) δ 165.90, 163.99, 149.40, 135.75, 128.48, 128.19, 115.42, 66.76.

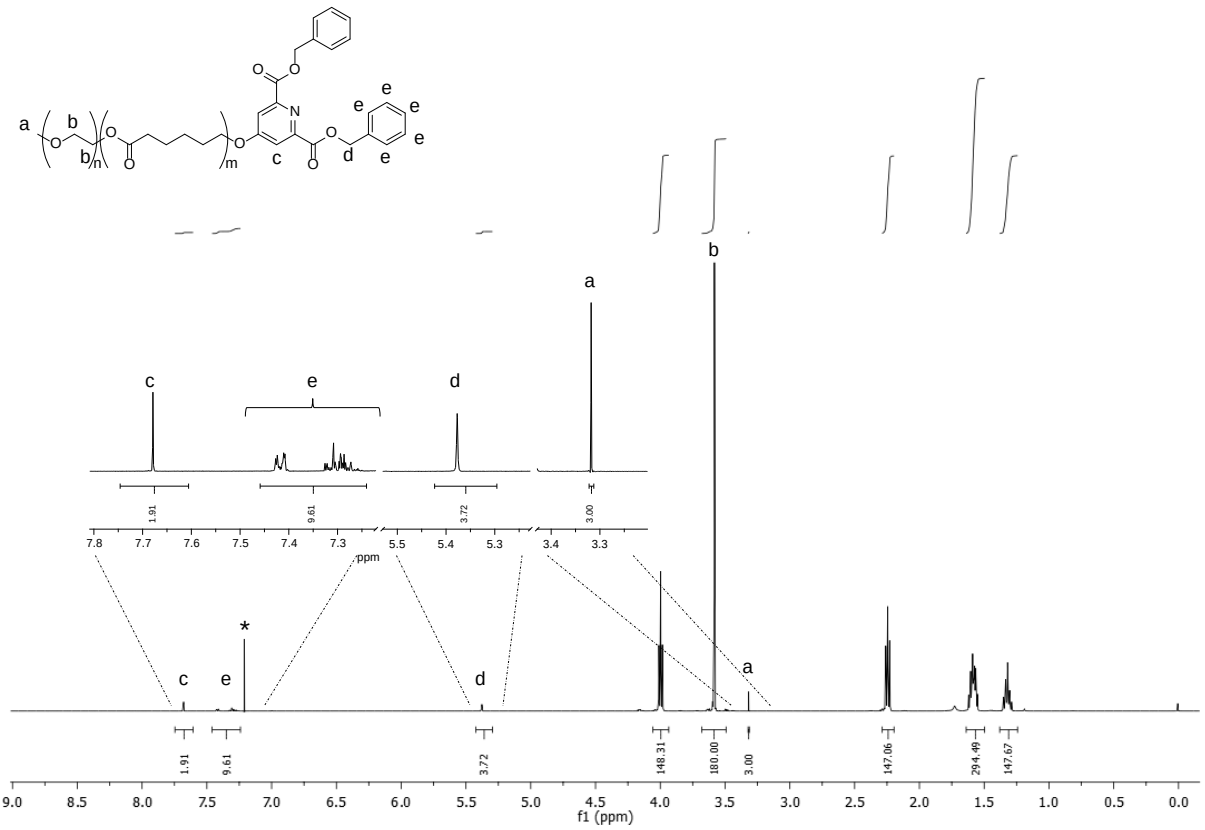

Figure S3. ^{1}H NMR spectrum of Bn_2dpa-PCL-PEG-OCH_3, **4.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, Pyr*H*), 7.54 – 7.29 (m, Ar*H*), 5.43 (s, CH_2Ph), 4.05 (t, *J* = 6.7 Hz, –CH_2CH_2O), 3.64 (s, PEG –CH_2CH_2–), 3.37 (s, PEG CH_3OCH_2), 2.31 (dt, *J* = 15.1, 7.6 Hz, –$CO_2CH_2CH_2$–), 1.70–1.56 (m, –$CH_2CH_2CH_2CH_2CH_2$–), 1.46–1.31 (m, –$CH_2CH_2CH_2$–).

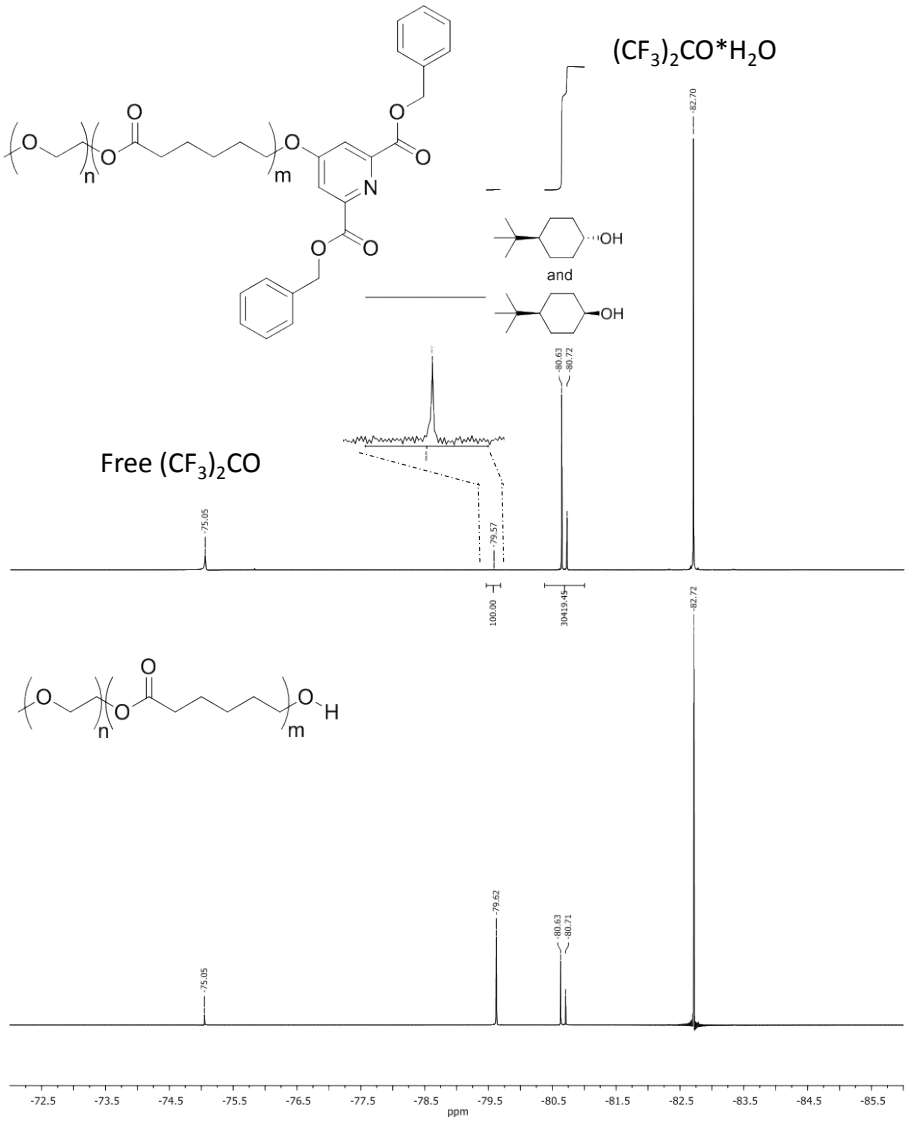

Figure S4. ^{19}F NMR spectrum of Bn_2dpa-PCL-PEG-OCH_3, **4**. The degree of functionalization was determined by the relative integration of the peak of hexafluoroacetone (HFA)-adduct of mPEG-PCL-OH (-79.57 ppm) versus the peak of HFA-adduct of 4-tert-butylcyclohexanol (-80.63 ppm and -80.72 ppm) as internal standard.[1] A 99% end-group functionalization was found.

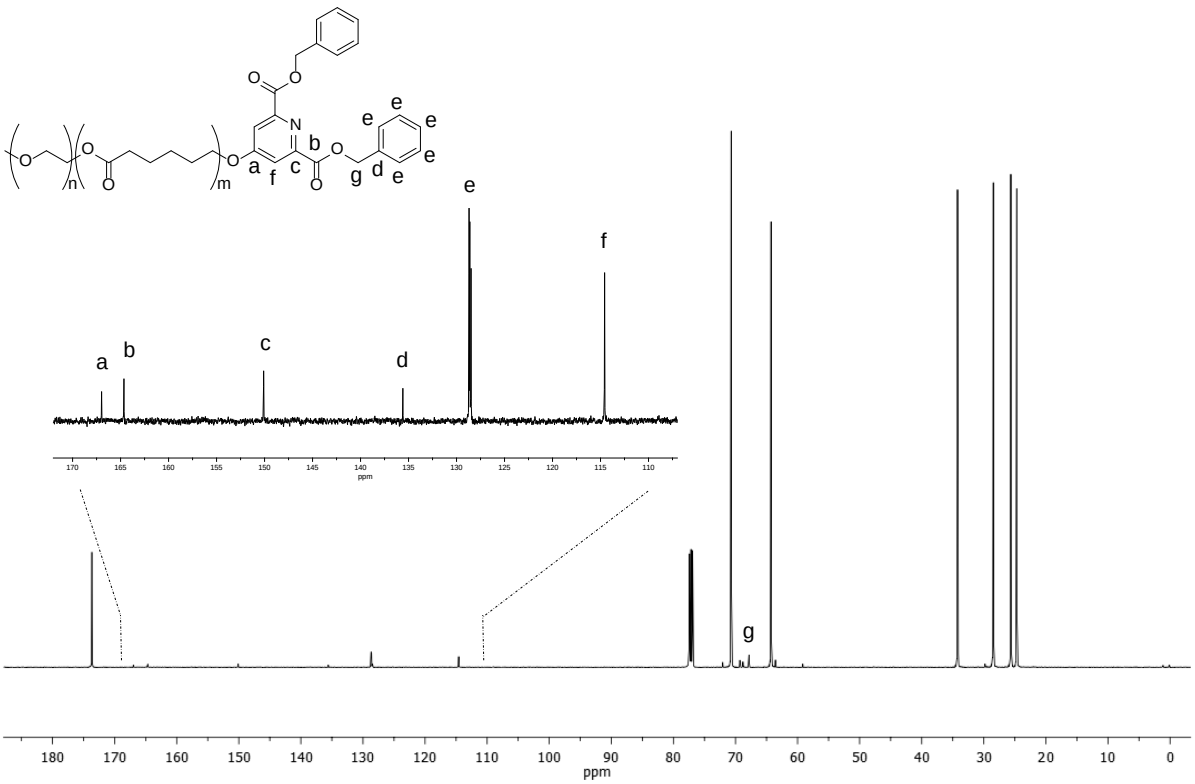

Figure S5. ^{13}C NMR spectrum of Bn_2dpa-PCL-PEG-OCH_3, **4**. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.65, 166.98, 164.65, 150.07, 135.57, 128.70, 128.63, 128.50, 114.58, 70.67, 67.83, 64.27, 59.17, 34.26, 28.46, 25.64, 24.69.

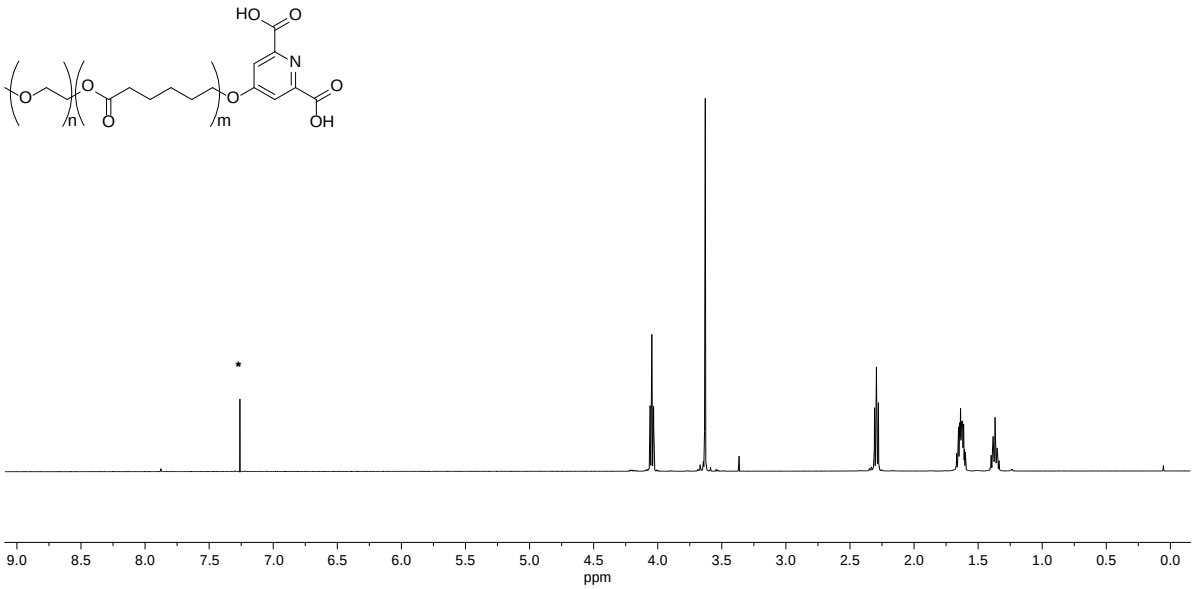

Figure S6. ^{1}H NMR spectrum of dpa-PCL-PEG-OCH_3, **5**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, Pyr*H*), 4.05 (t, *J* = 6.7 Hz, –CH_2CH_2O), 3.64 (s, PEG –CH_2CH_2–), 3.37 (s, PEG CH_3OCH_2), 2.30 (t, –$CO_2CH_2CH_2$–), 1.69–1.58 (m, –$CH_2CH_2CH_2CH_2CH_2$–), 1.42–1.33 (m, –$CH_2CH_2CH_2$–).

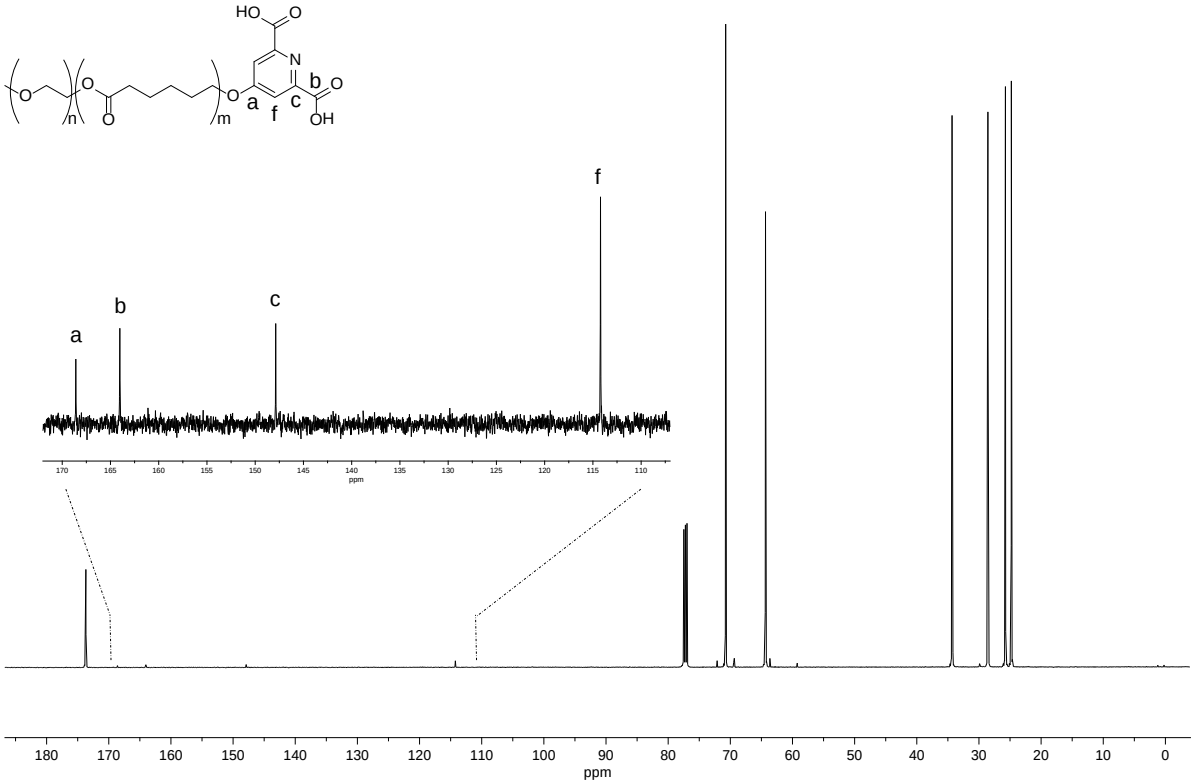

Figure S7. ^{13}C NMR dpa-PCL-PEG-OCH_3, **5**. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.68, 168.59, 164.03, 147.87, 114.19, 70.68, 64.27, 59.15, 34.24, 28.46, 25.64, 24.69.

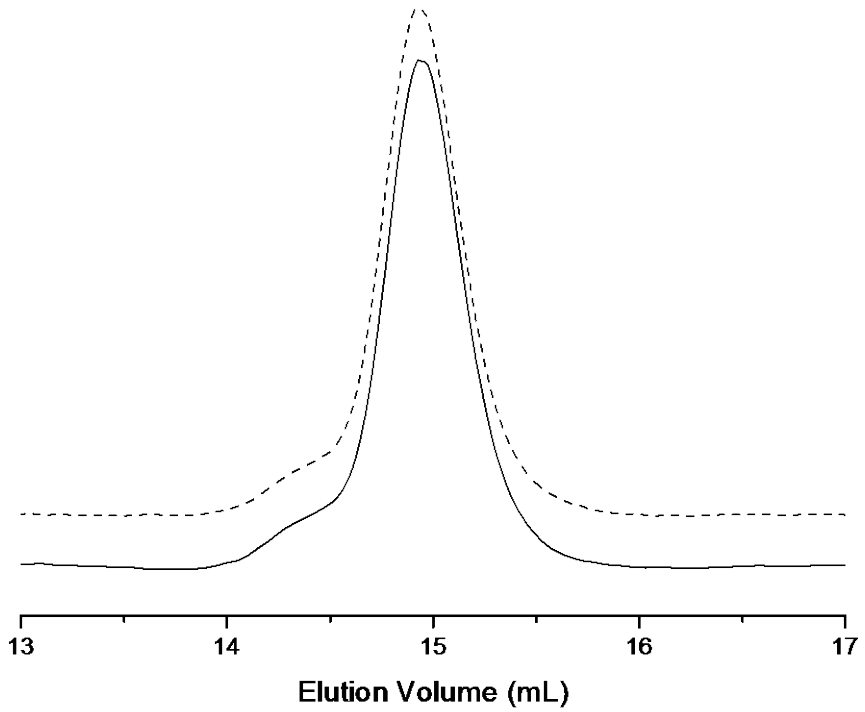

Figure S8. Gel permeation chromatography (GPC) traces of mPEG-PCL, **3.** (- - -) and Bn_2dpa-PCL-PEG-OCH_3, **4** (—) in THF (1 mL/min).

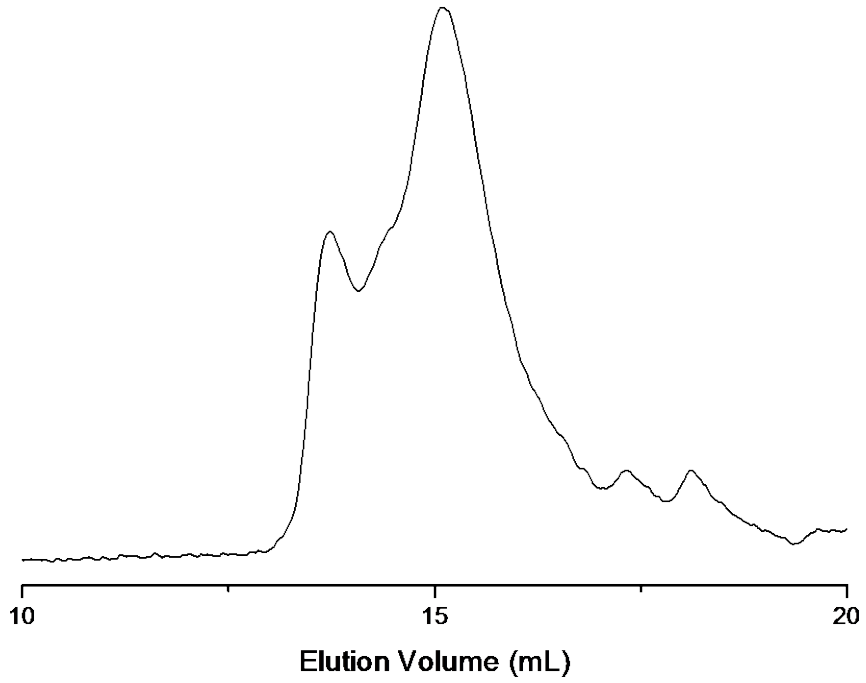

Figure S9. Gel permeation chromatography (GPC) traces of dpa-PCL-PEG-OCH_3, **5** in THF (1 mL/min). The carboxyl groups of the dpa-polymer chain end resulted in significant interactions with the GPC columns.

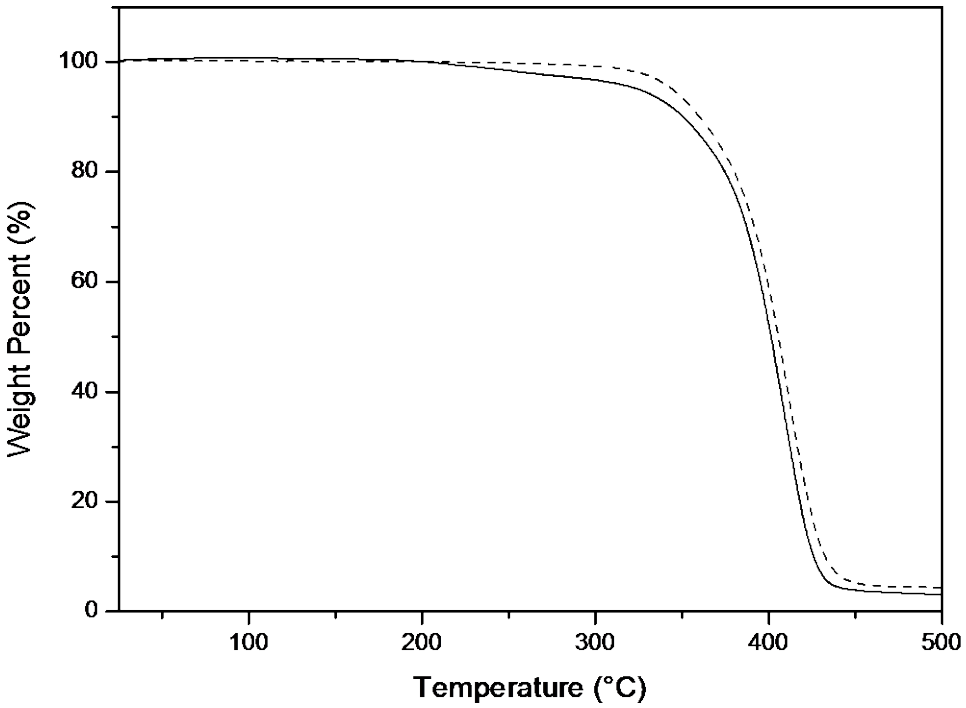

Figure S10. Thermogravimetric analysis (TGA) traces of Bn_2dpa-PCL-PEG-OCH_3, **4** (- - -) and dpa-PCL-PEG-OCH_3, **5** (—). The experiment was conducted at a heating rate of 10° C/min under a N_2 atmosphere.

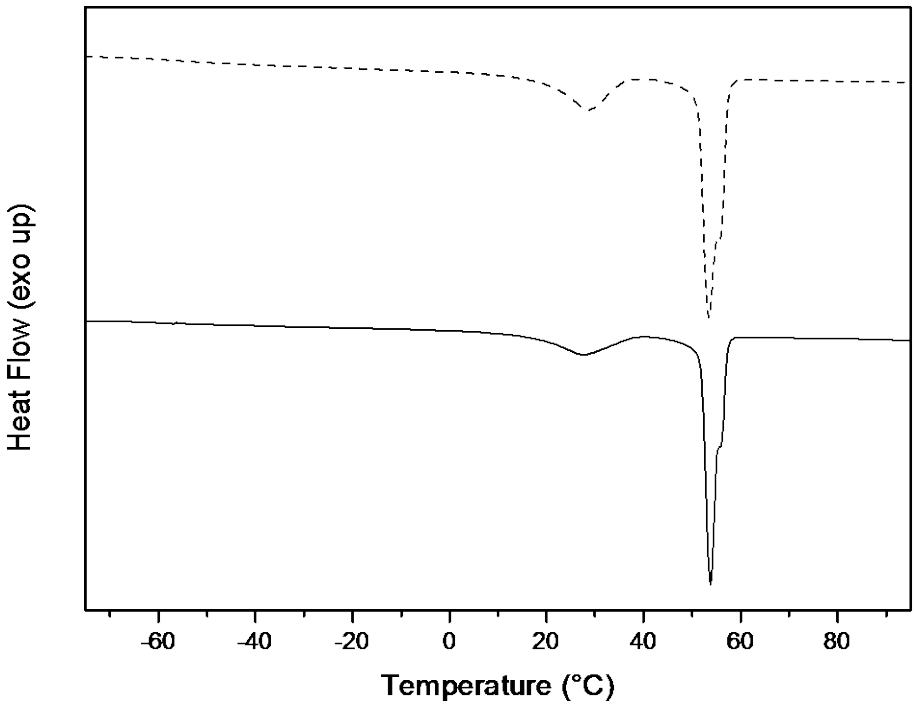

Figure S11. Modulated differential scanning calorimetry (DSC) curves of Bn_2dpa-PCL-PEG-OCH_3, **4** (- - -) and dpa-PCL-PEG-OCH_3, **5** (—). The experiment was conducted with heating and cooling rates of 10º C/min under N_2 atmosphere and data from the second heating cycle is reported.

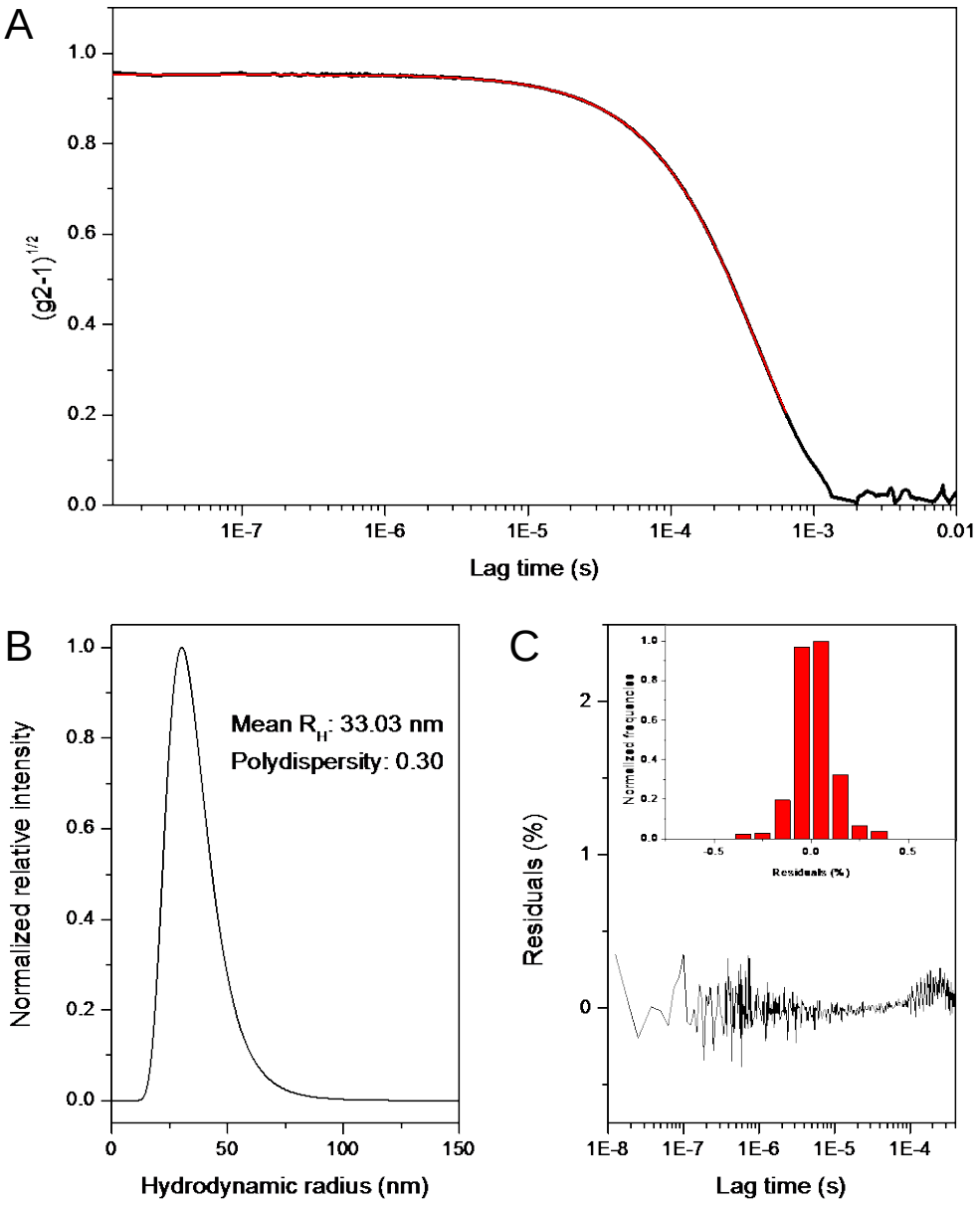

Figure S12. Dynamic light scattering (DLS) analysis of [Eu(**5**)$_3$](HNEt$_3$)$_3$ nanoparticles in water (0.5 mg/mL) prepared by addition of water into a DMF solution of [Eu(**5**)$_3$](HNEt$_3$)$_3$ (10 mg/mL). The intensity auto-correlation functions (g2) were recorded at a scattering angle of 90° for 180 s at 25 °C in water. A viscosity of 0.893 mPa·s and a refractive index of 1.33 were used for calculation. (A) Square root of the autocorrelation function (black) and the corresponding fit using Schulz-Zimm distribution (red) are shown. (B) Intensity-weighted Schulz-Zimm distribution is shown. (C) Residuals of the measured data and the fitting with Schulz-Zimm distribution is shown.

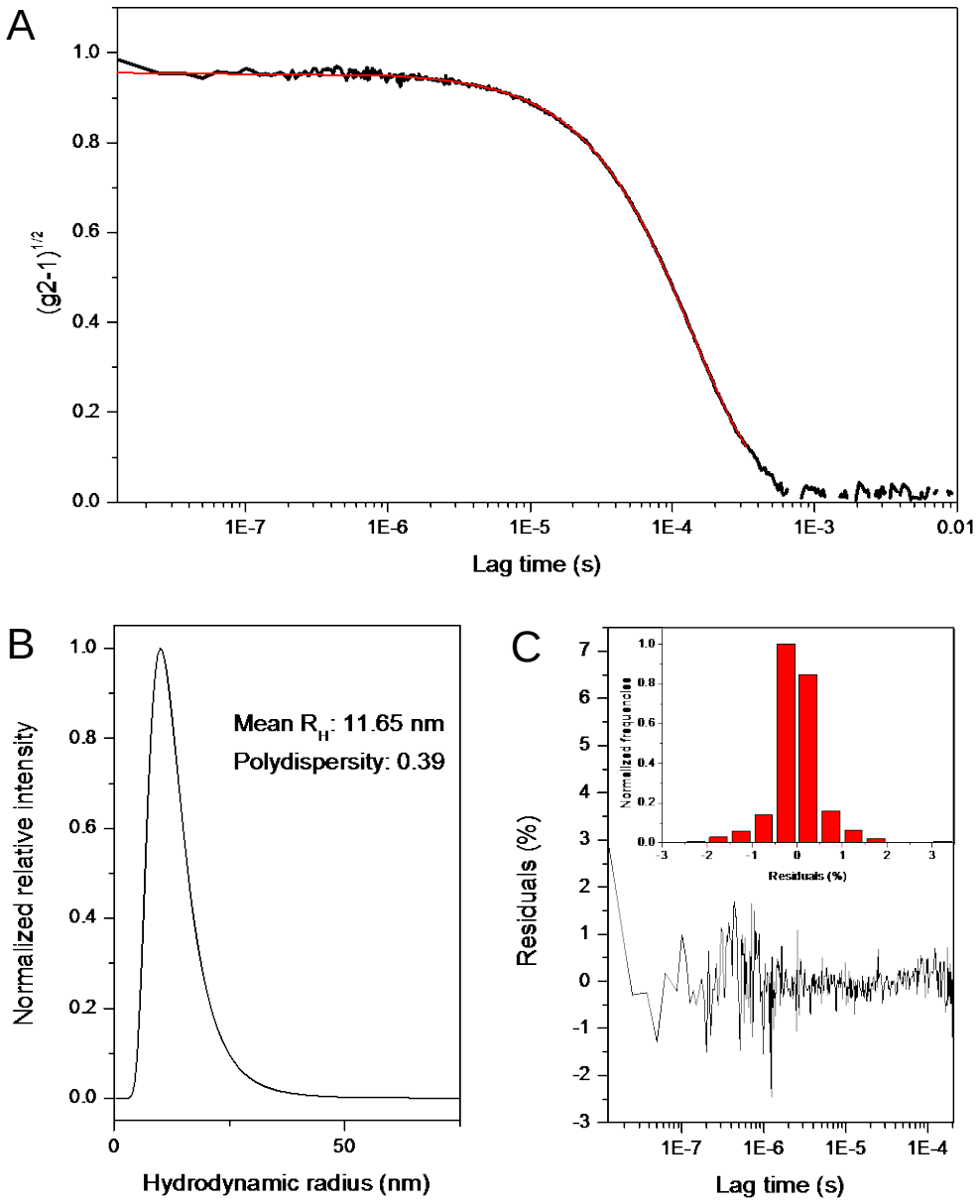

Figure S13. Dynamic light scattering (DLS) analysis of [Eu(**5**)$_3$](HNEt$_3$)$_3$ nanoparticles in water (0.5 mg/mL) prepared by addition of a DMF solution of [Eu(**5**)$_3$](HNEt$_3$)$_3$ (10 mg/mL) into water. The intensity auto-correlation functions (g2) were recorded at a scattering angle of 90° for 180 s at 25 °C in water. A viscosity of 0.893 mPa·s and a refractive index of 1.33 were used for calculation. (A) Square root of the autocorrelation function (black) and the corresponding fit using Schulz-Zimm distribution (red) are shown. (B) Intensity-weighted Schulz-Zimm distribution is shown. (C) Residuals of the measured data and the fitting with Schulz-Zimm distribution is shown.

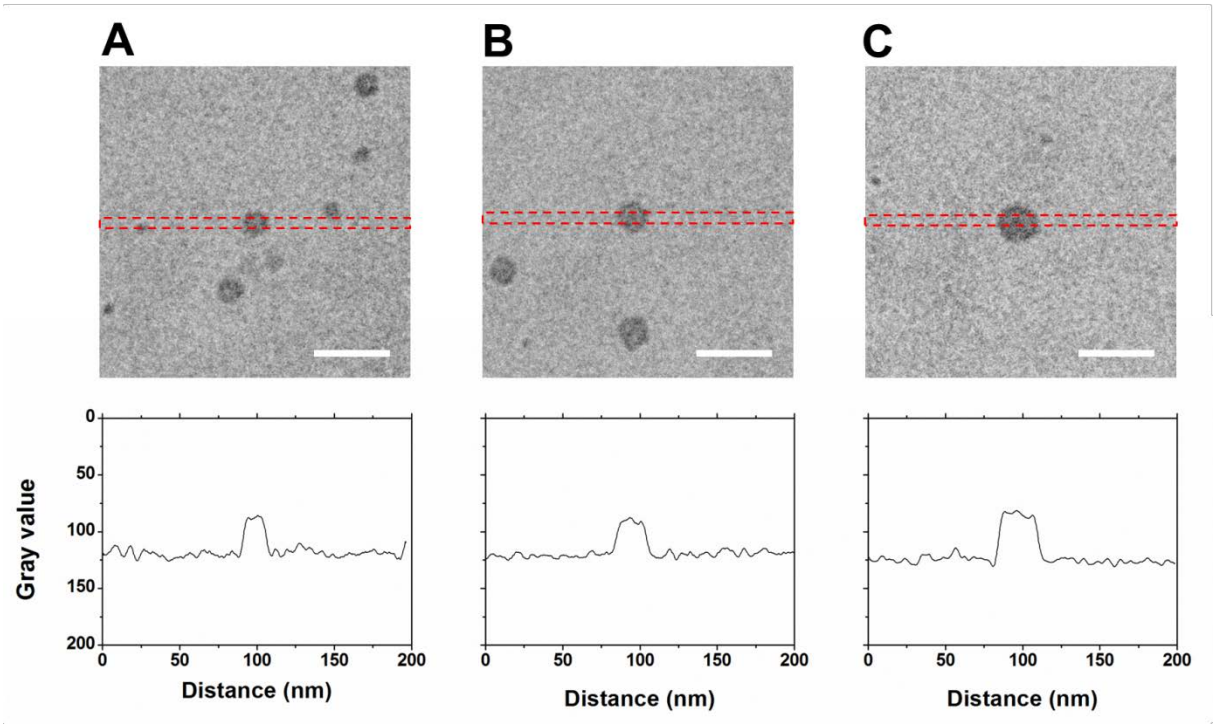

Figure S14. Representative cryo-TEM images of $[Eu(\mathbf{5})_3](HNEt_3)_3$ nanoparticle suspensions. Nanoparticle samples were prepared using a solvent displacement method by slowing adding a $[Eu(\mathbf{5})_3](HNEt_3)_3$ DMF solution to water. Cryo-TEM images of nanoparticles with increasing diameters ((A) d = 17 nm, (B) d = 21 nm and (C) d = 25 nm) and the corresponding intensity profiles are shown. Scale bars = 50 nm.

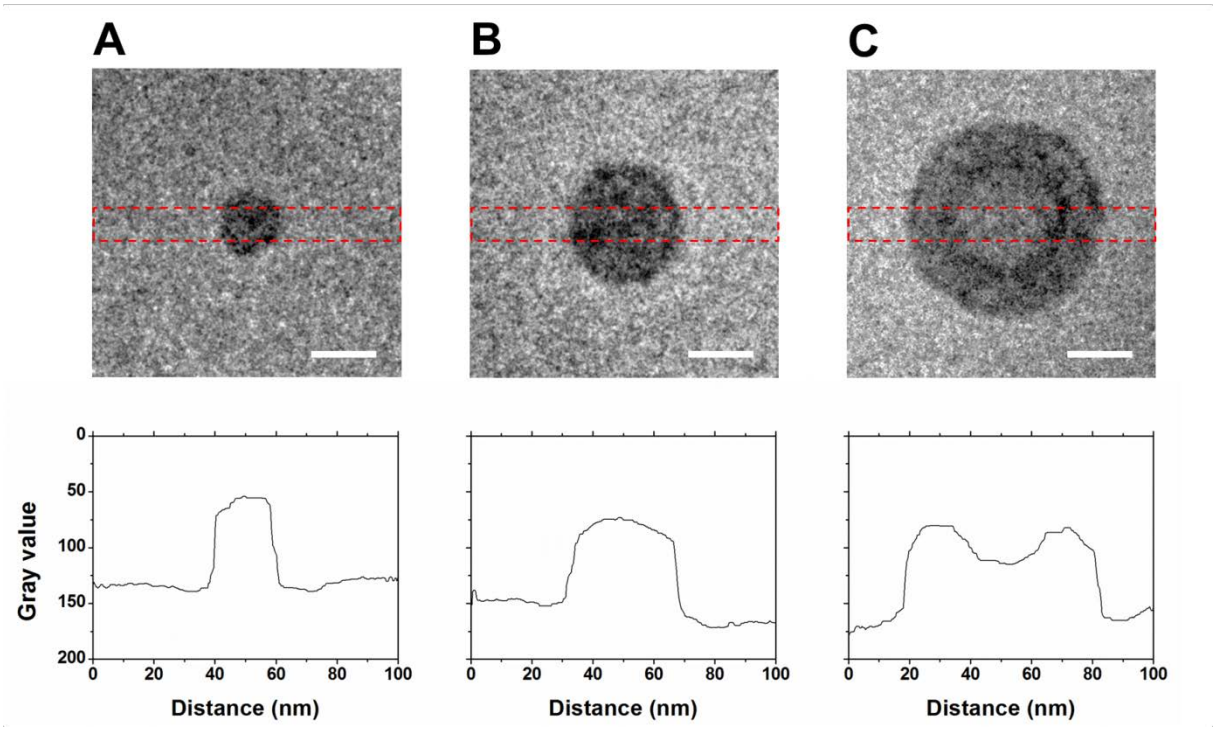

Figure S15. Representative cryo-TEM images of $[Eu(\mathbf{5})_3](HNEt_3)_3$ nanoparticle suspensions. Nanoparticle samples were prepared using a solvent displacement method by slowing adding water to a $[Eu(\mathbf{5})_3](HNEt_3)_3$ DMF solution. Cryo-TEM images of nanoparticles with increasing diameters ((A) d = 22 nm, (B) d = 41 nm and (C) d = 66 nm) and the corresponding intensity profiles are shown. Scale bars = 20 nm.

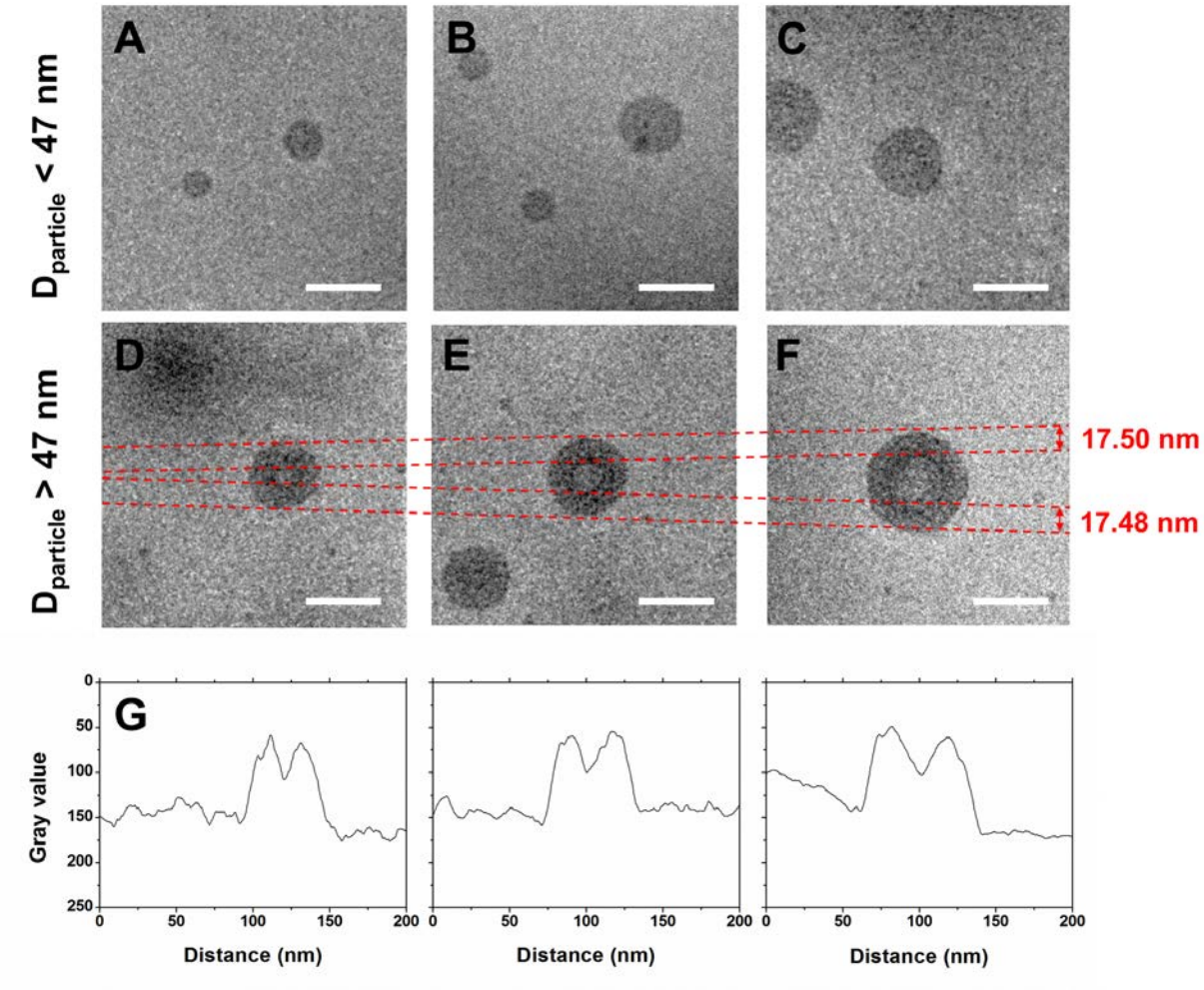

Figure S16. Representative cryo-TEM images of $[Eu(\mathbf{5})_3](HNEt_3)_3$ nanoparticle suspensions. Micelle-like nanoparticles were obtained by the slow addition of water to a $[Eu(\mathbf{5})_3](HNEt_3)_3$ DMF solution.. Nanoparticles with a diameter of less than 47 nm ((A) d < 24 nm, (B) d = 34 nm and (C) d = 44 nm) clearly resemble solid spheres. Images and intensity profiles of nanoparticles (G) with a diameter above 47 nm ((D) d = 48 nm, (E) d = 55 nm, and (F) d = 67 nm) exhibit a vesicle-like structure with a constant wall thickness of 17.5 nm. The intensity profile for the vesicle structure is represented below each respective cryo-TEM image. Scale bars = 50 nm.

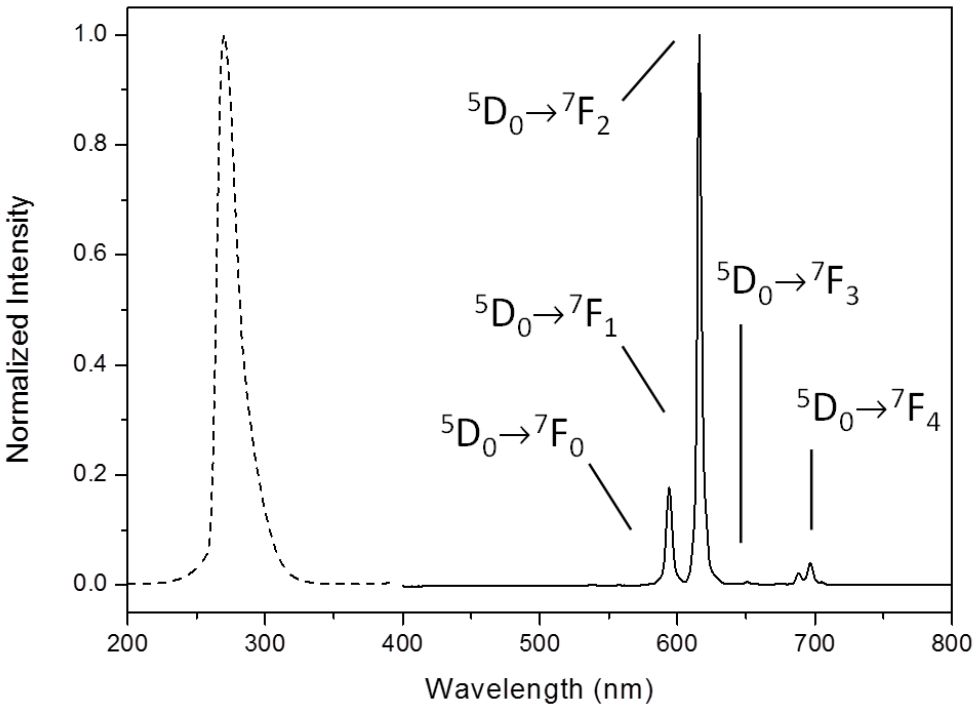

Figure S17. Excitation and emission spectra of $[Eu(\mathbf{5})_3](HNEt_3)_3$ in DMF (1 mg/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

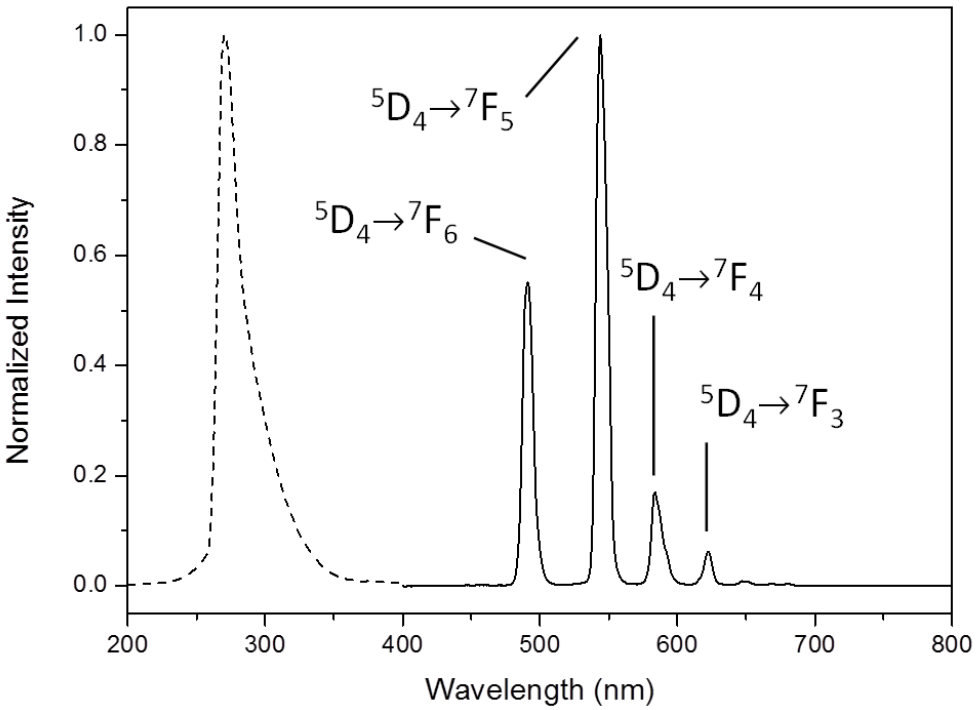

Figure S18. Excitation and emission spectra of $[Tb(\mathbf{5})_3](HNEt_3)_3$ in DMF (1 mg/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

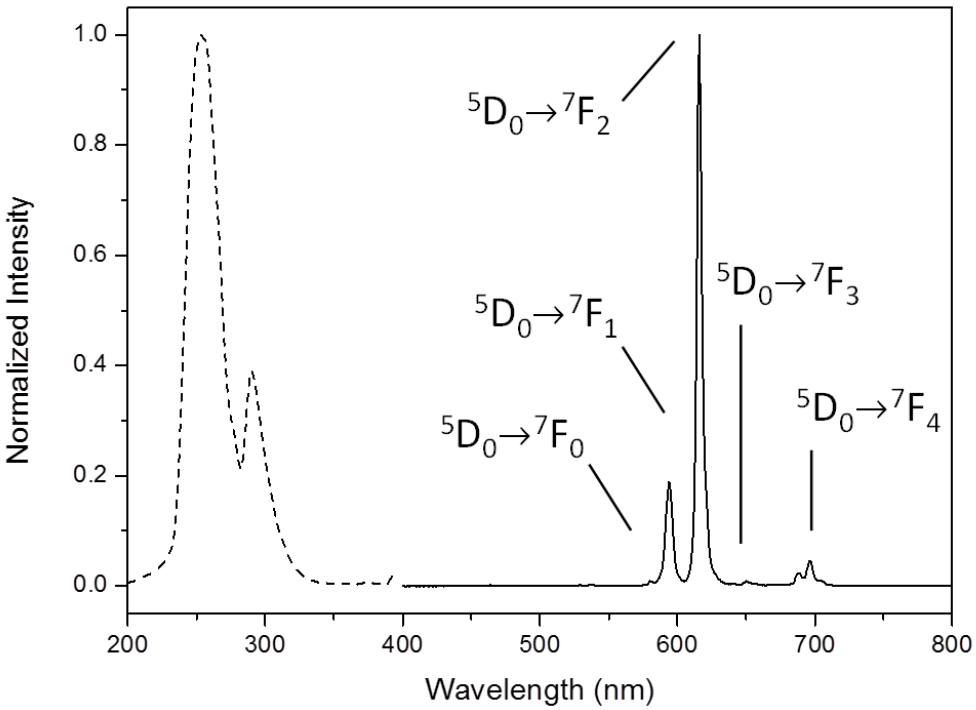

Figure S19. Excitation and emission spectra of $[Eu(\mathbf{5})_3](HNEt_3)_3$ in THF (1 mg/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

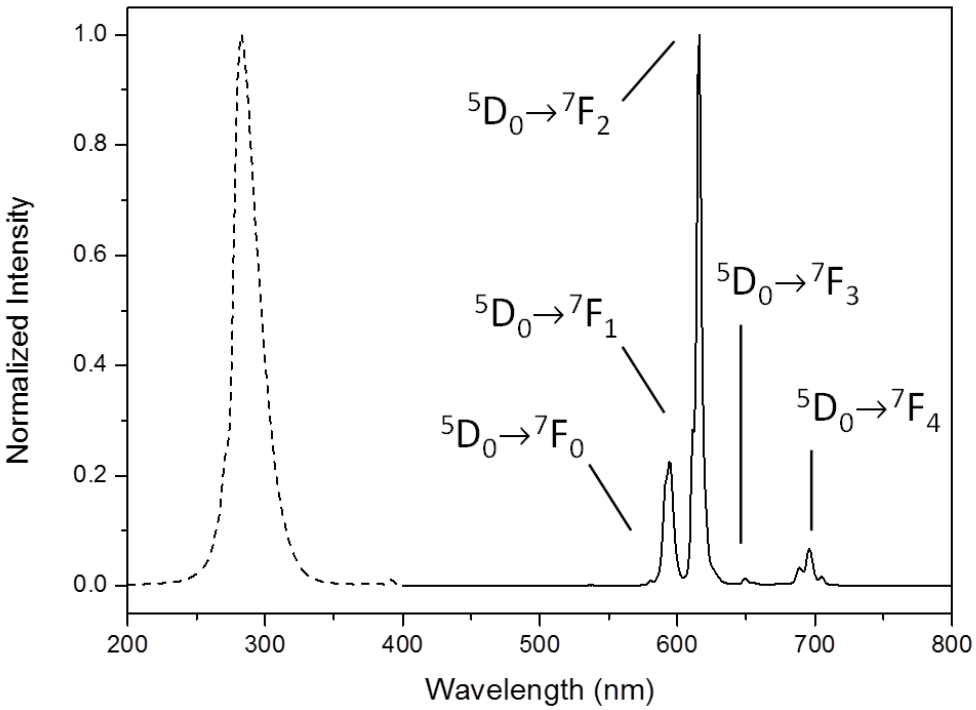

Figure S20. Excitation and emission spectra of $[Eu(dpa)_3](HNEt_3)_3$ in DMF (1.6×10^{-4} g/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

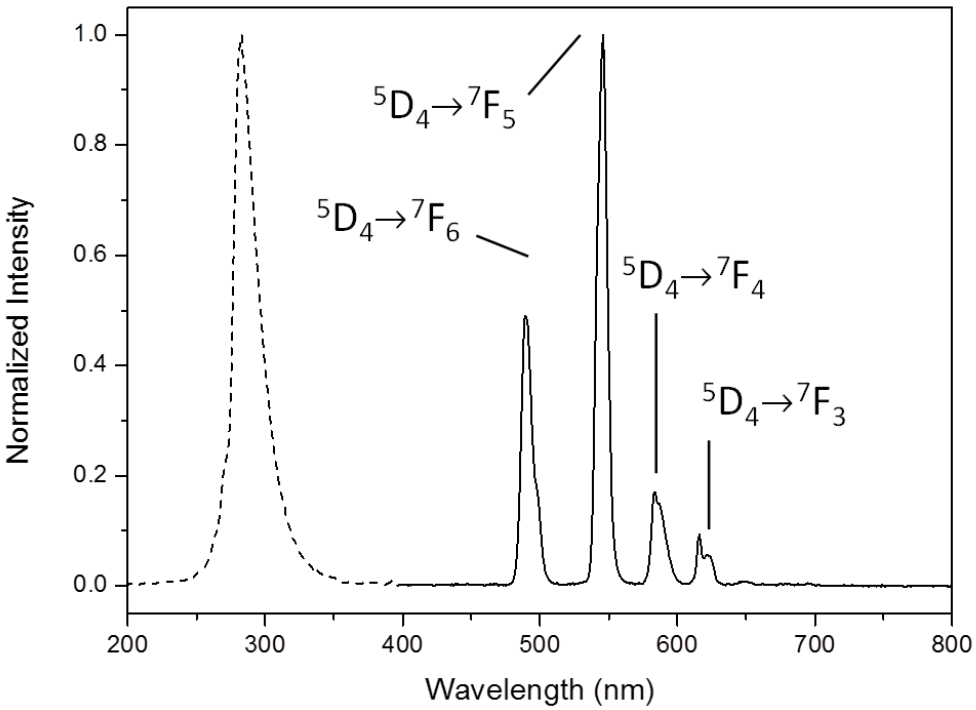

Figure S21. Excitation and emission spectra of $[Tb(dpa)_3](HNEt_3)_3$ in DMF (1.6×10^{-4} g/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

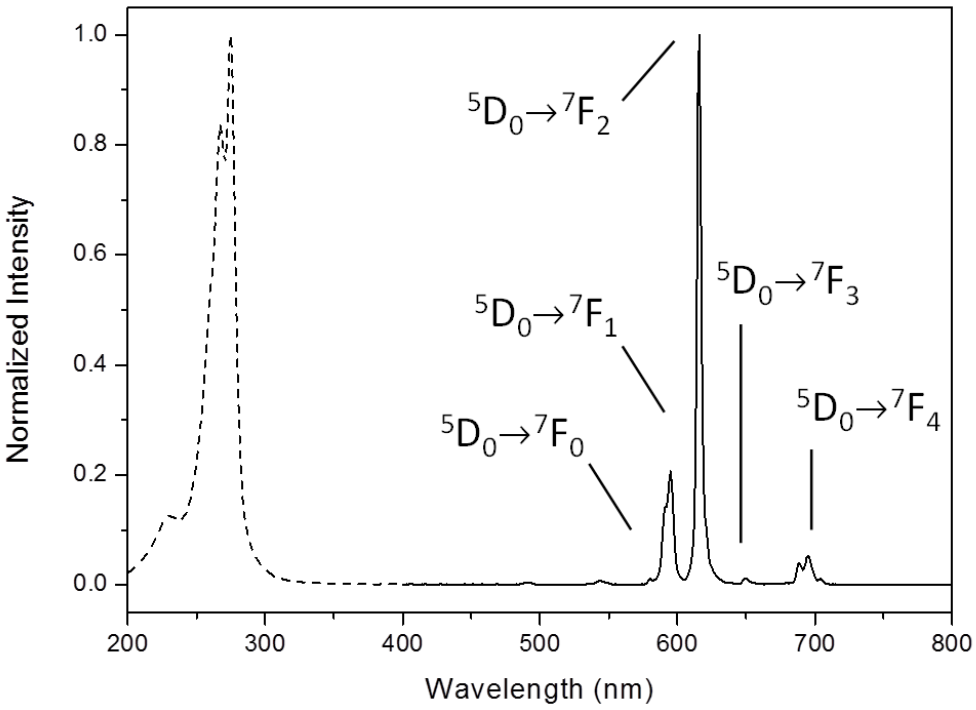

Figure S22. Excitation and emission spectra of $[Eu(dpa)_3](HNEt_3)_3$ in water (1.6×10^{-4} g/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

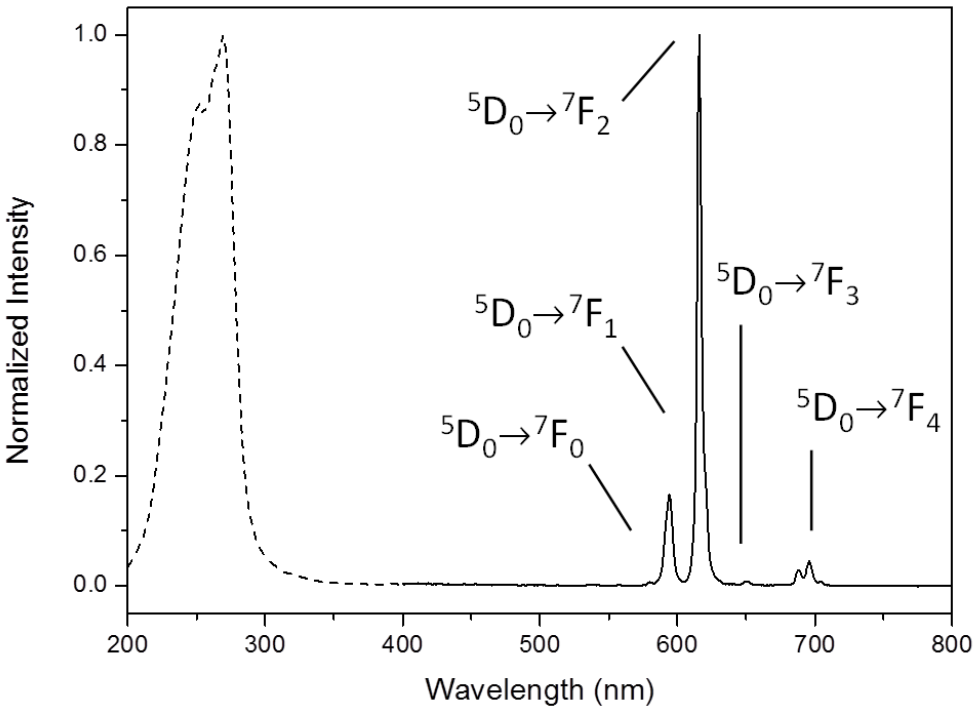

Figure S23. Excitation and emission spectra of [Eu(**5**)$_3$](HNEt$_3$)$_3$ nanoparticles in PBS (0.5 mg/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm.

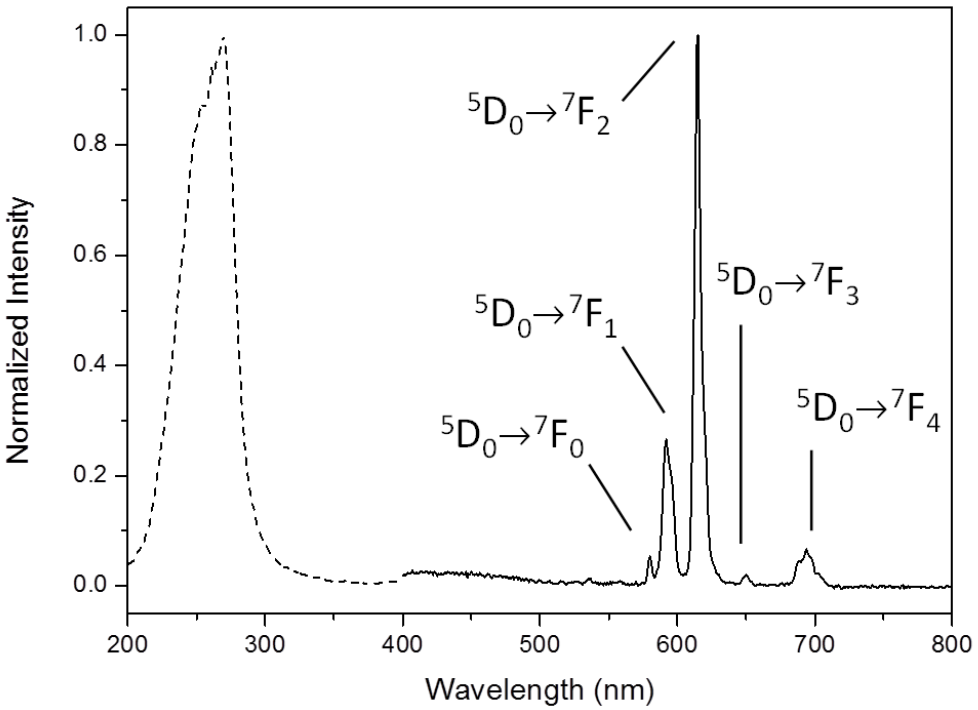

Figure S24. Excitation and emission spectra of [Eu(**5**)$_3$](HNEt$_3$)$_3$ nanoparticles in water (0.5 mg/mL). The excitation spectrum (- - -) was recorded with a fixed emission at 615 nm. The emission spectrum (—) was recorded with a fixed excitation at 270 nm. Nanoparticles were prepared by the addition of **5** in DMF/triethylamine to stirring water and followed by dialysis against water (2 days). A solution of $EuCl_3$ in water was then added to the nanoparticle suspension and the emission spectrum was recorded after a delay of 5 minutes.

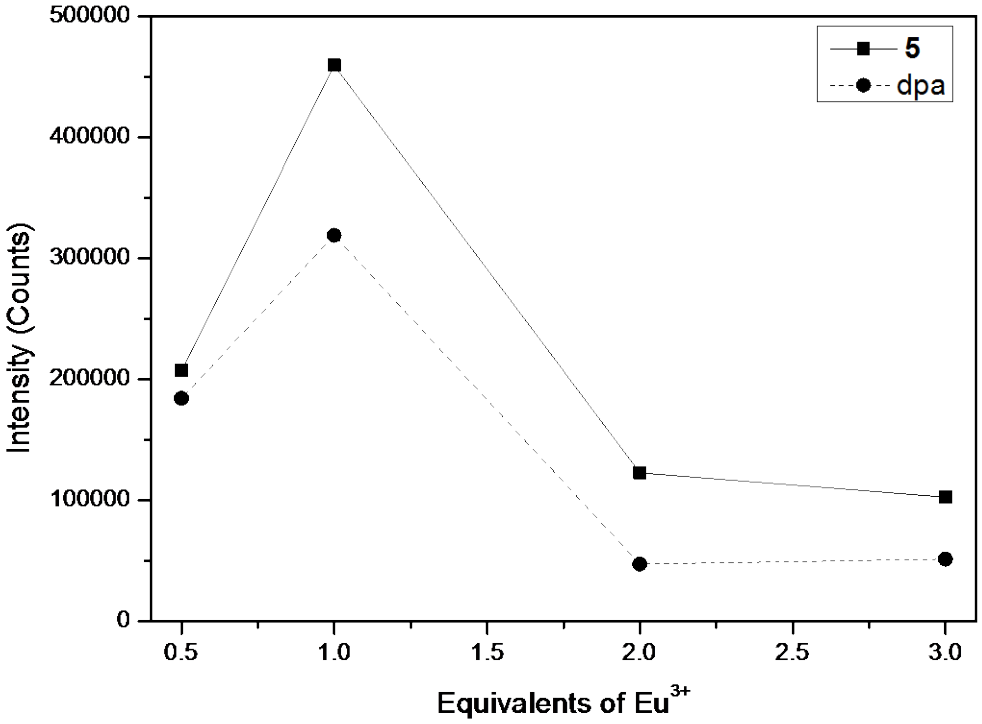

Figure S25. Europium titration experiment. Emission intensity at 615 nm was recorded versus the equivalents of Eu^{3+} added to 3 equivalents of ligand (dpa or **5**) in DMF.

References

(1) Keizer, H. M.; van Kessel, R.; Sijbesma, R. P.; Meijer, E. W. *Polymer* **2003**, *44*, 5505-5511.