SUPPORTING INFORMATION

Photoswitching of Bis-Spiropyran Using Near-Infrared Excited Upconverting Nanoparticles

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Experimental

Synthesis

1) Synthesis of $LiYF_4:Tm^{3+}$, Yb^{3+} (UCNPs).

Thulium oxide (Tm_2O_3, 99.99+ %), ytterbium oxide (Yb_2O_3, 99.99%), yttrium oxide (Y Y_2O_3, 99.99+ %), triflouroacetic acid (CF_3COOH, 99%), lithium trifluoroacetate (CF_3COOLi, 98%), oleic acid (technical grade, 90%), and 1-octadecene (technical grade, 90%) were all purchased from Sigma-Aldrich and were used without further purification. $LiYF_4:Tm^{3+}$, Yb^{3+} UCNPs were synthesized via the thermal decomposition method previously demonstrated by our group[1-3], which was comprised of a two-step process. In the first step, a 10 mL mixture of water/trifluoroacetic acid (1:1) was added to a

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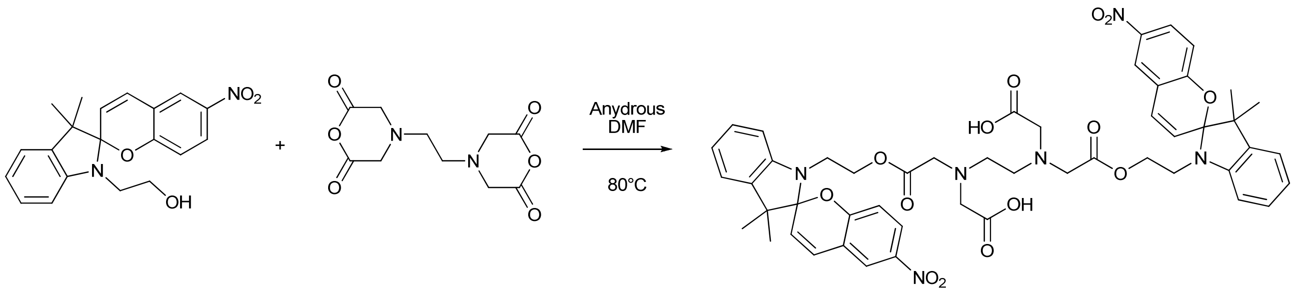
[1] V. Mahalingam, F. Vetrone, R. Naccache, A. Speghini and J. A. Capobianco, Colloidal Tm^{3+}/Yb^{3+}-doped $LiYF_4$ Nanocrystals: Multiple Luminescence Spanning the UV to NIR Regions via Low Energy Excitation, *Adv. Mater.*, **21**, 4025-4028 (2009)

[2] V. Mahalingam, R. Naccache, F. Vetrone and J. A. Capobianco, Sensitized Ce^{3+} and Gd^{3+} Ultraviolet Emissions via Tm^{3+} in Colloidal $LiYF_4$ Nanocrystals, *Chem.-Eur. J.*, **15**, 9660-9663 (2009)

[3] V. Mahalingam, R. Naccache, F. Vetrone, J. A. Capobianco, Preferential Suppression of High-Energy Upconverted Emissions of Tm^{3+} by Dy^{3+} ions in Tm^{3+}/Dy^{3+}/Yb^{3+}-doped $LiYF_4$ Colloidal Nanocrystals, *Chem. Commun.*, **47**, 3481-3483 (2011)

round-bottom flask containing 6.25 × 10^{-6} mol of Tm_2O_3 (0.0024 g, 0.5 mol % Tm^{3+}), 3.13 × 10^{-4} mol of Yb_2O_3 (0.1232 g, 25 mol % Yb^{3+}), and 9.31 × 10^{-4} mol of Y_2O_3 (0.2103 g), and the cloudy solution was heated to reflux at 80 °C until it was clear. The resulting solution was then dried at 60 °C to form the trifluoroacetate lanthanide precursors. In the second step, 12.5 mL of oleic acid and 12.5 mL of 1-octadecene were added to a 3-neck round bottom flask (solution A) and degassed at150 °C for 30 min, and then maintained at the same temperature under argon atmosphere. Approximately 2.50× 10^{-3} mol (0.2999 g) of CF_3COOLi was added to the dried precursor solids along with 7.5 mL of oleic acid and 7.5 mL of 1-octadecene (solution B), the resulting solution was degassed at 45 °C, 75 °C, and 125 °C for 5 min, respectively. Meanwhile, solution A was heated to 315 °C. At this moment, solution B was injected into solution using a syringe and pump system at a rate of 1.5 mL/min (Harvard Apparatus Econoflow). The reaction mixture was left to stir vigorously for 90 min under Ar gas. After cooling down to room temperature, absolute ethanol was added to the reaction solution to precipitate UCNPs, which were subsequently isolated *via* centrifugation (3000 rpm, 15 min). The pellets were washed with a 1:3 hexane/ethanol mixture twice to remove any impurities.

2) *Synthesis of Bis-Spiropyran*



Scheme S1: Reaction scheme used to prepare bis-spropyran

1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (200 mg, 0.57 mmol) and Ethylenediaminetetraacetic dianhydride (73 mg, 0.285 mmol) were dissolved in 5 mL of anhydrous DMF in an inert atmosphere. The solution mixture was heated to 80 °C for 24 h. Subsequently, the solution was allowed to cool to room temperature and water was added to precipitate the molecule, which was subsequently isolated by filtration and dried under vacuum. The target molecule was obtained as a pinkish solid with a 80 % yield. ^{1}H NMR (300MHz , CDCl3) δ= 8.80 (br. s., 2 H), 7.98 (s, 2 H), 7.96 (s, 2 H), 7.16 (t, J = 7.4 Hz, 2 H), 7.07 (d, J = 7.2 Hz, 2 H), 6.94 (d, J = 10.2 Hz, 2 H), 6.87 (t, J = 7.2 Hz, 1 H), 5.87 (d, J = 9.7 Hz, 2 H), 4.42 - 2.84 (m, 20 H), 1.26 (br. s., 4 H), 1.14 (br. s., 5 H). ^{13}C NMR □(75 MHz, CDCl3):δ = 172.26, 169.54, 159.29, 146.50, 141.12, 135.79, 128.55, 127.87, 125.97, 122.91, 122.00, 121.57, 120.10, 118.48, 115.52, 106.54, 106.37, 63.28, 55.89, 55.27, 54.54, 52.79, 42.25, 25.91, 19.88. HRMS (ESI): m/z calcd for $C_{50}H_{52}N_6O_{14}+H^+$: 961.3620 [M+H$^+$]; found: 961.3614

3) Ligand Exchange Reaction with Bis-Spiropyran

UCNPs conjugated with bis-spiropyran (BSP-UCNPs) were synthesized by a ligand exchange reaction between oleate-capped UCNPs ($LiYF_4$:Tm^{3+}, Yb^{3+}) and bis-spiropyran. Typically, 100 mg of UCNPs were dispersed in 5 mL tetrahydrofuran (THF) followed by the addition of 10 mg of bis-spiropyran in 1 mL of THF. The mixture was stirred at room temperature for 48 h and the resulting solution was subsequently centrifuged at 3000 rpm for 15 min. After centrifugation the clear supernatant was eliminated and the pellet was re-dispersed with THF and washed twice. Free unbound bis-spiropyran molecules were removed by further centrifugations and the resulting pink deposit was subsequently dispersed in THF for use.

Characterization

4) Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of the as-synthesized bis-spiropyran molecules, oleate-capped UCNPs, and the BSP-UCNPs conjugate were measured on a Nicolet 6700 FTIR spectrometer by using the KBr method.

5) Transmission Electron Microscopy (TEM)

TEM analysis of the colloidal dispersion of UCNPs were performed using a Philips CM200 microscope operating at 200 kV equipped with a charge-coupled device (CCD) camera (Gatan). Prior to analysis, a 20 mg sample was dispersed in 2 g of toluene to yield an approximate 1 wt% solution. A few drops of the resulting solution were evaporated on a formvar/carbon film supported on a 300 mesh copper grid (3 mm in diameter).

6) X-Ray Powder Diffraction (XRPD)

XRPD patterns were measured using a Scintag XDS-2000 Diffractometer equipped with a Si(Li) Peltier-cooled solid state detector, Cu Kα source at a generator power of 45 kV and 40 mA, divergent beam (2 mm and 4 mm), and receiving beam slits (0.5 mm and 0.2 mm).

The scan range was set from 20-80° 2θ with a step size of 0.02° and a count time of 2 s. The sample was measured using a quartz “zero background” disk.

7) Upconversion Luminescence Spectroscopy

The upconversion visible emission spectra of the oleate-capped UCNPs and the BSP-UCNPs were obtained upon 980 nm excitation, using a Coherent 6-pin fiber-coupled F6 series 980 nm laser diode (power of 615 mW), coupled to a 100 μm (core) fiber. For the upconversion studies, the samples (1 wt% in THF) were placed in 1 cm path-length quartz cuvettes (Hellma, QS). The upconverted visible emissions were collected at right angle with respect to the incident beam and subsequently dispersed by a 1m Jarrell-Ash Czerny-Turner double monochromator with an optical resolution of ~0.15 nm. The visible emissions were detected by a thermoelectrically cooled Hamamatsu R943-02 photomultiplier tube. A preamplifier, model SR440 Standard Research Systems, processed the photomultiplier signals and a gated photon counter model SR400 Standard Research Systems data acquisition system was used as an interface between the computer and the spectroscopic hardware. The signal was recorded under computer control using the Standard Research Systems SR465 software data acquisition/analyzer system.

The UV emissions were collected using a Spex Minimate ¼ m monochromator and detected with an Oriel 70680 photomultiplier tube. It should be noted that while the UV and visible emissions are measured with different detectors, they do in fact have overlapping wavelengths in the blue region. Thus, by measuring the overlapping regions with both monochromators, under identical conditions, the intensity of the UV emissions could be compared to the visible ones.

8) UV-visible absorption measurement

UV-visible absorption spectra of bis-spiropyran and BSP-UCNPs in THF solvent were recorded using Varian (Mulgrave, Victoria, Australia) Cary 5 and 5000 spectrophotometers.

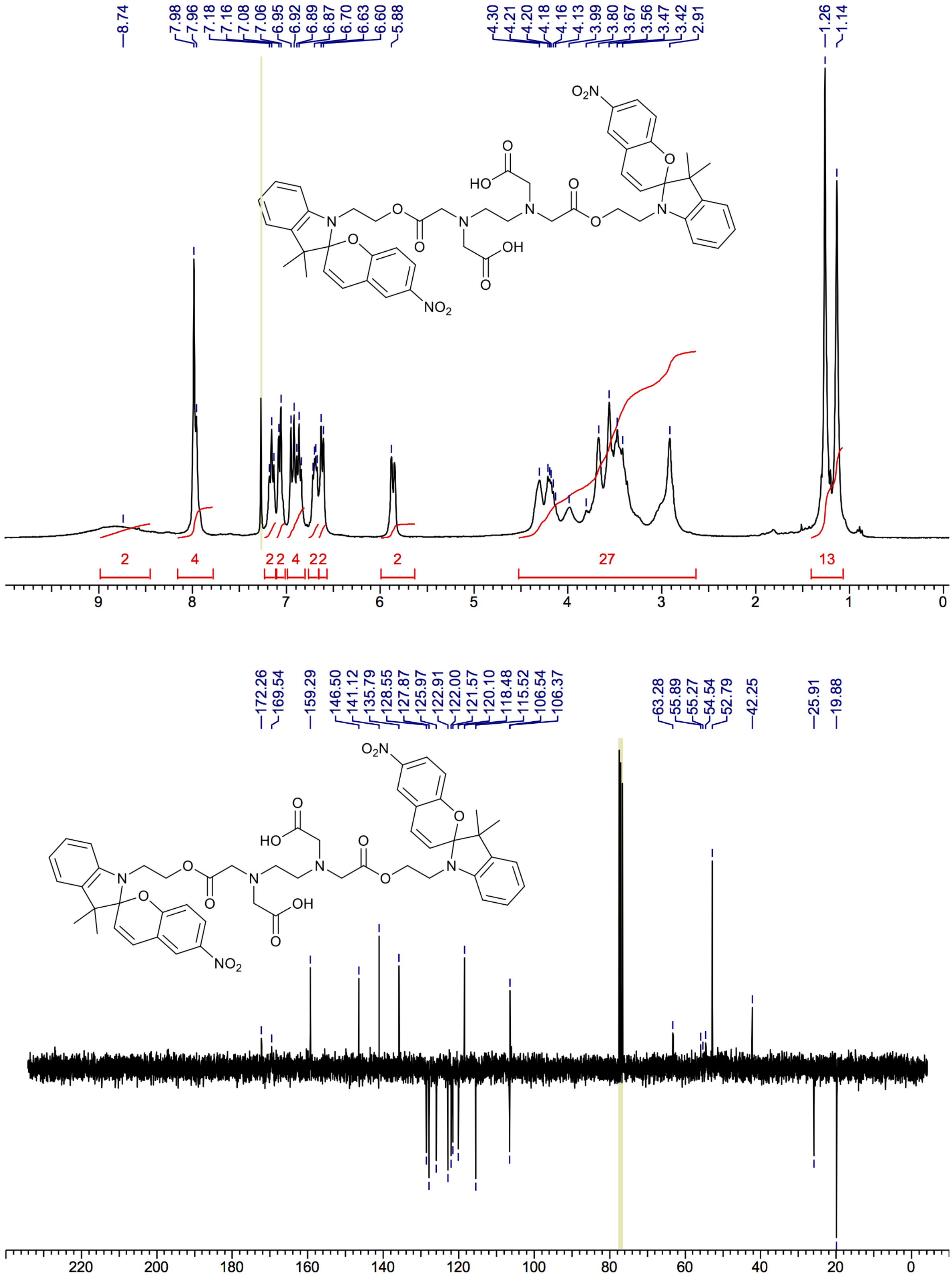


Fig. S1. ^{1}H NMR (top) and ^{13}C NMR (bottom) of bis-spiropyran.

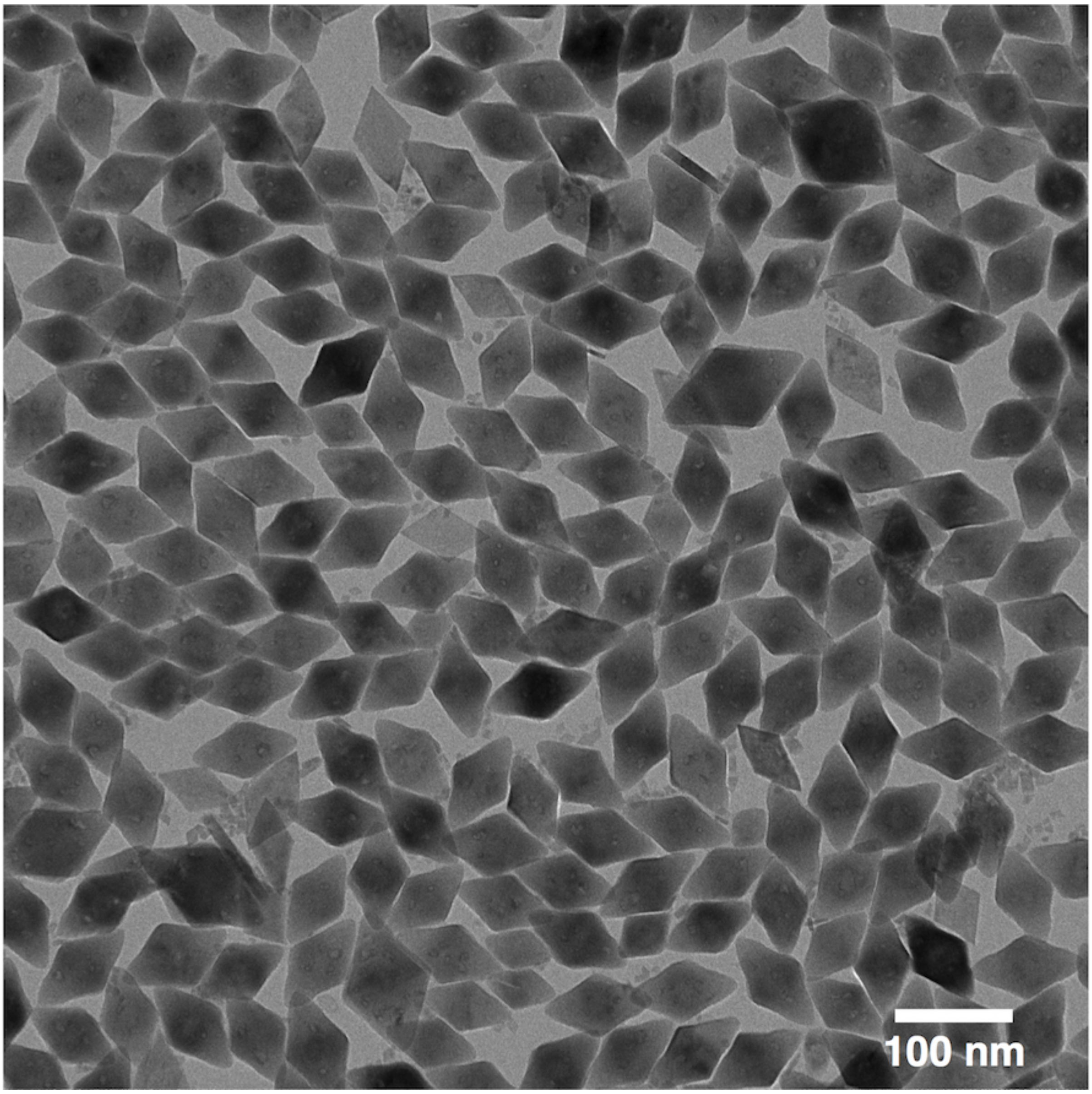


Fig. S2. Transmission electron microscopy image of oleate-capped UCNPs (1 wt% in toluene).

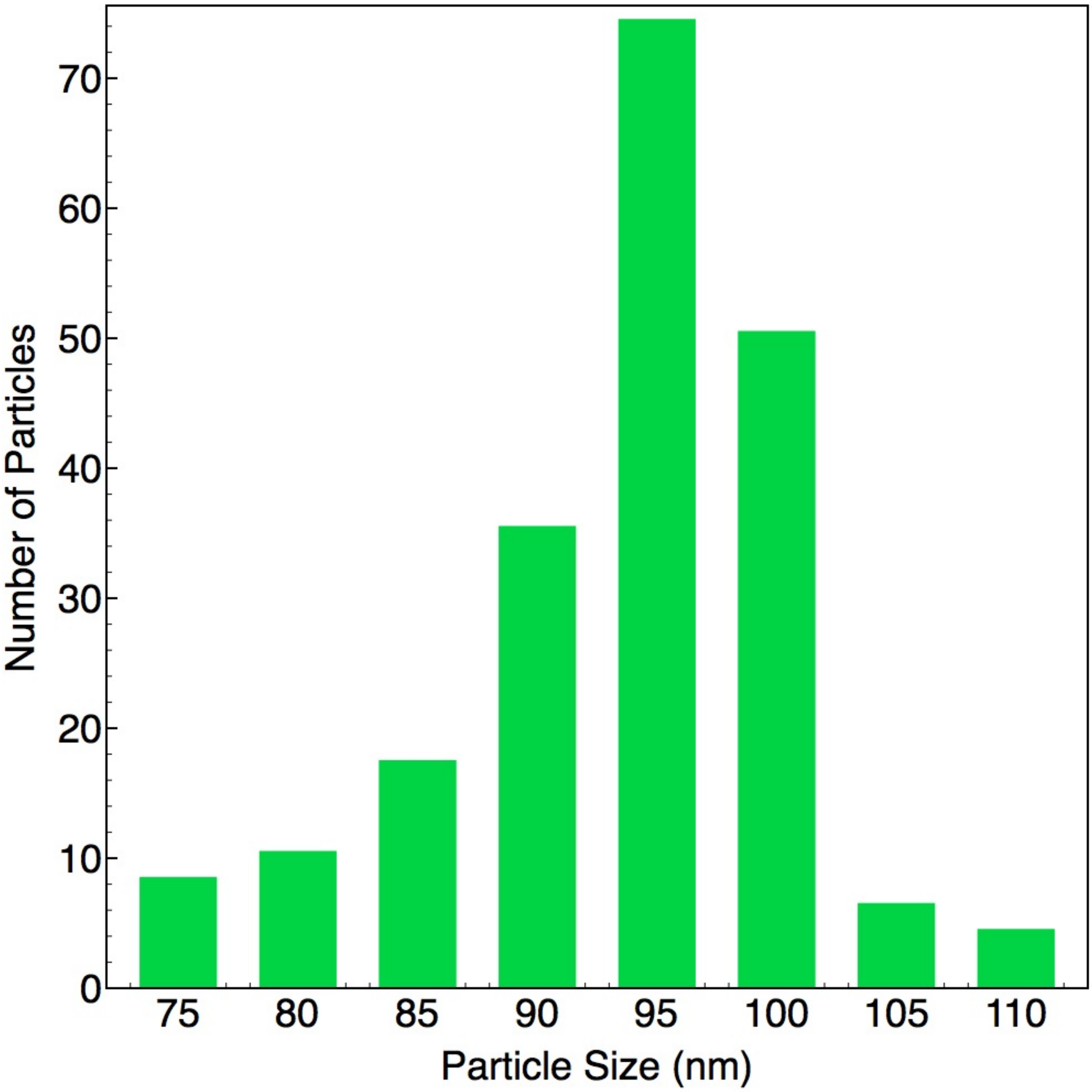


Fig. S3. Particle size distribution of the oleate-capped $LiYF_4:Tm^{3+}$, Yb^{3+} UCNPs obtained from the long axis. Average particle size was determined to be 89 nm.

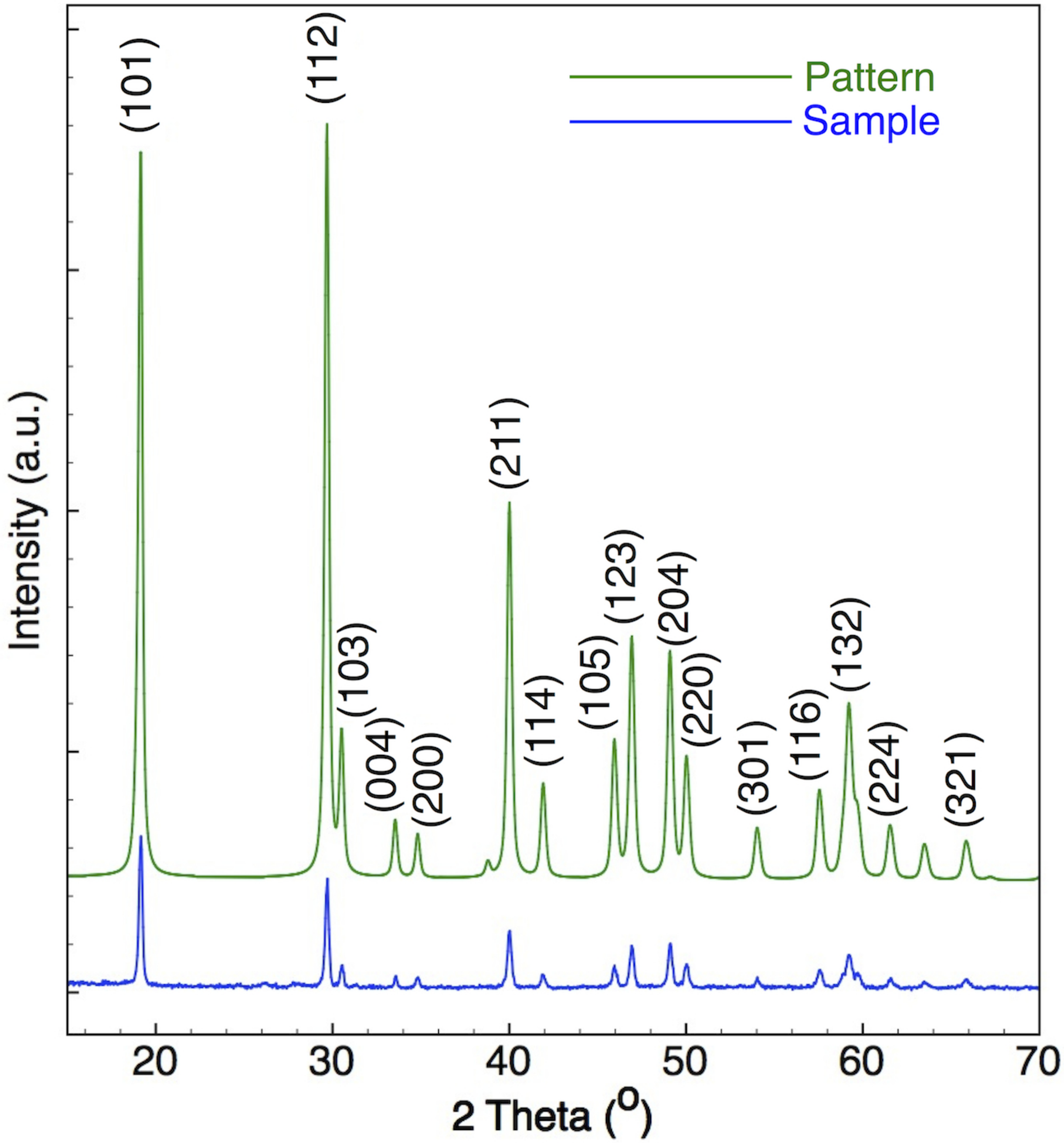


Fig. S4. Experimental (blue line) and standard (green line) X-ray diffraction patterns for the (0.5 mol%) Tm^{3+} and (25 mol%) Yb^{3+} co-doped $LiYF_4$ nanoparticles.

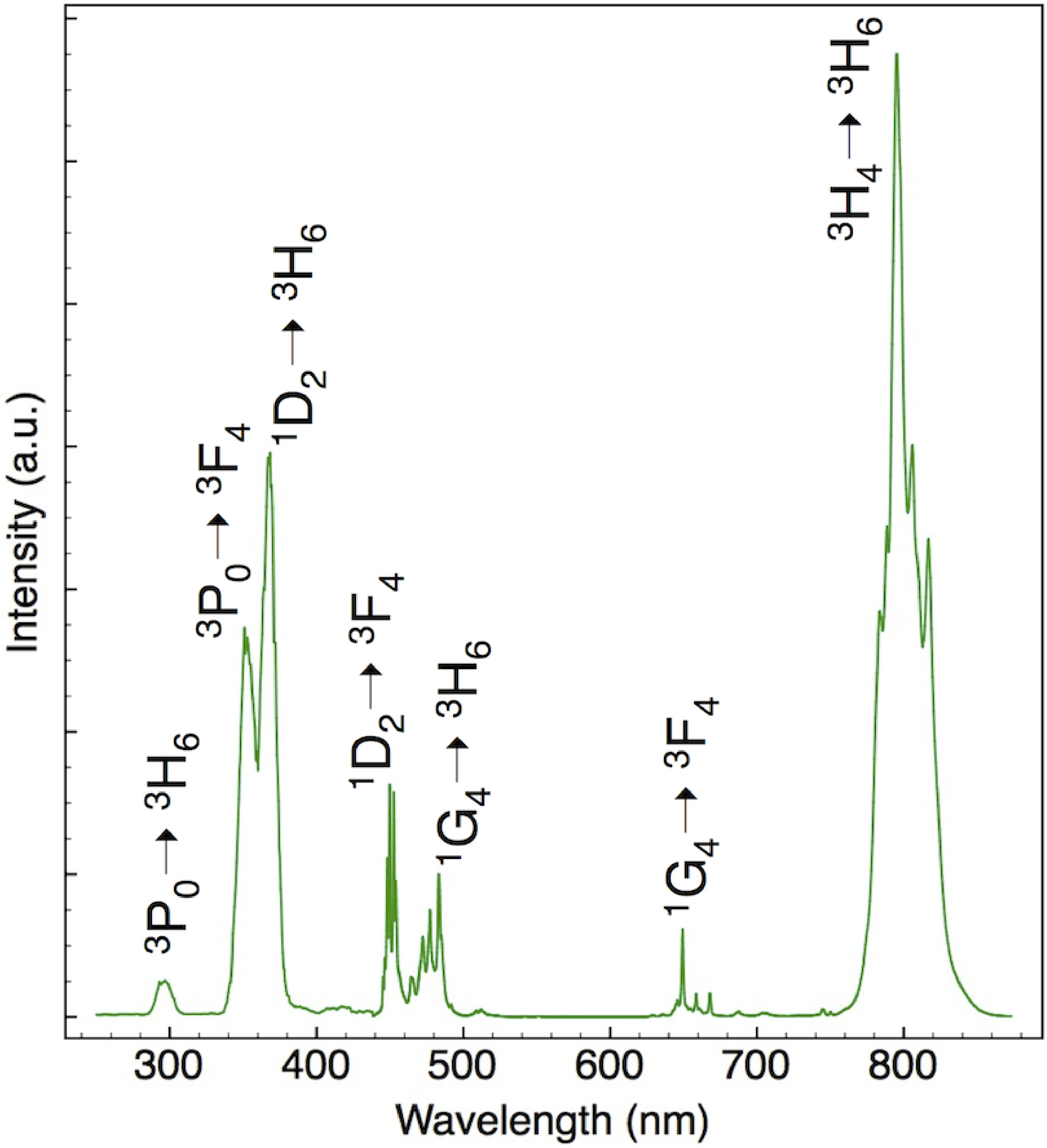


Fig. S5. Upconversion luminescence spectrum of oleate-capped $LiYF_4:Tm^{3+}$, Yb^{3+} UCNPs in toluene following 980 nm excitation.

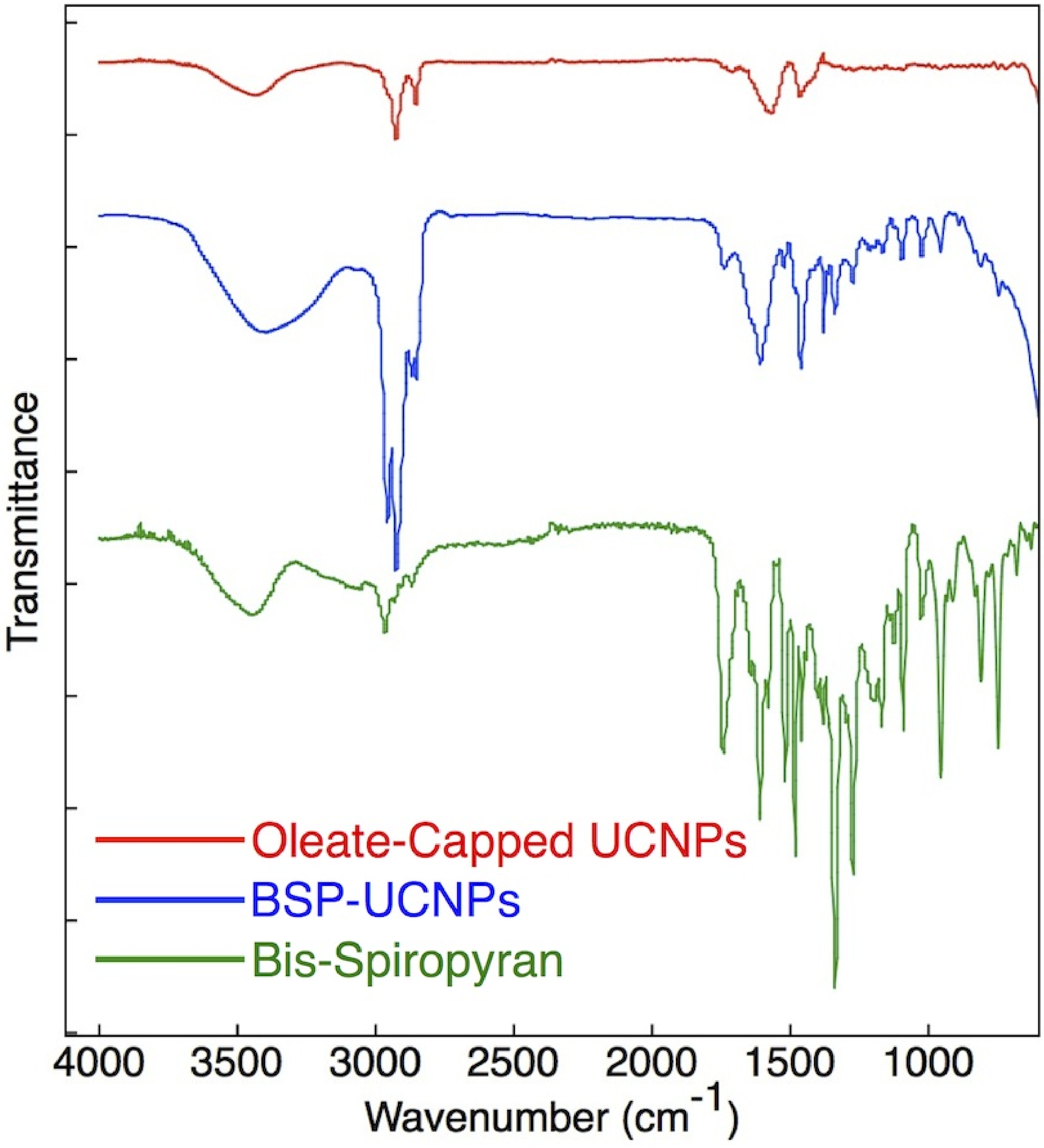


Fig. S6. Fourier transform infrared spectra of oleate-capped UCNPs (red line); BSP-UCNPs (blue line); and bis-spiropyran (green line).

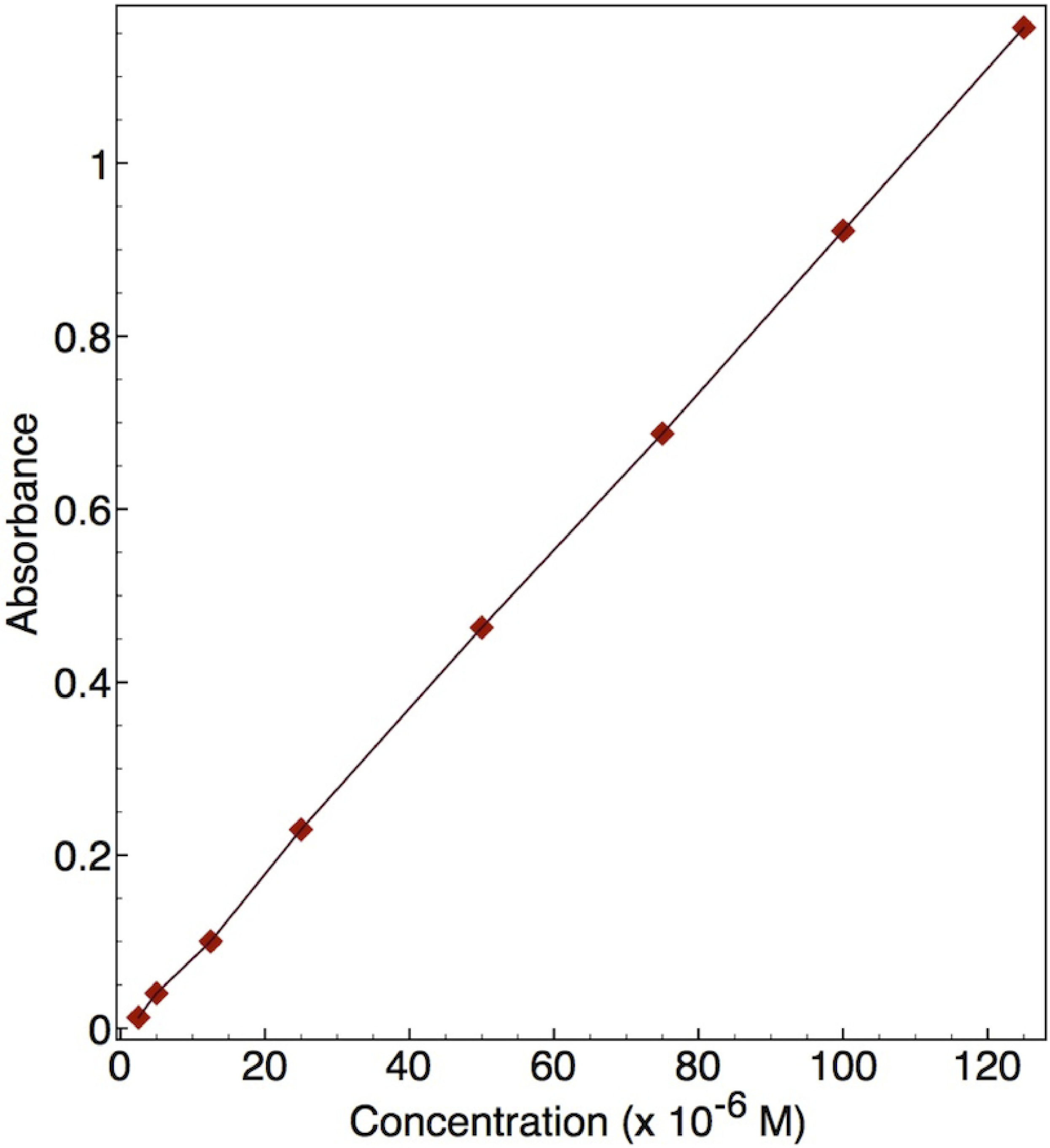


Fig. S7. Calibration curve of bis-spiropyran in THF (absorbance at 333 nm). The concentration of bis-spiropyran was determined to be 6.8 x 10^{-5} M in a solution of 0.2 wt% BSP-UCNPs in THF.

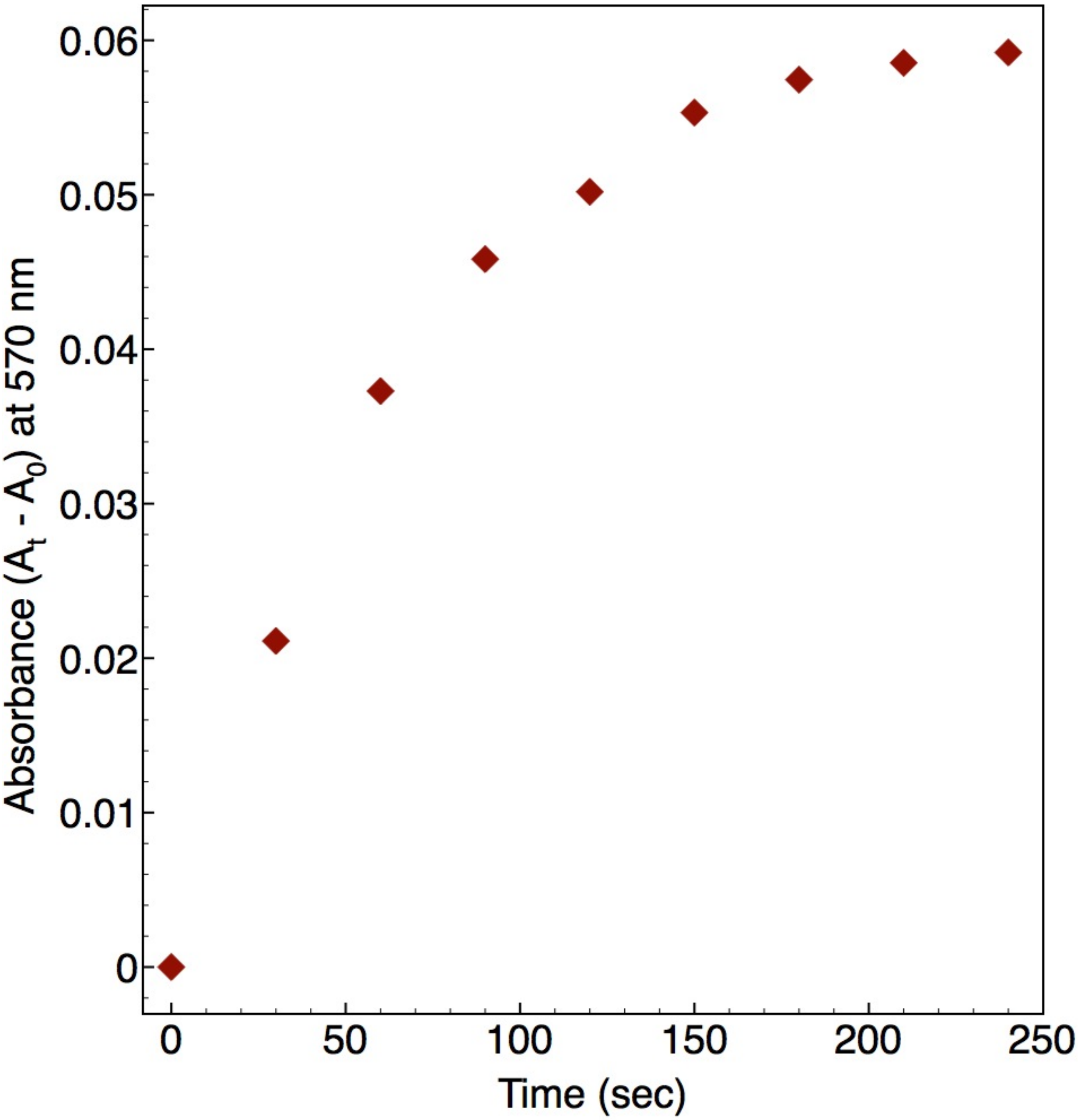


Fig. S8. Kinetic curve of BSP-UCNPs following 980 nm laser irradiation (at 570 nm).

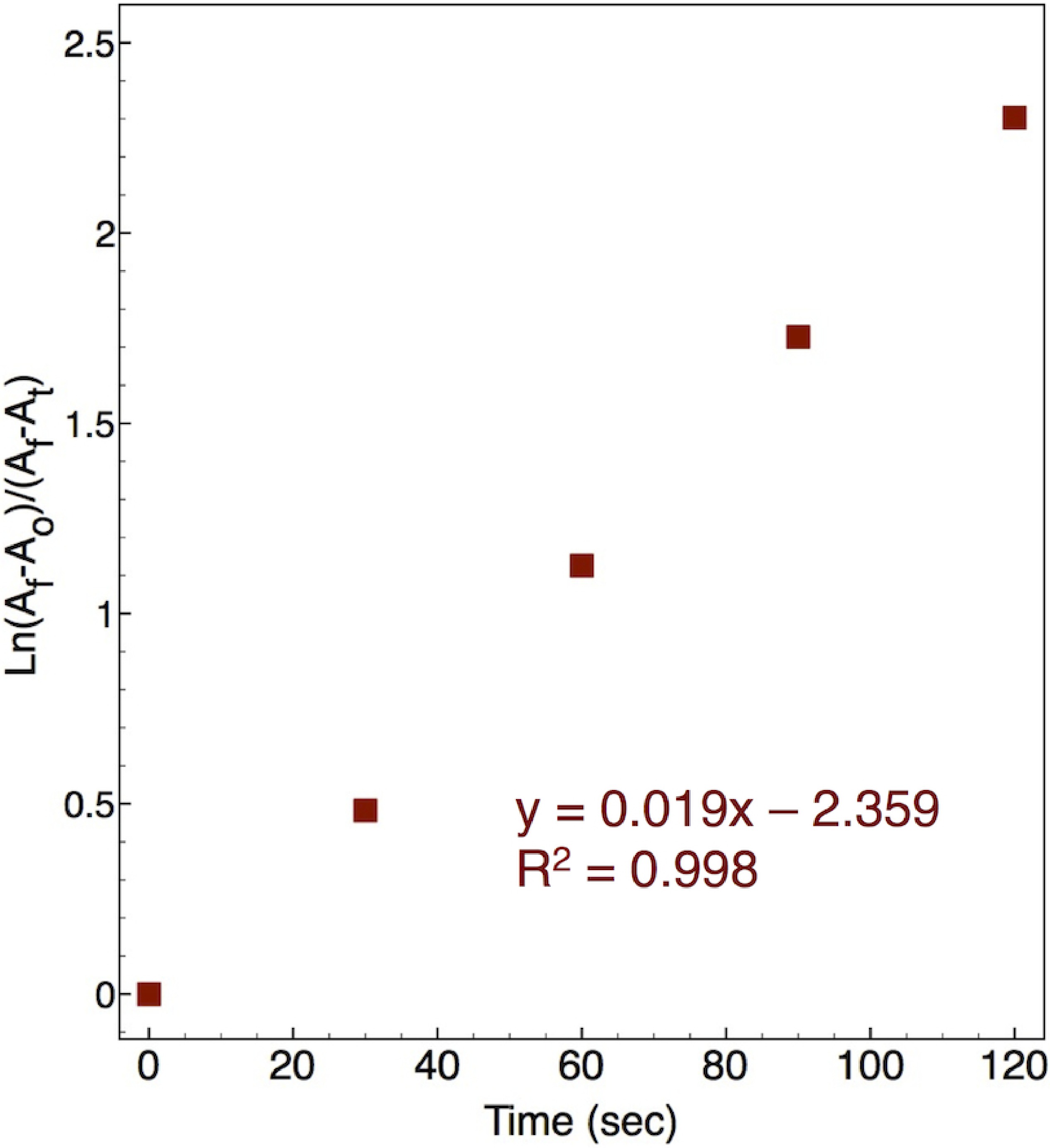


Fig. S9. Reaction order determination A_0, A_t and A_f: absorbance at $t = 0$, t, infinite time, respectively.