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Observation to Enhanced Luminescence by Single Lanthanide on Silver Nanorod

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Experimental Section

All reagents and spectroscopic grade solvents were used as received from Fisher or Sigma/Aldrich. Tris(dibenzoylmethanate)mono(5-amino-1,10-phenanthroline) europium chelate (Eu chelate) was commercially available from Sigma/Aldrich. Nanopure water (>18.0 MΩ·cm^{-1}) purified on a Millipore Milli-Q gradient system was used in all experiments.

Fabrication of Silver Nanorods.

The silver nanorods (AgNRs) were fabricated in a seed-mediated growth method. [R1-R3] First, the small silver nanoparticles with an average diameter of 4 nm were prepared in an aqueous solution as a seed solution. 20 mL of aqueous solution with 0.25 mM $AgNO_3$ and 0.50 mM sodium citrate was added by 1 mL of ice-cold 0.1 M $NaBH_4$ solution with rigorous stirring. The solution was changed from colorless to yellow representing the formation of 4 nm silver nanoparticles. Then, 30 μL of seed solution was added to 10 mL of aqueous solution containing 0.25 mM $AgNO_3$, 80 mM cetryltrimethylammoium bromide (CTAB), and 0.5 mM ascorbic acid. The reaction solution was stirred for 30 min. The solution was changed from yellow to green representing the formation of AgNRs. The AgNRs were collected by centrifugations followed by dispersing in 1 mL mixing solvent of water/ethanol (v/v = 1).

Deposition of Silica Shells on AgNR and Conjugation of Eu(III) Chelate.

Through a modified strategy of Stöber method, the silica layers were deposited on the external surfaces of AgNRs. [R3] Typically, 1 mL of AgNR solution was added to 1 mL of mixing solution of water/ethanol (v/v = 1) containing 1×10^{-3} M tetraethyl orthoorthosilicate. Subsequently, 10 μL of 30% ammonia solution was added with vigorous stirring. The solution was continuously stirred overnight at room temperature. The solution was observed to become slurry representing the formation of silica layers on the AgNRs. The suspension solution was removed by centrifugation, and the silica-coated AgNRs were collected followed by dispersing in 1 mL of mixing solvent of *N*,*N*-dimethylformamide (DMF)/alcohol (v/v=1/1). Tris(dibenzoylmethanate) mono(5-amino-1,10-phenanthroline)europium chelates (5×10^{-10} M) were dissolved in the solution for their absorptions into the silica layers on the metal rods (1×10^{-8} M). [R4] The solution was stirred for 12 h and the AgNRs were recovered by centrifugation. Then the AgNRs were dispersed in water for the measurements. Since the Eu(III) chelates were

dissolved in the solution with a very low molar ratio over the AgNRs (molar ratio of Eu(III) chelate/AgNR = 1/20), the Eu(III) chelates were believed to immobilize on the AgNRs mostly as single chelate on each AgNR.

Spectral and Microscope Measurements

Absorption spectral measurements were conducted on a Hewlett-Packard 8453 spectrophotometer. Ensemble luminescence spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer. Because of a slow decay time of Eu chelate and related samples, the emission data were collected with a time-gated method, in which the gate pulse width was 0.5 ms and the delay time was 0.1 ms.

The SMD measurements were performed on a time-resolved scanning confocal microscope (MicroTime 200, PicoQuant) which consists of an inverted confocal microscope coupled to a high-sensitivity detection setup. A single-mode pulsed laser diode (375 nm, 100 ps, 5 MHz) was used as the excitation source. An oil immersion objective (Olympus, 100×, 1.3 NA) was used to focus the laser beam on the sample and to collect the emission from the sample. The emission signals passed a dichroic mirror and focused onto a 75 μm pinhole for spatial filtering and were recorded on a single-photon avalanche diode (SPAD) (SPCM-AQR-14, Perkin-Elmer Inc.). A band-pass filter of 610/70 nm was used to eliminate the residual excitation signals. The data were collected with a TimeHarp 200 board and stored in time-tagged time-resolved mode (TTTR). Typically, the frequency of the laser source in the measurements was 5 MHz.

For the transmission electron microscope (TEM) measurements, the AgNR-containing solution was diluted to nanomolar concentration followed by casting onto a copper grid (200 mesh) with a standard carbon-coated Formvar film (200–300 Å). The sample was dried in air. The TEM measurements were performed on a side-entry Philips electron microscope at 120 keV. The distributions of nanoparticle sizes were analyzed with Scion Image Beta Release 2 on the basis of at least 200 images.

References and Notes

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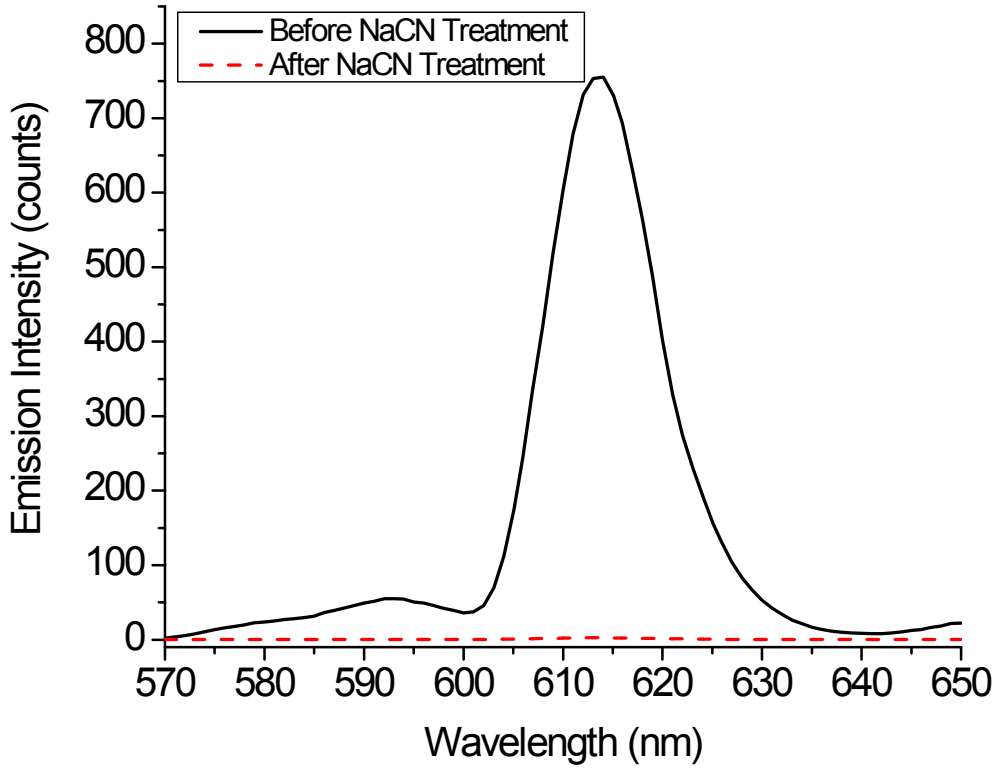

Figure S1. Emission spectral decrease for the Eu chelates on the AgNRs in aqueous solution prior to and after NaCN treatment. The emission spectra were collected upon excitation at 380 nm with a time-gated method. The gate pulse width was controlled to be 0.5 ms and the delay time was 0.1 ms.

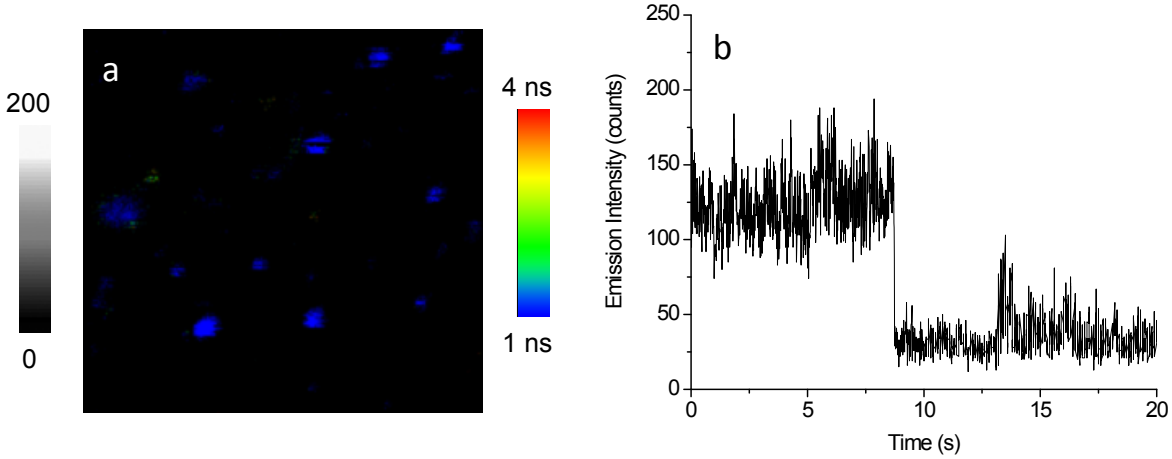

Figure S2. (a) Emission images from the individual Cy5-AgNR complexes upon excitation at 640 nm with a frequency of 40 MHz. The images were acquired on a time-resolved microscope. (b) Time-trace analysis to the single emission spots on Figure S2a.