Supporting Information

Ultrathin Two-Dimensional Nanosheets Meet Upconverting Nanoparticles: In Situ Near-Infrared Triggered Molecular Switching

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Experimental Section

General considerations. All syntheses were performed under ambient conditions and all the chemicals were of analytical grade and used without further purification. Both the raw materials for 2D SCO nanosheets {[Fe(1,3-bpp)$_2$(NCS)$_2$]$_2$ (1, 3-bpp = 1, 3-di(4-pyridyl)-propane)}-- $Fe(ClO_4)_2 \cdot 6H_2O$, KSCN, and 1, 3-bpp; and the raw materials for UCNPs--NaOH, NH_4F, ethanol, chloroform, toluene, cyclohexane, trifluoroacetic acid (CF_3COOH), and HCl were all obtained commercially purchased from Sinopharm Chemical Reagent

Co. Ltd (China), Beijing HWRK Chem Co., Ltd. (China), and Sinopharm Chemical Reagent Co. Ltd (China).

Characterization. The morphologies of the 2-D SCO nanosheets, the size and morphologies of UCNPs, and the morphologies and crystalline phase of 2D@UCNPs hybridized systems were characterized by using a Field emission scanning electron microscope transmission electron microscope (TEM; Tecnai-G2 20 E-TWIN 200 KV) and atom force microscopy (AFM, Cypher, Asylum Research). Before these microscope characterizations, the aqueous suspension of 2-D SCO nanosheets was dropping onto the holey carbon-coated carbon support copper grids, Si/SiO_2, and piranha-cleaned Si/SiO_2, respectively, and then naturally dried. Infrared spectra were recorded on a Shimadzu IR Prestige-21 FTIR-8400S spectrometer in the spectral range 4000−500 cm^{-1}, with the samples in the form of potassium bromide pellets. UCL spectra of UCNPs were measured with a fluorescence spectrometer (Edinburgh, LFS-920) using an external CW 980 nm laser (Xi'an Saipulin Laser Technology Institute, China) with a tunable power of 0−3 W acting as the excitation source. UV-vis absorption and the fluorescence spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer and a Horiba Fluoro-Max4 Spectro-fluorometer, respectively. Thermogravietric analysis (TGA) were performed by using a Mettler-Toledo TGA/DSC STARe System at a heating rate of 10K min^{-1}, under an atmosphere of dry N_2 flowing at a rate of 20 cm^3min^{-1} over a temperature range from 50 °C to 800 °C. The

irradiation experiments were performed by using a CW 980 nm NIR laser (SD980- 5000G3, Xi'an Saipulin Laser Technology Institute, China) with a laser power density of 1.5 W cm^{-2}.

Preparation of bulk precursors $[Fe(1,3\text{-bpp})_2(NCS)_2]_2$. Bulk precursors were synthesized according to literature. In a typical procedure, a methanol solution (15 mL) of 1, 3-bpp (0.991 g, 5.0 mmol) was added slowly into an methanol solution (10 mL) of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.434 g, 2.5 mmol), Potassium thiocyanate (0.485 g, 5.0 mmol) and a small amount of ascorbic acid (to avoid oxidation of Fe(II)) with continuous stirring, the yellow-colored solids were formed immediately. After stirred for about 1h, the solids were separated by suction filter and washed with methanol before dried vacuum. The typical yield was found to be 91% based on Fe(II), and the purity of them were checked by X-ray powder diffraction.

Synthesis of trifluoroacetate precursor: The powders samples of trifluoroacetate precursor $Y(CF_3CO_2)_3$, $Yb(CF_3CO_2)_3$ and $Er(CF_3CO_2)_3$ were prepared by reacting 2.00 mmol Y_2O_3, Yb_2O_3 and Er_2O_3 in a 20 mL 1:1 (v/v) solvent mixture of trifluoroacetic acid and DI water, respectively. [1] These mixtures were refluxed overnight at 80 °C under magnetic stirring, during which time, the precursors were formed and precipitated after cooling to RT. The precursors were then collected by filtrate and dried vacuum overnight.

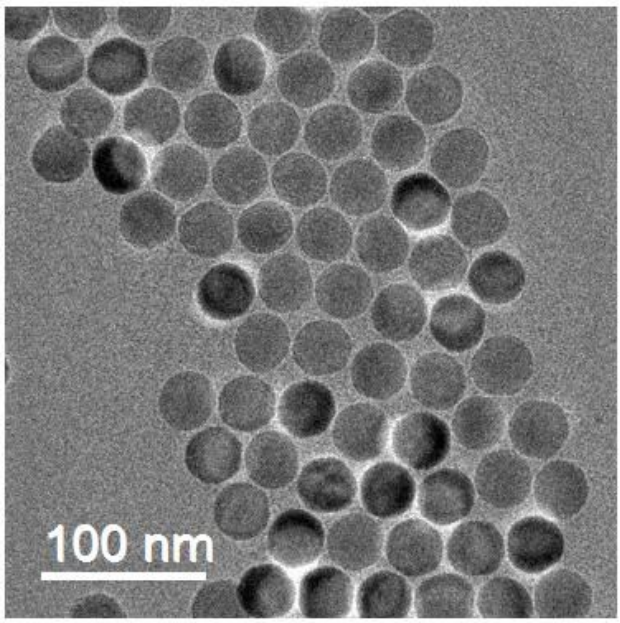

Figure S1. Additional TEM images of Yb^{3+} sensitized hexagonal-phase UCNPs.

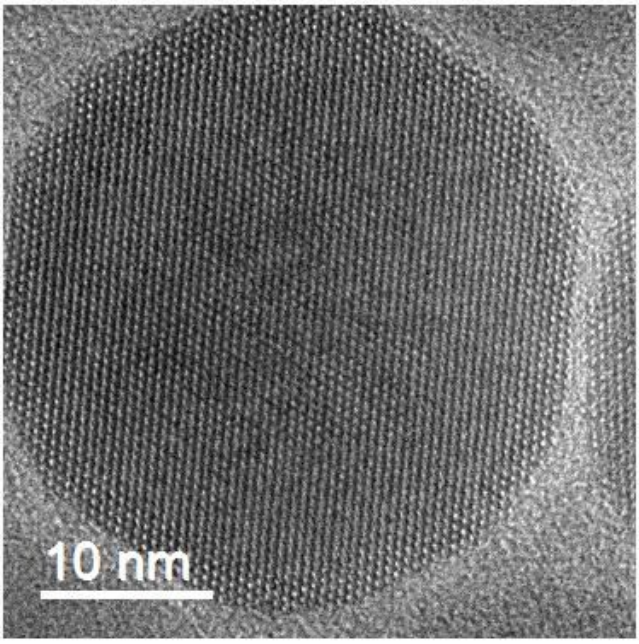

Figure S2. HRTEM photographs of Yb^{3+} sensitized hexagonal-phase UCNPs.

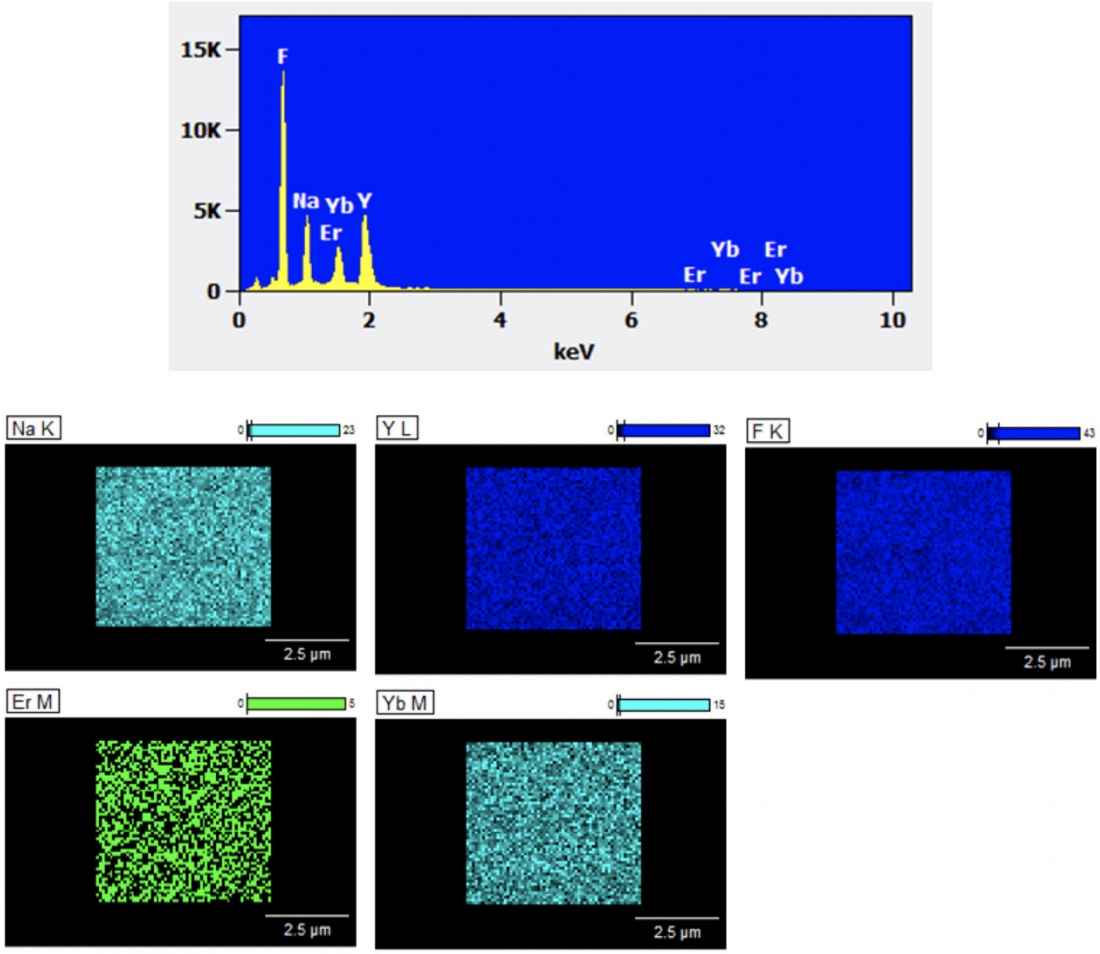

Figure S3. EDXA analysis of Yb^{3+} sensitized hexagonal-phase UCNPs.

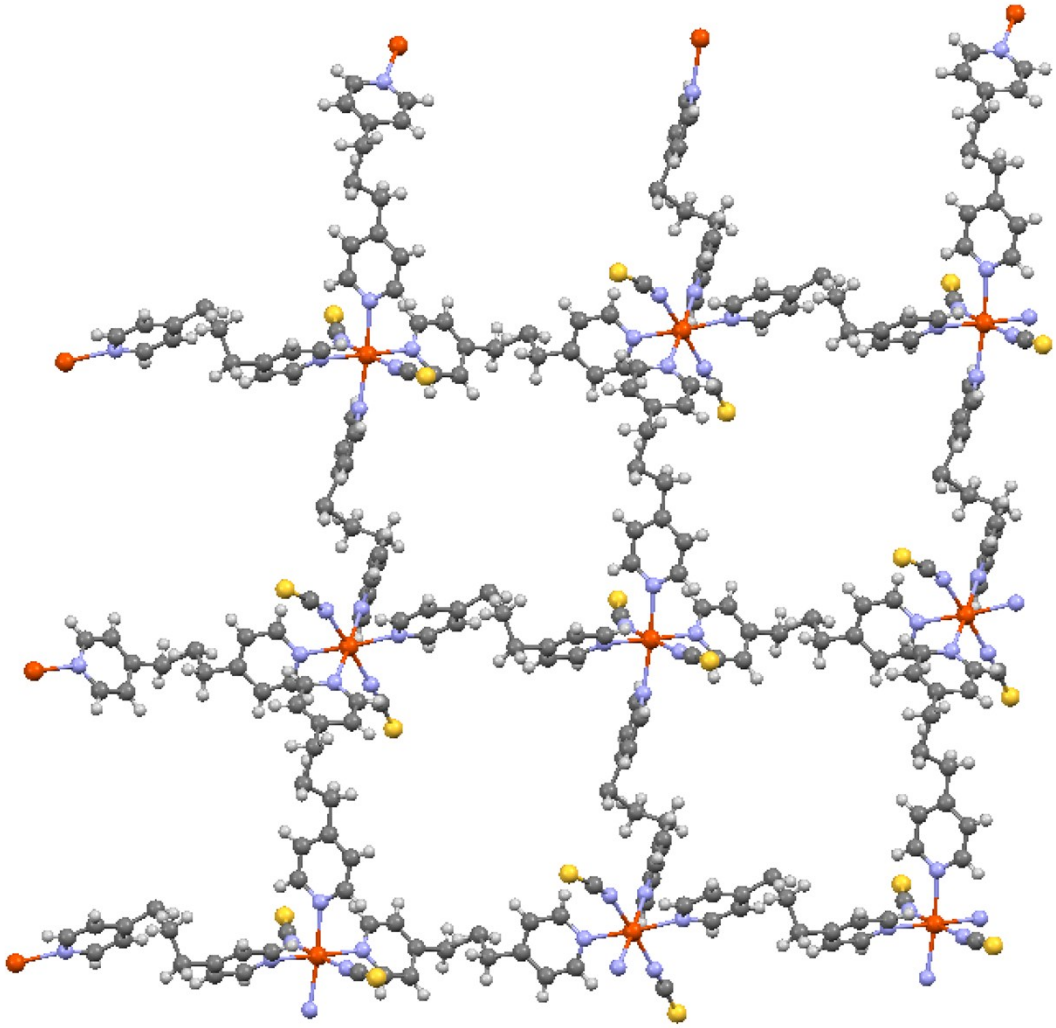

Figure S4. Crystal structure of bulk precursors $[Fe(1,3\text{-bpp})_2(SCN)_2]_2$.

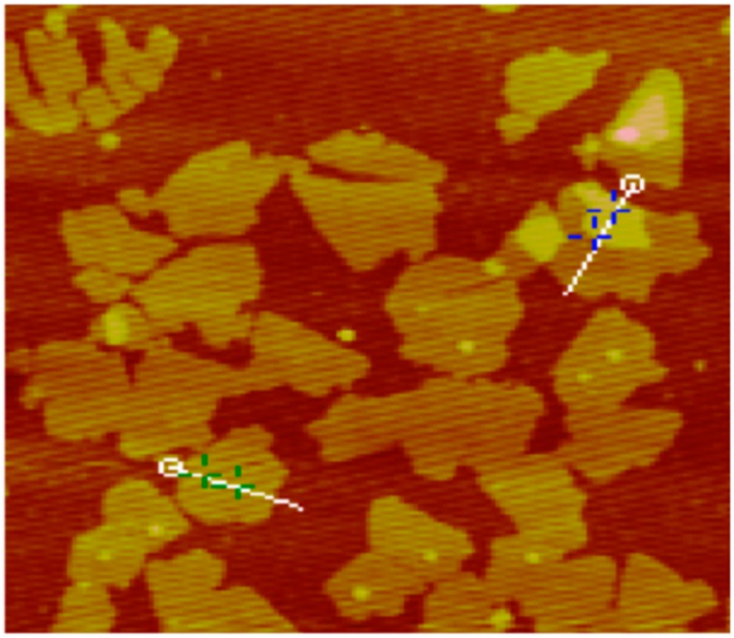

Figure S5. AFM topological image of 2D SCO nanosheets.

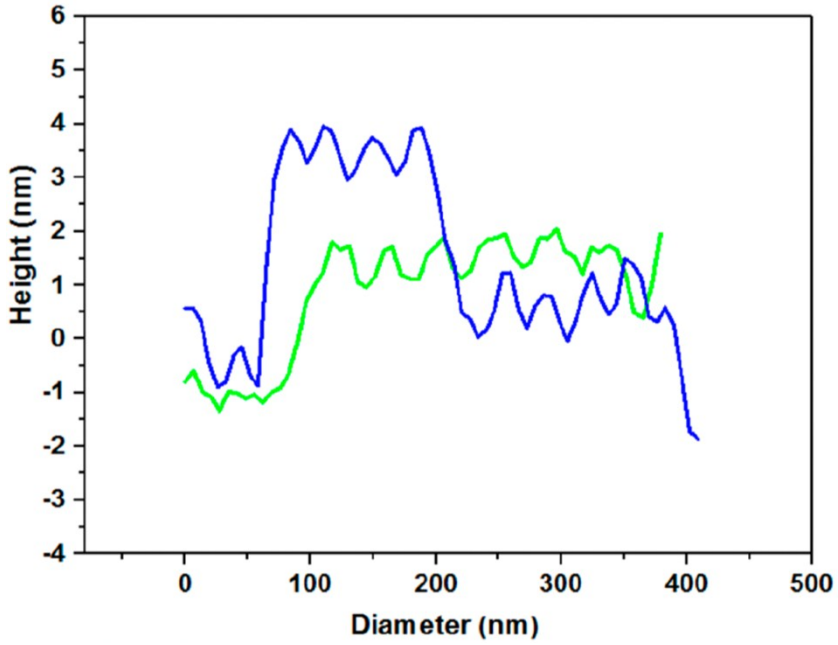

Figure S6. Height profile along the white lines for different regions for AFM topological image in Figure S5.

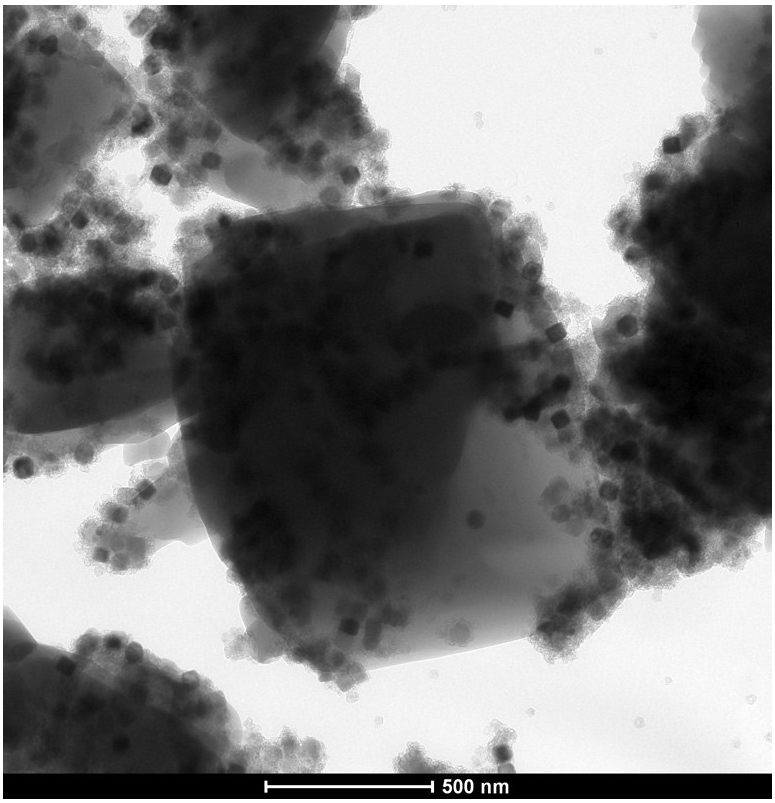

Figure S7. Additional TEM images of **2D@UCNPs** hybrid system.