Supplementary Information

Figure S1A
UV-Vis absorbance of NaY(Yb)F₄:Tm showing absorbance in the 910-1010 nm. Inset: full range scan.

Figure S1B
Effect of Laser excitation wavelength on emission of NaY(Yb)F₄:Tm.
Top: excitation with higher energy than absorbance. The absence of emission at 800 nm indicates that the material does not absorb this energy.
Middle, excitation at the absorbance edge and the simultaneous emission of the upconversion luminescence at 800 nm.
Bottom: excitation with higher wavelength (lower energy) showing no emission. Therefore, upconversion occurs since an 800 nm emission is only observed when exciting the material in the absorbance range. A red filter # KC19 (see methodology section), is used to cut-off any residual light from the excitation below 700 nm. The lines at 546 and 698 cm⁻¹ might be due to other rate earth impurities in Thulium (III) and Yittrium (III) nitrates.

Figure S1C
Optimization of the set up for upconversion emissions of NaY(Yb)F₄:Tm with excitation at 975 nm (+/- 5nm). A fraction of light is converted to the visible (477 nm) and IR (802 nm) light. KC19 (red filter) is used to cut-off any residual light from the excitation source below 700 nm. A blue filter # C3C23 is used to attenuate light above 700 nm. In the figure both excited and emitted lights are collected.
Figure S2
Products during the gas phase photoreaction, in the absence of methanol, under 980 nm excitation on (0.25 wt. % Au/CdS)-(NaYF₄-Yb-Tm) with a 1 to 1 ratio. Methane was not observed during the experimental run, traces of hydrogen were observed and some adventitious CO₂ (did not increase with time) indicating its non-catalytic origin.
Figure SF3 A. STEM-HAADF of NaYF$_4$ (Yb):Tm
Figure SF3 B. STEM-HAADF of NaYF$_4$ (Yb):Tm
Figure SF3 C. HRTEM of NaYF$_4$(Yb):Tm
Figure SF3 D. HRTEM and FFT of Au/CdS nanoparticles
Figure SF4 A. Optical density of the ref filter used during the UC experiments.
Figure SF4 B. Extension coefficient of the blue filter used during the UC experiment.
Methodology

0.538 g of Yttrium (III) nitrate hexahydrate (Sigma Aldrich 99+; rare earth impurities is < 0.25%), 0.260 g of Ytterbium (III) nitrate pentahydrate (Sigma Aldrich 99.999 %) and 0.015 g of Thulium (III) nitrate pentahydrate (Sigma Aldrich 99.9 %; rare earth impurities < 0.15%) were dissolved in 75 mL de-ionized water. 5.777 g of citric acid was dissolved into the pre-mentioned mixture to obtain a concentration of 0.4 M and citric acid to rare earth metal ratio of 4. In a separate flask, 3.78 g of NaF were dissolved in 75 mL of de-ionized water to obtain a 1.2 M concentration. The two mixtures were left under stirring for 1 hour after which, the NaF solution was added to the rare earth metal solution dropwise. After mixing the two solutions, they were left stirring for 30 minutes then transferred into a Teflon-lined autoclave (where only ¾ of the autoclave was filled with solution). The solution was then treated hydrothermally at 180°C for 24 hours. After completion, the product was washed three times with de-ionized water and once with ethanol.

Gold nanorods colloidal suspension is acquired from Sigma Aldrich with a 10 nm diameter and 41 nm in length. Au concentration is estimated to be greater than 30 µg/mL in H₂O. The amount of cetyl trimethylammonium bromide, C₁₉H₄₂NBr (CTAB) ligand on the metal (used to stabilize the nanorods) is estimated to be < 0.1 wt. %. CdS is prepared by precipitation of Na₂S and Cd(NO₃)₂ followed by calcination under inert atmosphere at 600°C for four hours. 0.25 wt. % Au/CdS is made by mixing 120 mg of CdS with 10 mL of gold colloidal suspension and drying at 90°C overnight under stirring.

15 mg of 0.25 wt. % Au nanorods/CdS are mixed with 15 mg of (NaYF₄ – 28mol% Yb – 0.75mol% Tm) and sonicated in ethanol for several minutes. The mixture is then deposited on glass and the solvent dried at 70°C. Inside a 6 mL reactor, one drop of methanol (ca. 0.05 mL) is added along with the coated slide and the reactor is sealed. The catalyst is then excited with ≈ 0.15W at 980 nm (spot size ≈ to 3 mm) light provided from a 100 fs pulsed laser (Coherent), filters were provided from Concept Design Production (CDP) Systems Corp (SF4 contains information related to the filers uSTCD and a Hysep Q column under N₂ carrier gas. The blank experiment (Figure S2) is conducted in the same manner with the exclusion of methanol to eliminate the possibility of ligand (CTAB) contribution.

Raman analysis were performed using a Thermo Scientific™ DXR™. Catalyst samples were analysed from 50 to 3400 cm⁻¹ with multiple scans (16scans) with exposure time of 0.5 seconds, the wavelength of the laser used for the analysis was 532 nm, with the power of 8mW and the spot size was 2.1µm. The aperture opening was 50µm and grating had 900 lines per mm. High-Resolution Transmission Electron Microscopy (HRTEM) was carried out at 200 kV with a JEOL JEM 2100 instrument equipped with a LaB₆ source. The point-to-point resolution of the microscope was 0.19 nm. Samples were deposited on holey-C-coated Cu grids from alcohol suspensions.