Electronic Supplementary Information for:

Spatially confined photoexcitation with triplet-triplet annihilation upconversion

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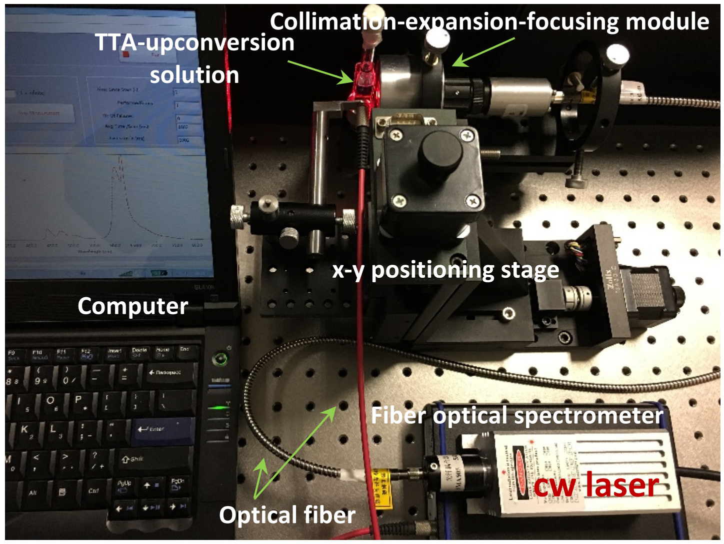

Figure S1. The optical mechanics set up used in the study. The 2D scanning of the fiber against the luminesencing area is performed with an electronic x-y positioning stage, which is controlled by computer.

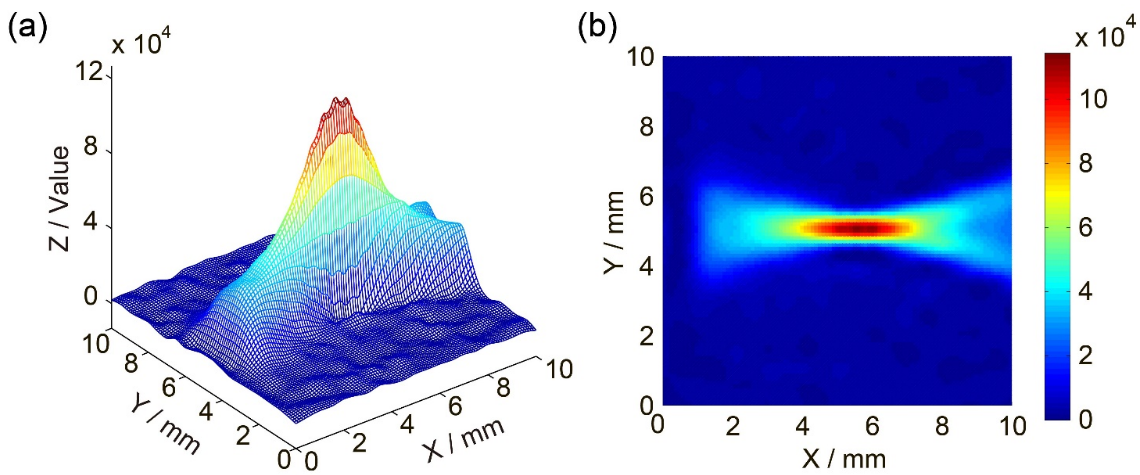

Figure S2. Spatially resolved phosphorescence intensity of **Ru-1,** excited with focusing beam of a cw 532 nm laser, <u>laser power: 0.2 mW</u> (power density at focal point is 30 mW/cm^2). (a) 3D map and (b) 2D map showing the integrated phosphorescence intensity of the range 548 nm – 750 nm of the luminescencing area at different X-Y coordinate position; $c = 1.0 \times 10^{-5}$ M, in deaerated CH_3CN, 20 °C. The results show the spatially resolved excitation is unsatisfactory, as compared to that obtained with the TTA upconversion system (e.g. as compared to Figure 4 in the manuscript).

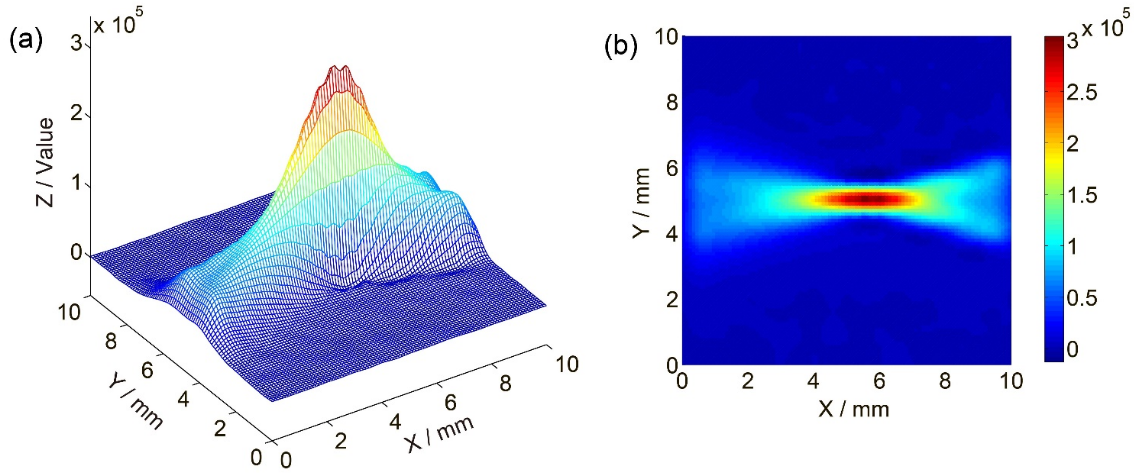

Figure S3. Spatially resolved phosphorescence of **Ru-1,** excited with focusing 532 nm cw green laser, <u>laser power: 1.6 mW</u> (power density at focal point is 0.2 W/cm^2). (a) 3D picture and (b) 2D picture showing the phosphorescence integrated intensity at the range from 550 nm – 750 nm at different X-Y coordinate position; $c = 1.0 \times 10^{-5}$ M, in deaerated CH_3CN, 20 °C. The results show the spatially resolved excitation is unsatisfactory, as compared to the TTA upconversion system.

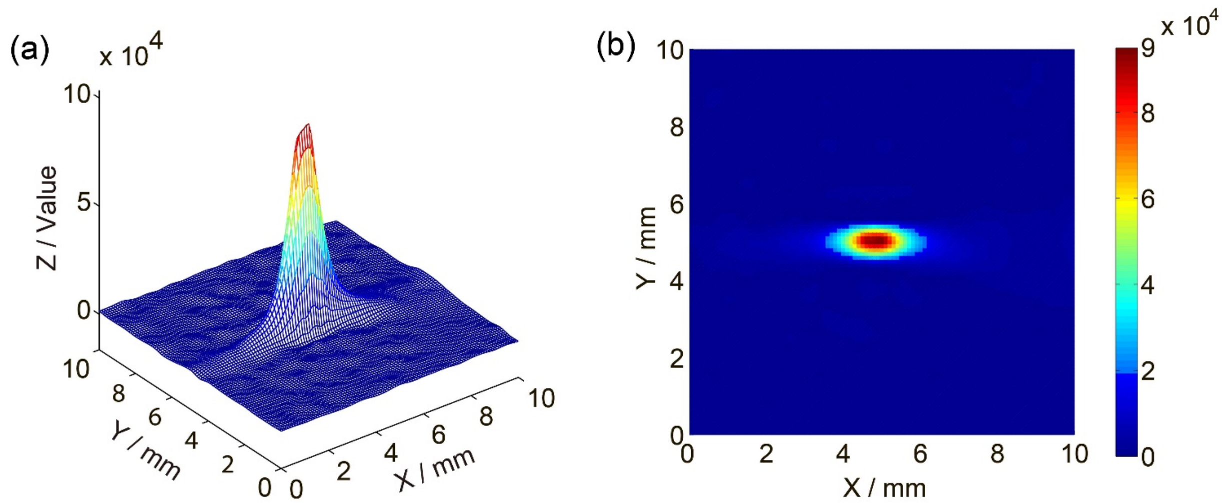

Figure S4. Spatially resolved upconversion intensity with triplet photosensitizer **Ru-2** and triplet acceptor/emitter **DPA,** excited with focusing 532 nm cw green laser, laser power: 2.4 mW (power density at focal point is 0.3 W/cm^2). (a) 3D picture (b) 2D picture reflecting upconversion value (integration at the range from 385 nm to 500 nm) at different X-Y coordinate position; [**Ru-2**] = 1.0×10^{-5} M, [**DPA**] = 4×10^{-5} M, in deaerated CH_3CN, 20 °C. The results show the spatially resolved excitation of the TTA upconversion is satisfactory, as compared to that of **Ru-2** alone (Figure S5 in this ESI file).

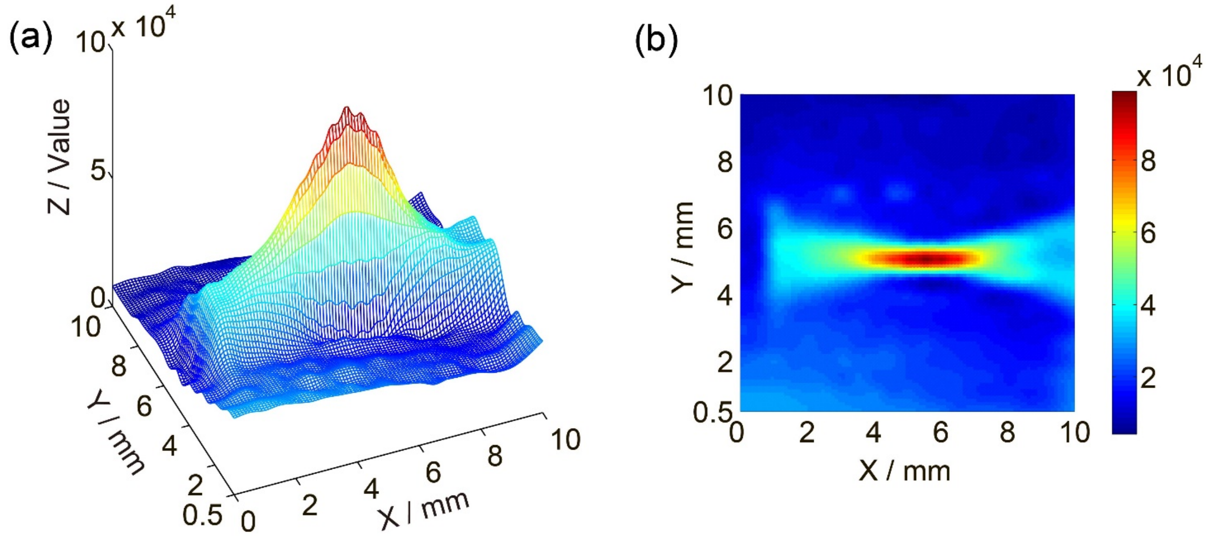

Figure S5. Spatially-resolved phosphorescence intensity of **Ru-2,** excited with focusing 532 nm cw green laser, laser power: 0.05 mW (power density at focal point is 6 mW/cm^2). (a) 3D map and (b) 2D map demonstrating the integrated phosphorescence intensity in the range 548 nm – 710 nm at different X-Y coordinate position. c = 1.0 × 10^{-5} M, in deaerated CH_3CN, 20 °C. The results show the spatially resolved excitation is unsatisfactory, as compared to the TTA upconversion system with **Ru-2** (Figure S4 in this ESI file).

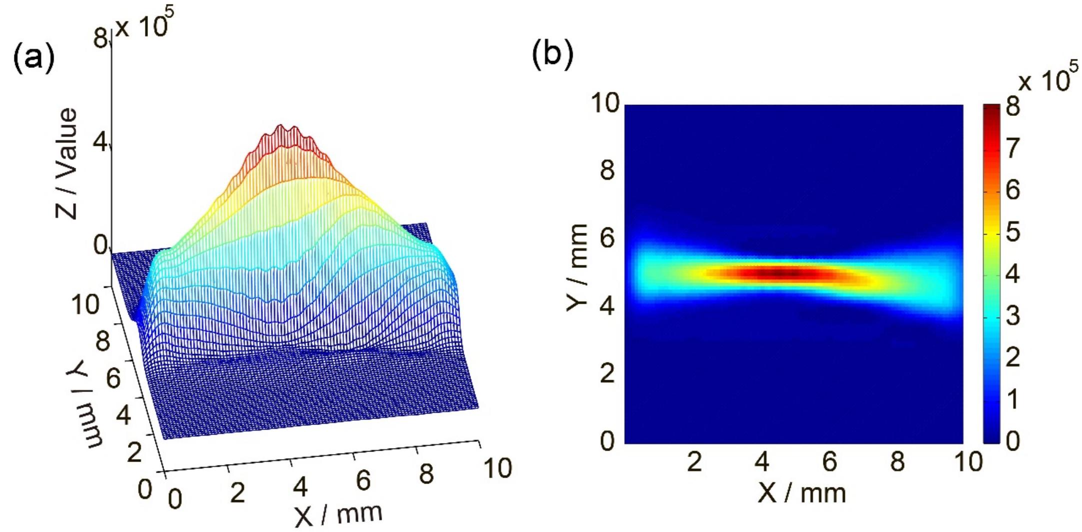

Figure S6. Spatially-resolved phosphorescence intensity of **Ru-2** alone**,** excited with a focusing 532 nm cw laser, laser power: 2.4 mW (power density at focal point is 0.3 W/cm^2). (a) 3D map (b) 2D picture reflecting the integrated phosphorescence intensity in the range of 545 – 800 nm at different X-Y coordinate position; c = 1.0 × 10^{-5} M, in deaerated CH_3CN, 20 °C.

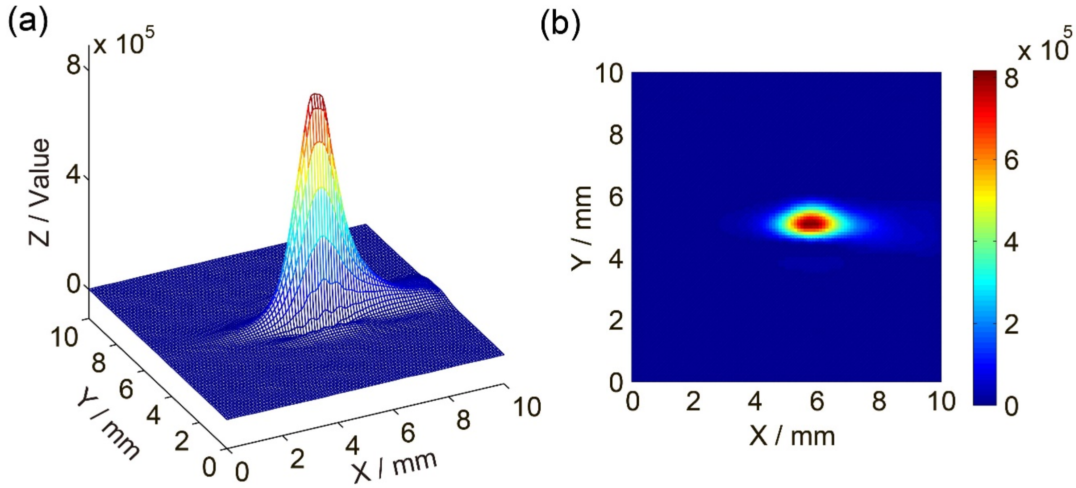

Figure S7. Spatially-resolved integrated upconversion intensity with sensitizer **PtOEP** and triplet acceptor/emitter **DPA,** excited with a focusing 532 nm cw laser, laser power: 0.8 mW (power density at focal point is 0.1 W/cm^2). (a) 3D map (b) 2D map reflecting the integrated upconversion intensity value (integration is in the range 380 nm – 520 nm) at different X-Y coordinate position; [**PtOEP**] = 1.0 × 10^{-5} M, [**DPA**] = 4 × 10^{-5} M, in deaerated ethanol, 20 °C. The results show the spatially resolved excitation of TTA upconversion is satisfactory, as compared to the **PtOEP** alone (Figure S8 in this ESI file).

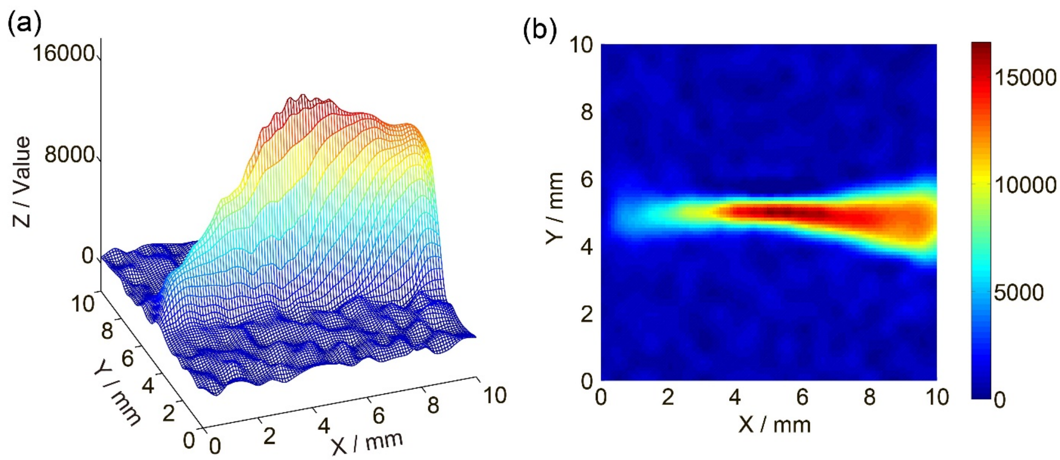

Figure S8. Spatially-resolved integrated phosphorescence intensity of **PtOEP,** excited with a focusing 532 nm cw laser beam, laser power: 0.04 mW (power density at focal point is 0.005 W/cm^2). (a) 3D map and (b) 2D map showing the integrated phosphorescence intensity value (integration in the range from 626 – 687 nm) at different X-Y coordinate position; [**PtOEP**] = 1.0 × 10^{-5} M, in deaerated ethanol, 20 °C. The results show the spatially resolved excitation of **PtOEP** alone is unsatisfactory, as compared to the TTA upconversion system with **PtOEP** (Figure S7 in this ESI file).

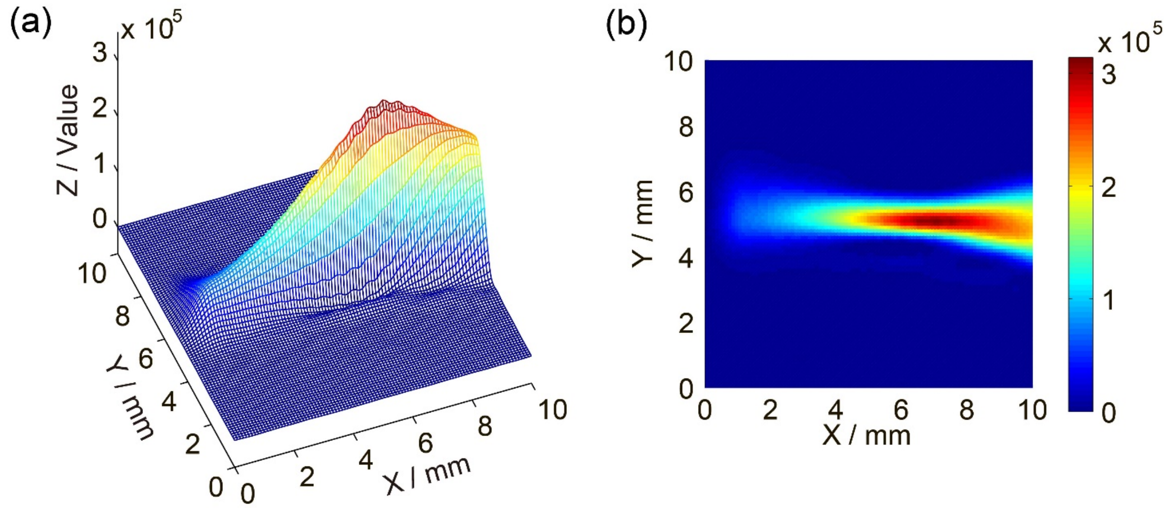

Figure S9. Spatially-resolved integrated phosphorescence intensity of **PtOEP,** excited with 532 nm fiber laser, laser power: 0.8 mW (power density at focal point is 0.1 W/cm^2). (a) 3D map and (b) 2D map showing the integrated phosphorescence intensity value (integration in the range 610 – 740 nm) at different X-Y coordinate position; [**PtOEP**] = 1.0×10^{-5} M, in deaerated ethanol, 20 °C.

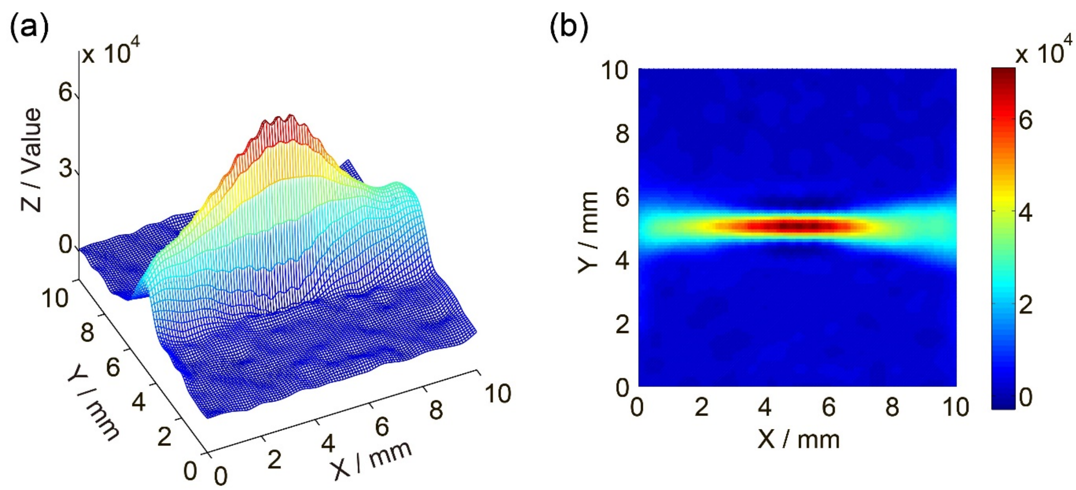

Figure S10. Spatially-resolved integrated fluorescence intensity of **BDP,** excited with a focusing 532 nm cw laser, laser power: 0.05 mW (power density at focal point is 6 mW/cm^2). (a) 3D map and (b) 2D map showing the integrated fluorescence intensity in the range from 483 nm – 600 nm at different X-Y coordinate position; $c = 1.0 \times 10^{-5}$ M, in toluene, 20 °C.

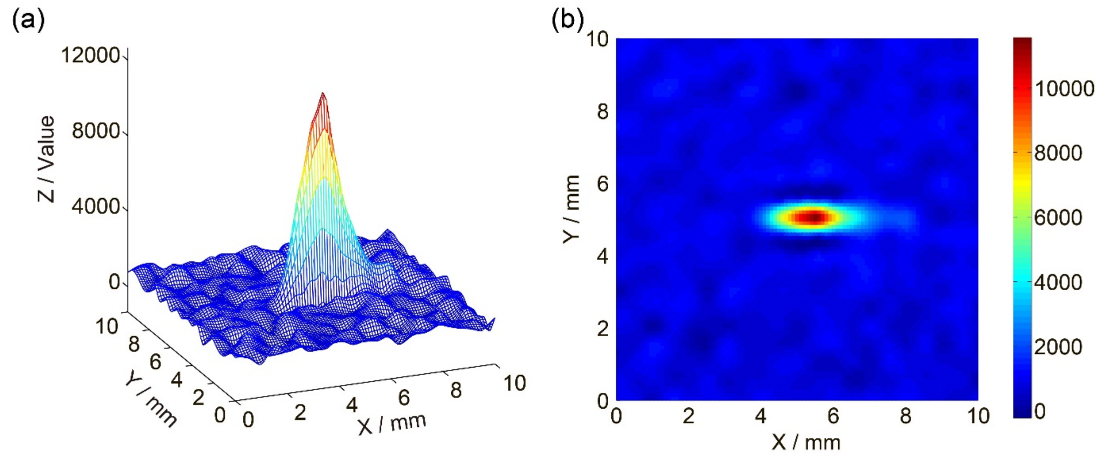

Figure S11. Spatially-resolved integrated upconversion intensity with sensitizer **IBDP-IBDP** and triplet acceptor/emitter **Perylene,** excited with a focusing 635 nm cw laser, laser power: 0.3 mW (power density at focal point is 0.04 W/cm^2). (a) 3D map and (b) 2D map showing the integrated upconversion intensity value (integration is in the range 428 nm – 528 nm) at different X-Y coordinate position; [**IBDP-IBDP**] = 1.0×10^{-6} M, [**Perylene**] = 1×10^{-5} M, in deaerated toluene, 20 °C. The results show the spatially resolved excitation of the TTA upconversion system with **IBDP-IBDP** is satisfactory, as compared to the excitation of **IBDP-IBDP** alone (Figure S12 in this ESI file).

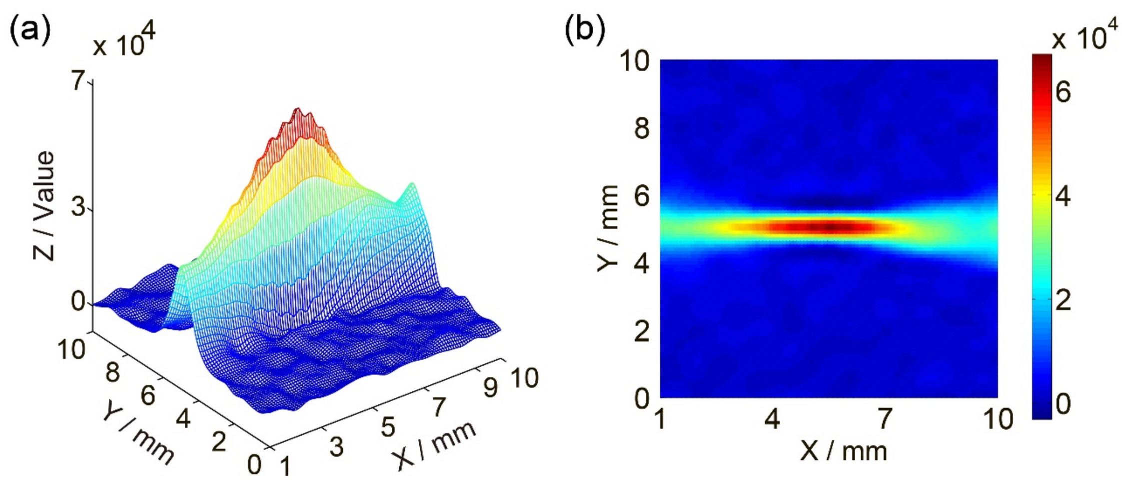

Figure S12. Spatially-resolved integrated fluorescence intensity of **IBDP-IBDP,** excited with a focusing 635 nm cw laser, laser power: 0.01 mW (power density at focal point is 0.001 W/cm^2). (a) 3D map and (b) 2D map showing the integrated fluorescence intensity in the range from 550 nm – 800 nm at different X-Y coordinate position; $c = 1.0 \times 10^{-6}$ M, in toluene, 20 °C. The results show the spatially resolved excitation of **IBDP-IBDP** alone is unsatisfactory, as compared to the TTA upconversion system with **IBDP-IBDP** (Figure S11 in this ESI file).

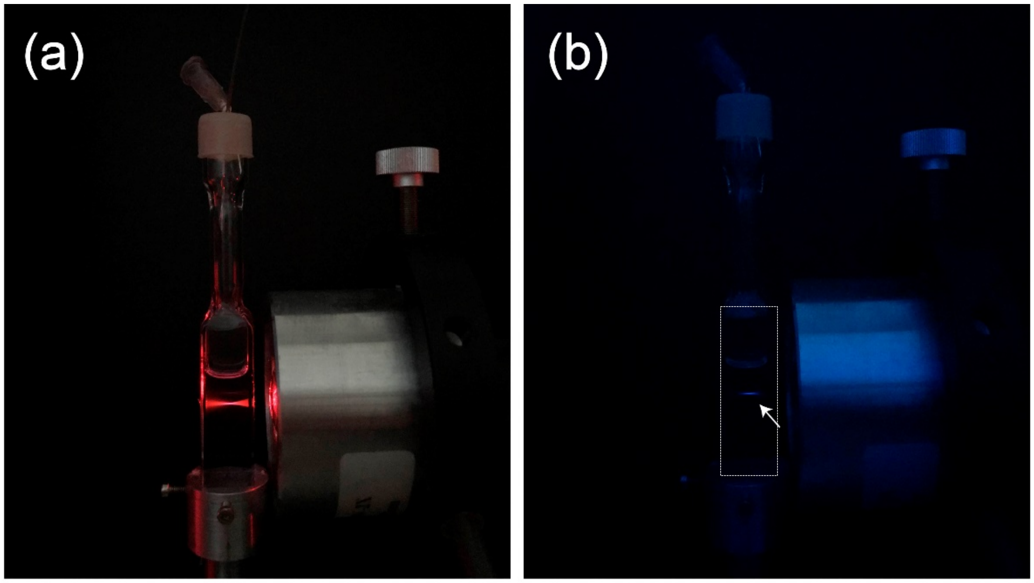

Figure S13. Photographs of the TTA-UC with [**IBDP-IBDP**] = 1 × 10^{-5} M, [**Perylene**] = 1 × 10^{-4} M, excited with 635 nm red laser, laser power: 0.3 mW (power density at focal point is 0.04 W/cm^2). (a) The photograph was taken without any filter; (b) taken with 400–520 nm bandpass filter. The dotted line frame shows the position of the cuvette. The blue TTA upconverted light at the focusing point is indicated by the arrow.

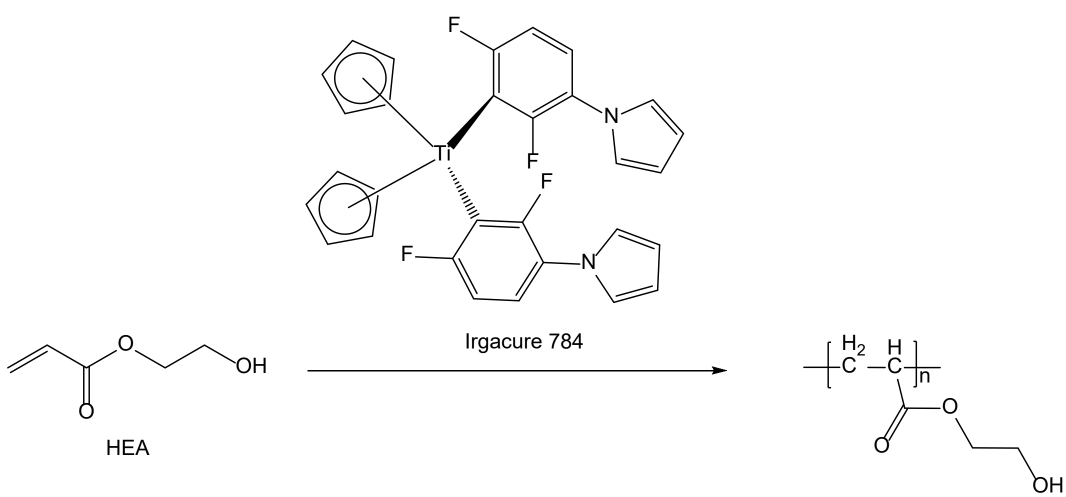

Figure S14. PhotoPolymerization reaction of 2-hydroxylethyl acrylate (HEA) with photoinitiator (Irgacure 784).

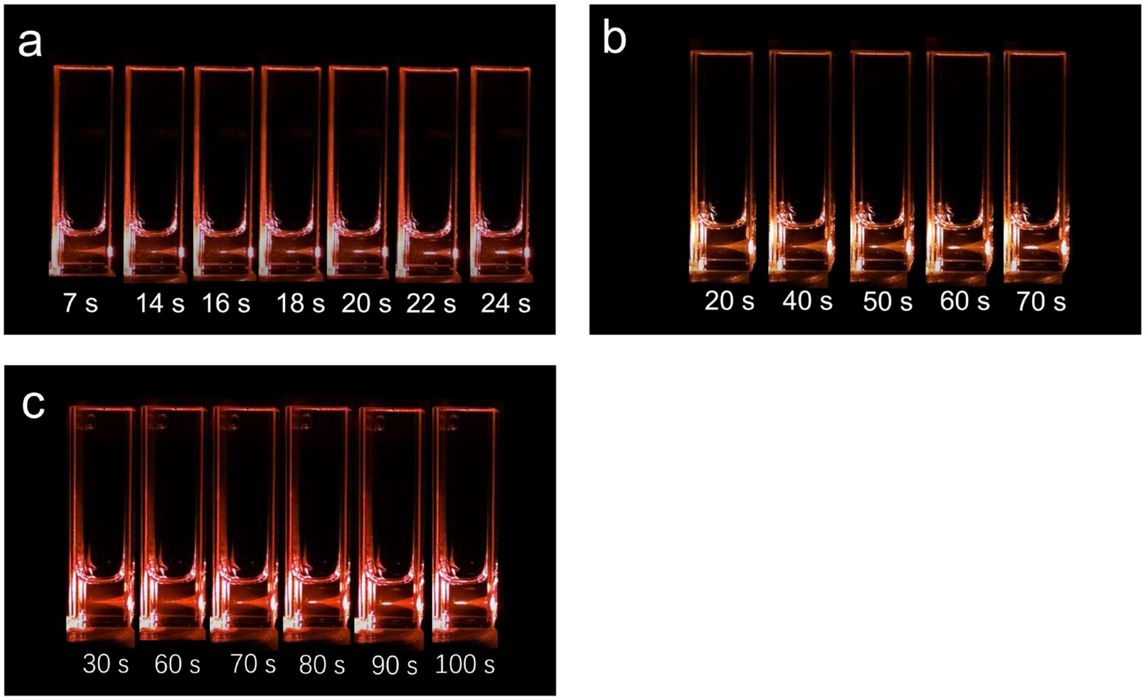

Figure S15. Photographs of TTA upconversion-driving nanomicell-based localized photoexcitation /spatially confined photopolymerization (the bright spot is the polymer thread formed by the localized photopolymerization) at different irradiation time under different laser power densities. Laser power densities at focal point are (a) 0.41 W/cm^2, (b) 0.26 W/cm^2, and (c) 0.15 W/cm^2, and the photopolymerization at different irradiation time. The irradiation time for generating ca. 1 mm length polymer thread are ca. 3 s, 6 s, and 9 s, respectively. TTA-upconversion system: [**IBDP-IBDP**] = 1.0×10^{-5} M, [**Perylene**] = 1.0×10^{-4} M; Photopolymerization system: Monomer: 2-hydroxylethyl acrylate (HEA); Photoinitiator: Irgacure 784, irradiated with 635 nm laser.

Methods

In the optical setup depicted in Fig. 1, the output beam of the low power, continuous wave (cw) diode pumped solid state laser (VD-IIIA DPSSL, Xi'an Minghui Optoelectronics Technology Co., LTD, China) was coupled into a collimating-beam expanding-focusing assembly, the focusing laser beam is with a focal distance of ca. 11.5 mm and the beam diameter entering the cuvette is ca. 4 mm, the focusing of the laser beam is achieved in the middle of the 1 cm cuvetter. A fiber optic spectrometer (AvaSpec-ULS2048L-USB2, Avantes, Netherlands) was used for recorded the spatially resolved emission spectra. The emission was collected with the optical fiber (diameter of 0.6 mm), and the scanning of the X,Y plane was carried out with a motorized two dimensional positioning stage (with precision of 0.625 μm, TSA30-C, Zolix, China). Normally a 21 × 21 data matrix for an area of 10 × 10 mm were collected for every experiment. The spatially resolved spectra were collected by positioning of the optical fiber, which is connected with the optical fiber spectrometer, with the 2D positioning stage. The control of the optical mechanics setup, the collection of the spatially-resolved spectra were implemented with a software developed based on Labview. The spectral data were processed with software of Labview, Origin 5.0 and MATLAB R2014a. The photographs of the upconversion were taken with a Samsung NV 5 CCD digital camera (Samsung Ltd., South Korea), and the 3D graphs showing the emission intensity of the photographs was processed with MATLAB R2014a.

Preparation of the nanomicelles: The preparation of the nanomicells is according to the literature [*Adv. Funct. Mater.*, **2016**, *26*, 8447–8454]. The **IBDP-IBDP** and **Perylene** were dissolved in 4 mL THF solution (*c*[**IBDP-IBDP**] = 1×10^{-5} M, *c*[**Perylene**] = 1×10^{-4} M). Then Kolliphor EL (0.32 mL) and 1,2-propanediol (0.1 mL) were added to the starting THF solution. The obtained mixture was sonicated for 30 minutes. THF was removed under reduced pressure, then deionized water (2 mL) was added to obtain the nanomicell mother solution.

Preparation of the nanomicelle photopolymerization solution: For each measurement, Irgacure 784 (2 mg) was added into 0.5 mL HEA (heating with dryer to fully solubilized it), then nanomicell mother solution (0.5 mL) was added. The mixture was filtered out by Syringe-driven Filter (Nylon, 0.22 μm) to obtain the clear and transparent nanomicelle photopolymerization solution for measurement.