Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Time–Oxygen & Light Indicating *via* Photooxidation Mediated Upconversion

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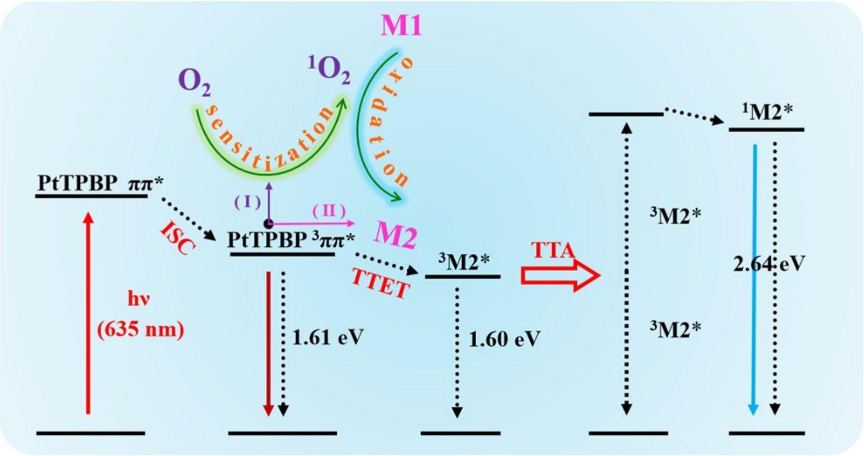


Scheme S1. The underlying process for the photoactivated TTA-upconversion. In the beginning, M1 & PtTPBP comprises a stealth upconversion system because M1 is nonluminous. In the subsequent photoactivation process (path I), O_2 is sensitized by the triplet sensitizer PtTPBP, and $^1O_2$ is formed and captured by M1 to produce M2. M1 acts as an internal reductant that depletes oxygen species and protects the generated M2 from further photooxidation. Then, TTET (path II) and TTA process are able to proceed. Consequently, efficient upconversion emission from M2 & PtTPBP is switched on in situ without additional deaeration. TTET: triplet-triplet energy transfer. TTA: triplet-triplet annihilation.

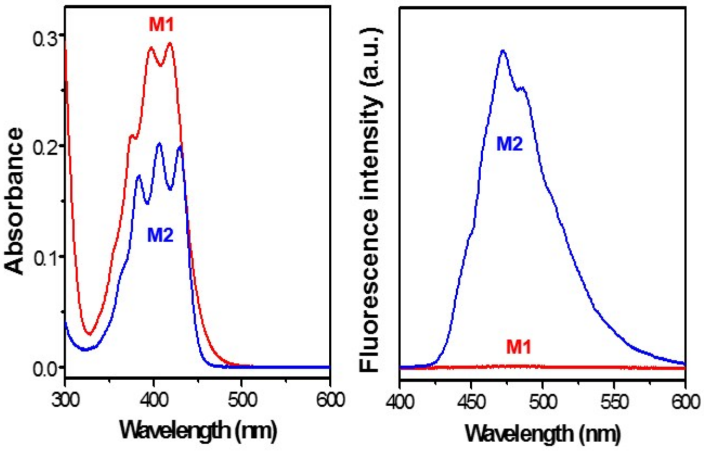


Figure S1. UV-vis absorption spectra (left) and fluorescent emission spectra (right, λ_{ex} = 380 nm) of M1 (1 μM) or M2 (1 μM) in toluene.

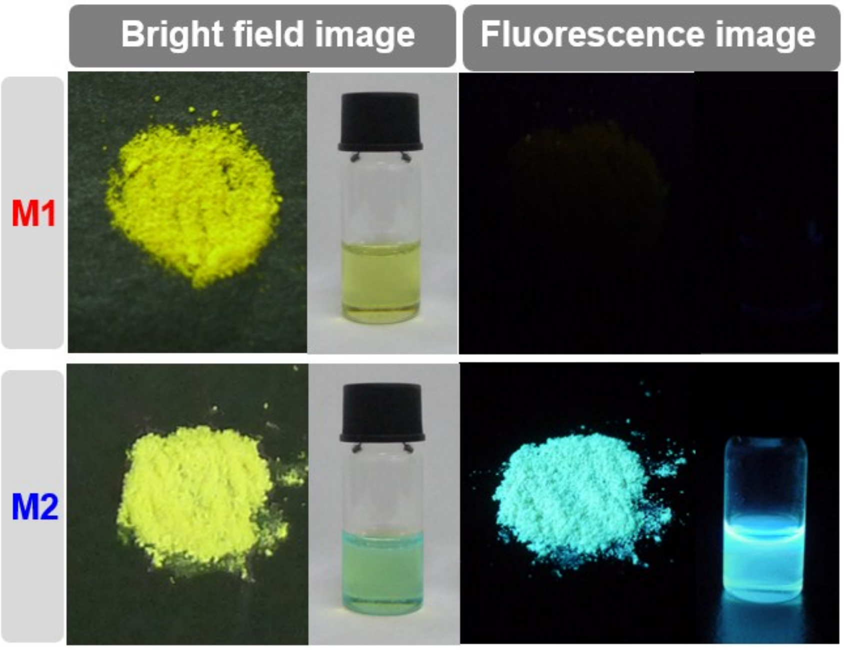


Figure S2. Photographs of bright-field imaging and fluorescent imaging of M1 and M2 in toluene solution (Concentration: [M1] = 10 μM; [M2] = 10 μM) and in powder. A 365 nm ultraviolet lamp was used as excitation source for the fluorescence imaging.

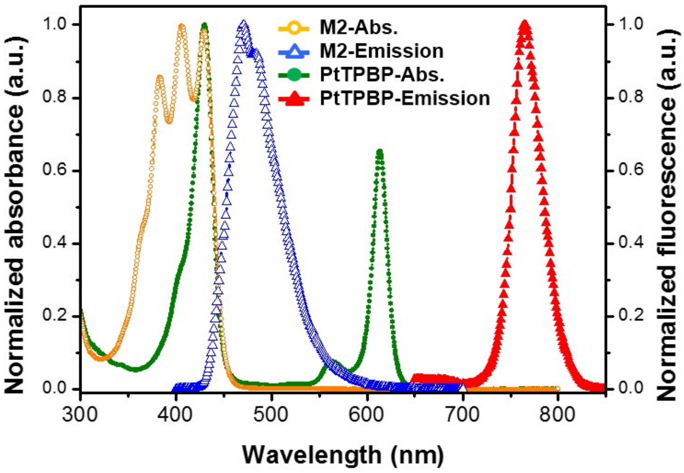


Figure S3. Absorbance spectra (circle) and fluorescent emission spectra (triangle) of M2 (hollow) and PtTPBP (solid) in toluene. All are normalized to an arbitrary maximum of 1.

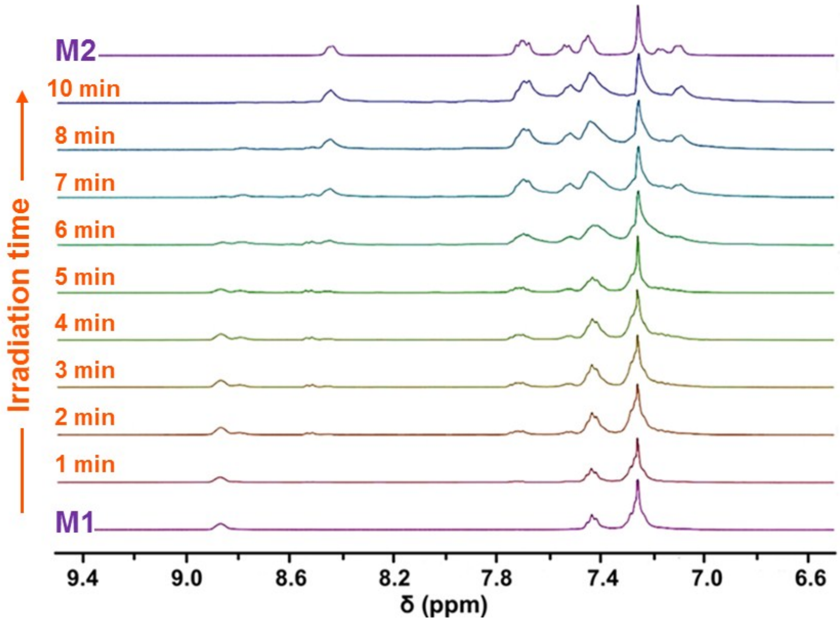


Figure S4. Change in ^{1}H NMR spectroscopy of the couple system M1 & PtTPBP in $CDCl_3$ solution under irradiation with 635 nm laser at the power density of 100 mW cm^{-2}. (Concentration: [M1] = 11.0 mM, [PtTPBP] = 2.0 mM). Herein, ^{1}H NMR spectroscopies of the pure compounds M1 and M2 (as standards for reference) were also shown. Time-courses of the reaction process monitored by ^{1}H NMR spectroscopies confirmed the success conversion of M1-to-M2 in the presence of PtTPBP and 635 nm laser in air-saturated solution.

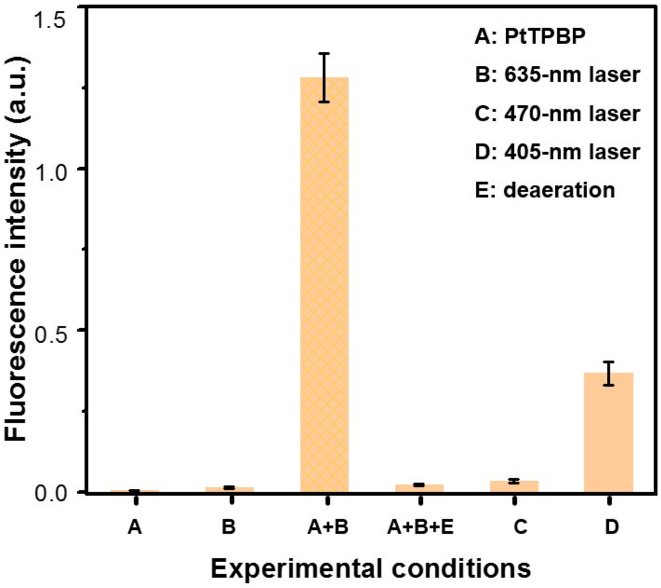


Figure S5. Comparison of fluorescent intensities of M1 (30 μM) in different conditions (A: in the presence of 0.1 μM PtTPBP as the sensitizer; B: under irradiation at 635 nm laser for 1 h; E: under deaeration condition by Ar degassing; C: under irradiation at 470 nm laser for 1 h; D: under irradiation at 405 nm laser for 1 h). All of excitation power density of 635 nm, 470 nm or 405 nm laser was fixed at 5 mW cm^{-2}. After oxidation processes, the fluorescent spectra of all the samples were recorded on fluorescent spectrometer with excitation wavelength at 380 nm. And the fluorescent intensities at 470 nm were used for comparison.

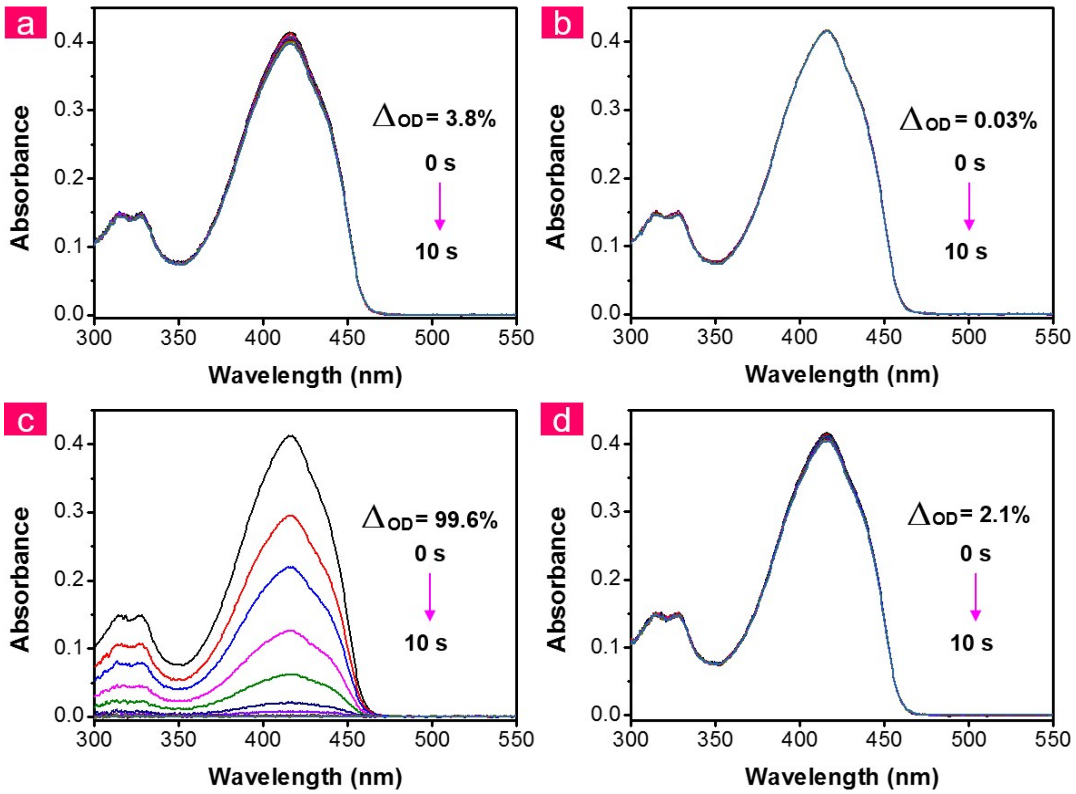
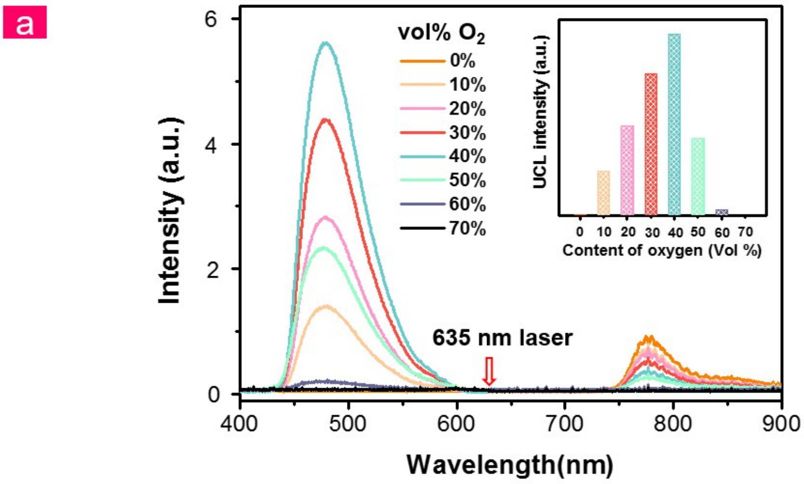
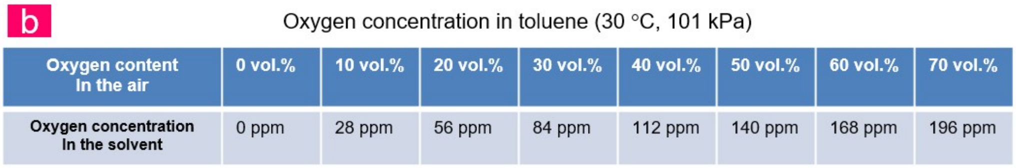


Figure S6. Simulation tests of the different photooxidiation reaction rate using DPBF as indicating molecules. Sensitizer PtTPBP and correlative 635 nm laser were used. The absorption of PtTPBP was deducted from the spectra. And absorption in 415 nm decreased with the oxidiation of DPBF. (a) Concentration of DPBF and PtTPBP were 2×10^{-4} M and 1×10^{-7} M, respectively. And power density of 635 nm laser was fixed at 5 mW cm^{-2}. (c) Concentration of DPBF and PtTPBP were 2×10^{-4} M and 1×10^{-5} M, respectively. And power density of 635 nm laser was fixed at 100 mW cm^{-2}. (b) and (d) DPBF alone was irradiated with 635 nm laser. And power density of laser was fixed at 5 and 100 mW cm^{-2}, respectively.





Oxygen concentration in toluene (30 °C, 101 kPa)

Oxygen content In the air	0 vol.%	10 vol.%	20 vol.%	30 vol.%	40 vol.%	50 vol.%	60 vol.%	70 vol.%
Oxygen concentration In the solvent	0 ppm	28 ppm	56 ppm	84 ppm	112 ppm	140 ppm	168 ppm	196 ppm

Figure S7. (a) Emission spectra of the toluene solution containing the couple system of M1 & PtTPBP (Concentrations: [M1] = 1.5 mM, [PtTPBP] = 10 μM) under 635 nm irradiation (100 mW cm^{-2}) in different mixture atmosphere with content of O_2 in the range of 0 ~ 70 Vol.%. Inset: changes in upconversion luminescence (UCL) intensities. All the samples were put in the specific gas filled chamber for 1 hour to reach gas diffusion equilibrium. The spectra were directly measured after laser irradiation for 10 seconds. (b) The oxygen content in the atmosphere and correlative oxygen concentration in the solvent. 1 ppm = 1 mg L^{-1}.

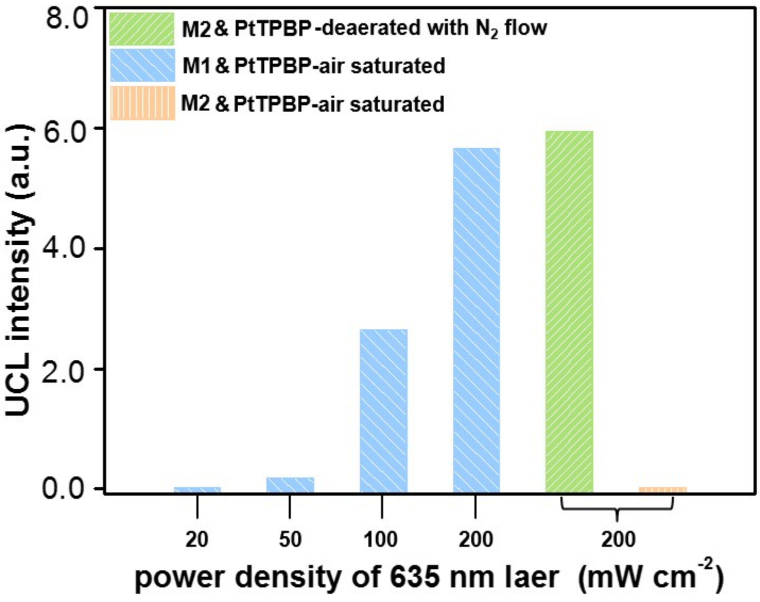


Figure S8. Comparison of upconversion luminescence (UCL) intensities of M1 & PtTPBP in air-saturated toluene (blue), M2 & PtTPBP in air-saturated toluene (yellow) and M2 & PtTPBP deaerated with N_2 flow (green, as a reference), under 635 nm irradiation with different power density for 20 s. Concentrations of M1, M2 and PtTPBP in toluene solution are 1.5 mM, 1.5 mM and 10 μM, respectively.

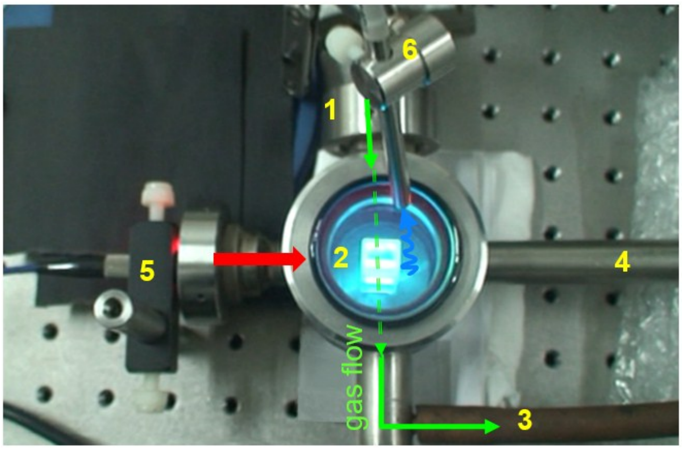


Figure S9. Photograph of the setup for upconversion luminescence (UCL) measurement system. O_2 and N_2 with proportional flow are blended in advance. The mixture atmosphere aerates into the setup from passage ***1***, passes through chamber ***2***, and then exhausts from passage ***3*** that is connected to a bottle of saturated salt solution. ***1*** and ***3*** are equipped with valves to tune the flow and a pressure gauge is installed at the end of passage ***4***. The top of the chamber is transparent and is covered with a short-pass filter (edge wavelength at 628.5 nm, Semrock). 635 nm laser is fixed closed to the transparent end of passage ***5***. The sample in chamber is irradiated by 635 nm laser, and UCL emission is detected by a fiber optic spectrometer (***6***). The percentages of oxygen in gas mixture could be regulated to a desired composition through carefully adjustment of flow-control valves ***1*** and ***3*** while keeping the pressure constant. All the samples were put in the specific gases composed of O_2 and N_2 filled chamber for 1 hour to reach gas diffusion equilibrium.

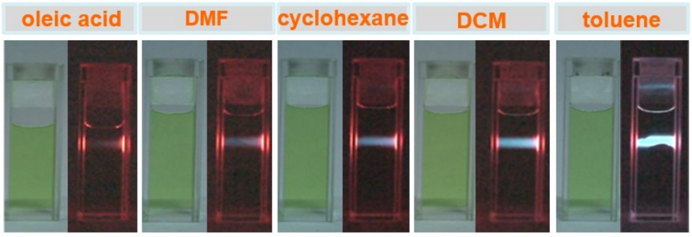


Figure S10. The photos of photooxidation-induced upconversion emission images (right) and their corresponding bright-field images (left) of the couple system M1 & PtTPBP (concentration: [M1] = 1 mM, [PtTPBP] = 10 μM) in the several solvents, under 635 nm irradiation (100 mW cm^{-2}) for 10 seconds. A short-pass filter (edge wavelength at 628.5 nm) was used to cut off the excitation light. The different solvents include oleic acid, *N*,*N*-dimethylformamide (DMF), cyclohexane, dichloromethane (DCM) and toluene, respectively.

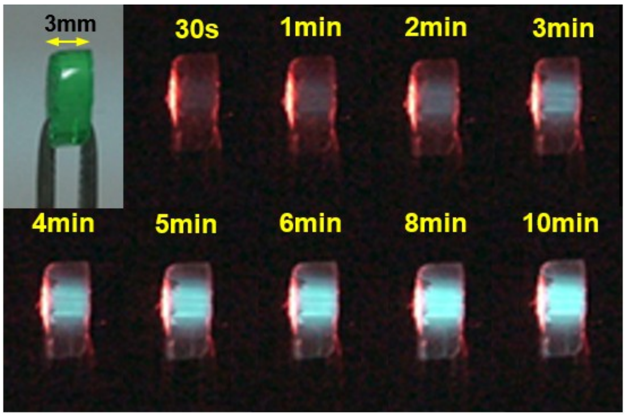


Figure S11. Photos show time-course of photooxidation-induced upconversion emission images of the M1 & PtTPBP system in polyurethane matrix, under 635 nm irradiation within 10 minutes. Power density of 635 nm laser was fixed at 200 mW cm^{-2}. A short-pass filter (edge wavelength at 628.5 nm) was used to cut off the excitation light.

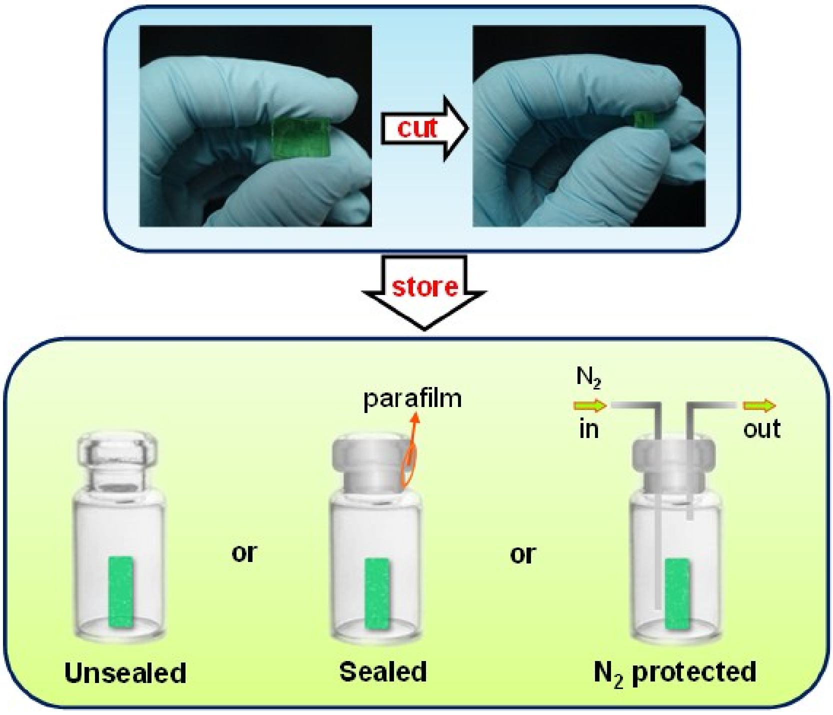
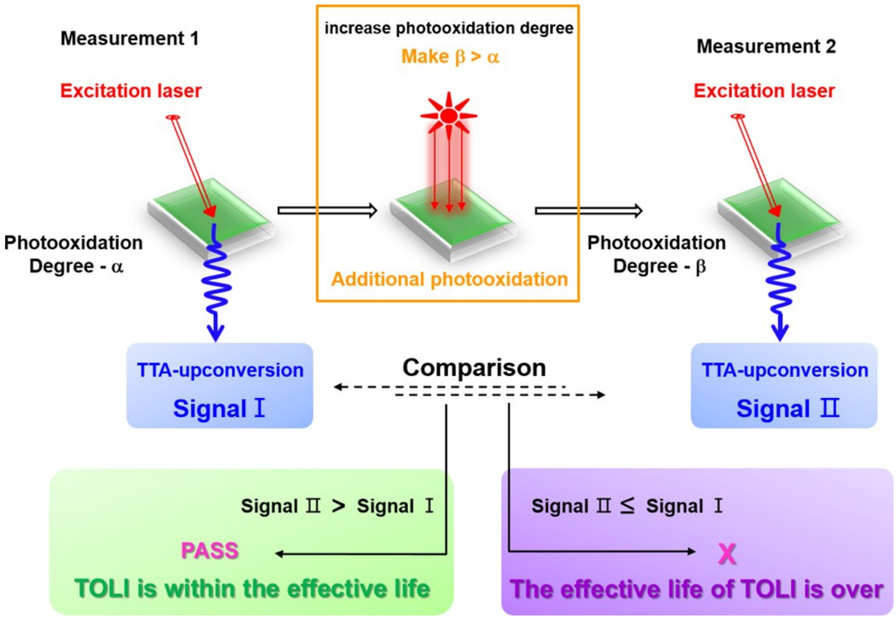


Figure S12. The time–oxygen & light indicator (TOLI) in different storage conditions for photoactivated upconversion emission measurement. For the storage condition **I**, the bottles were sealed and stored in darkness. For storage condition **II**, condition **III** and condition **IV**, the bottles were stored under indoor light, keeping sealed, unsealed and protected with N_2 atmosphere, respectively. For storage condition **V**, the bottles were filled with N_2 protection atmosphere and stored under outdoor sunlight. For storage condition **VI**, the bottles were stored under outdoor sunlight, keeping unsealed. A 635 nm laser fixed at 200 mW cm^{-2} was used as excitation source, and the UCL intensity was measured with the fiber optic spectrometer. Before storage, some of the bottles were unsealed (the oxygen concentration is ~300 ppm) while the other were sealed with parafilm or filled with N_2 atmosphere (the oxygen concentration is measured to be ~1 ppm). The TOLIs containing M1 & PtTPBP were prepared from the same polyurethane film (3 mm in thickness).



Scheme S2. Illustration of the test program for ascertaining the photooxidation state of TOLI accurately. Similar to the shelf-life of a product, the effective life of a TOLI is defined to mean the period of arriving at the maximum UCL signal. The photooxidation-based deterioration process is indicated with upconversion signals. And there is a negative correlation between the upconversion intensity and product quality when the TOLI is still within its effective life. This method is used to confirm whether the TOLI is still within its effective life. The photooxidation state of TOLI is judged from comparison of two successive measurements. An upward trend between the measured UCL intensities indicates that the TOLI is still within its effective life. Otherwise, the effective life of TOLI is over.

Other supplementary materials.

Movies 1 and Movies 2.

Moviel: Upconversion performance of the toluene solutions containing M1 & PtTPBP and M2 & PtTPBP, respectively. M2 & PtTPBP and M1 & PtTPBP in air-saturated toluene were filled in two open quartz cuvettes, respectively. Power density of 635 nm laser was fixed at 100 mW cm^{-2}. Laser light passes through M2 & PtTPBP solution in the left and then irradiate M1 & PtTPBP in the right. Concentrations of M1, M2 and PtTPBP were 1.5 mM, 1.5 mM and 10 μM, respectively.

Movie2: Upconversion performance of 3 mm thick polyurethane containing M1 & PtTPBP. The film was irradiated with 635 nm laser (200 mW cm^{-2}) for 10 min. A short-pass filter (edge wavelength at 628.5 nm) was used to cut off the laser light. Ten times faster playback speed was used to show the phenomenon more obviously.