Near Infrared Light-driven Water Oxidation in a Molecule-based Artificial Photosynthetic Device Using an Upconversion Nanophotosensitizer

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Experimental Section

Preparation and Characterization of the UCNPs and UCNPs/Pt(II)-TCPP nanophotosensitizer:

In a typical procedure of the synthesis of $NaYF_4$: Yb/Er nanoparticles, $LnCl_3$ (0.118 g $YCl_3•6H_2O$, 0.038 g $YbCl_3•6H_2O$, 0.0038 g $ErCl_3•6H_2O$) was added to a 50mL flask containing 3 mL of oleylamine and 7mL 1-octadecene. The mixture was heated at 150 °C for 30 min to remove the water from the $LnCl_3•xH_2O$. After cooling down to 50 °C, 5 mL of a methanol solution containing NH_4F(1.36 mmol) and NaOH (1 mmol) was added and the resultant solution was stirred for 30 min. After the methanol was evaporated, the solution was heated to 305 °C under argon for 1.5 h and then cooled down to room temperature. The resulting nanoparticles (yield 65 mg) were precipitated by addition of ethanol, collected by centrifugation at 6000 rpm for 5 min, washed with ethanol several times, and re-dispersed in 6 mL of cyclohexane.

The ligand exchange process was carried out to transfer hydrophobic upconversion nanoparticles into hydrophilic ones using poly(allylamine) as ligand. A poly(allylamine) solution in water (20%, 0.1 mL) was dispersed in 10 mL ethanol. The hydrophobic UCNPs solution (~5mg, purified and dispersed in 2mL of cyclohexane) were mixed with the poly(allylamine) solution and stirred vigorously over 24 h at 30 °C. After centrifugation, the obtained nanoparticles were redispersed in water. After phase transfer, the poly(allylamine) terminated UCNPs give amino group at the end which can be used for covalently coupling with carboxyl ended molecules.

To covalently conjugate Pt(II)-TCPP to UCNPs, 5mL of dimethylformamide (Sigma-Aldrich) solution containing 0.5 mg of Pt(II)-TCPP, 1 mg of 1-ethyl-3-(3-dimethyl- aminopropyl)carbodiimide (Sigma-Aldrich), and 1 mg of N-hydroxysulfosuccinimide sodium salt (Sigma-Aldrich) was incubated at room temperature for 2 h, and then 0.5 mg of amino-functionalized UCNPs (centrifuged from water solution) was added into the solution and stirred vigorously for 24 h. UCNPs/Pt(II)-TCPP conjugates were then centrifuged and washed with water to remove any unreacted Pt(II)-TCPP. The amount of Pt(II)-TCPP attached to UCNPs was calculated from the Pt(II)-TCPP absorption spectrum.

Characterization:

The structure and morphology of the nanoparticles were characterized by using a Bruker D8-advance X-ray diffractometer (XRD) with Cu Ka radiation (λ = 1.5418 Å). The transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN D573 electron microscope operated at 300 kV. The dynamic light scatting was performed on a Malvern Zetasizer Nano ZS90. UV/Vis absorption spectra were measured on a Hewlett-Packard/Agilent 8453 Diode-Array UV-Vis Spectrophotometer using 10 mm path-length quartz cuvettes. Steady-state emission spectra were measured on a SpexFluorolog 3 spectrometer, equipped with double grating monochromators. The excitation light source was a CW semiconductor diode laser at 980 nm and the detector a Peltier cooled R636-10(Hamamatsu) photomultiplier tube. The emission spectra were corrected for the wavelength response of the detection system. Time-resolved luminescence of UCNPs/Pt(II)-TCPP nanophotosensitizer solutions was measured with a HamamatsuR9110 PMT in a single-photon counting setup (Fast Comtec). For excitation a 980 nm laser pulse (~10 ns, 100 Hz) generated by a Nd:YAG laser system (Solar Inc.) was used. The diameter of the irradiated area is restricted by focal lenses to ~ 50 μm.

Light driven oxygen evolution measurements:

The photocatalytic oxygen evolution was monitored by means of a Clark-type oxygen electrode sensor (Hansatech Instruments, DW2/2 unit with an S1 electrode). A CW 532 nm green laser (Changchun New Industries, CNI model with PSU-H-LED) or a CW semiconductor diode laser of 980 nm was used as the illumination light source. The laser power was varied, and was measured using a power meter (Coherent). The reaction vessel was cooled with flowing water adjusted to T = 20 °C. The signal was calibrated using air saturated aqueous solutions ($[O_2]$ = 276.3 μM, T = 20 °C) and N_2-purged solutions ($[O_2] \approx 0$). In each measurement, the photocatalytic mixture solution was first purged with N_2 to provide an oxygen-free solution. In order to confirm the oxygen generation resulting from light driven water oxidation, the illumination by laser starts after ~2 minutes of flat zero $[O_2]$ signal in dark. The maximum turnover frequency (TOF_{max}) was determined at the steepest slope of the oxygen evolution curve.

Quantum yield determination under 980 nm laser excitation

The light-driven water oxidation reaction with UCNPs/PtTCPP as photosensitizer and persulfate as sacrificial electron acceptor is expressed below and the indirectly photoexcited Pt-TCPP on UCNPs/PtTCPP is denoted by Pt(II)-TCPP*. The Pt(III)-TCPP means the radical cation of Pt-porphyrin.

$$\begin{array}{l}
\text{Pt(II)-TCPP}^{*} + S_2O_8^{2-} \longrightarrow \text{Pt(III)-TCPP} + SO_4^{\bullet -} + SO_4^{2-} \\
\text{Pt(II)-TCPP} + SO_4^{\bullet -} \longrightarrow \text{Pt(III)-TCPP} + SO_4^{2-} \\
4\text{Pt(III)-TCPP} + 2H_2O \xrightarrow{\text{WOC}} O_2 + 4H^{+} + 4\text{Pt(II)-TCPP} \\
\hline
2S_2O_8^{2-} + 2H_2O + 2h\nu \longrightarrow O_2 + 4H^{+} + 4SO_4^{2-}
\end{array}$$

The quantum yield of water oxidation by photoexcited Pt(II)-TCPP $\Phi_{Pt\text{-}TCPP}(O_2)$ is two times the number of moles of oxygen produced divided by the number of moles of photoexcited Pt(II)-TCPP in the total illumination time.
The $\Phi_{Pt\text{-}TCPP}(O_2)$ can be expressed as :

$$\Phi_{Pt\text{-}TCPP}(O_2) = 2 \times \frac{Number\ of\ oxygen\ generation}{incident\ NIR\ photons\ \times \Phi(upconversion)\ \times\ \Phi(EnT)}$$

The quantum yield of water oxidation, by NIR-photons $\Phi_{NIR}(O_2)$ in whole process :

$$\Phi_{NIR}(O_2) = \Phi(\text{upconversion}) \times \Phi(\text{EnT}) \times \Phi_{Pt\text{-}TCPP}(O_2)$$

There is ~4% reflection loss at the glass/air interface and the transmission of borosilicate glass reaction vessel is about 90% at 980 nm. Hence the incident photon flux (I_0) is shown below table by photons/s.
Φ (upconversion) is the quantum yield of upconverted green emission and is related to 0.3% according to the reference.1
Φ(EnT) is the efficiency of upconverted green emission convert to photoexcited Pt(II)-TCPP. According to the steady state fluorescence study, the Φ(EnT) can be up to 96.3% including Förster resonant energy transfer and re-absorption.

980 nm laser power	I_0 : photons/s	Φ(upconversion)	Φ(EnT)	excited Pt-TCPP number : mol/s
750 mW	3.19×10^{18}	0.003	0.963	1.5×10^{-8}
500 mW	2.13×10^{18}	0.003	0.963	1.0×10^{-8}

250 mW	1.06×10^{18}	0.003	0.963	5.1×10^{-9}

The quantum yield of water oxidation was calculated by 15 minutes total irradiation time

980 nm laser power	$[O_2]$ nmol/ml at 15 mins	reaction volume /ml	illumination time /s	O_2 mol	Total molecules of photoexcited Pt-TCPP /mol	$\Phi_{Pt\text{-}TCPP}(O_2)$ / %	$\Phi_{NIR}(O_2)$ / %
750 mW	150	1.5	900	2.3×10^{-7}	1.4×10^{-5}	3	9×10^{-3}
500 mW	97	1.5	900	1.5×10^{-7}	9.2×10^{-6}	3	9×10^{-3}
250 mW	52	1.5	900	7.8×10^{-8}	4.6×10^{-6}	3	9×10^{-3}

In conclusion, the total quantum yield of NIR photons induced O_2 generation is about 9×10^{-3} % for UCNPs/PtTCPP nanophotosensitizer under the three 980 nm excitation density levels.

Reference:

1. J. C. Boyer, F. C. J. M. Veggel, Nanoscale, 2010, **2**, 1417.

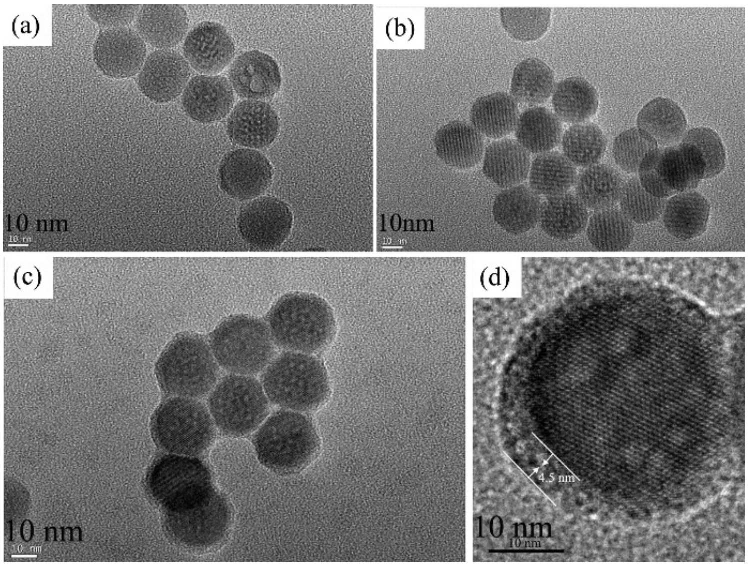

Fig. S1. (a) TEM image of $NaYF_4$: Yb^{3+}, Er^{3+} UCNPs; (b) TEM image of UCNP/Pt(II)-TCPP nanoconjugates; (c - d) TEM image of UCNP/Pt(II)-TCPP nanoconjugates after staining with phosphotungstic acid to enhance the contrast and the visualization of the polymer shells, which was measured to be about 4.5 nm.

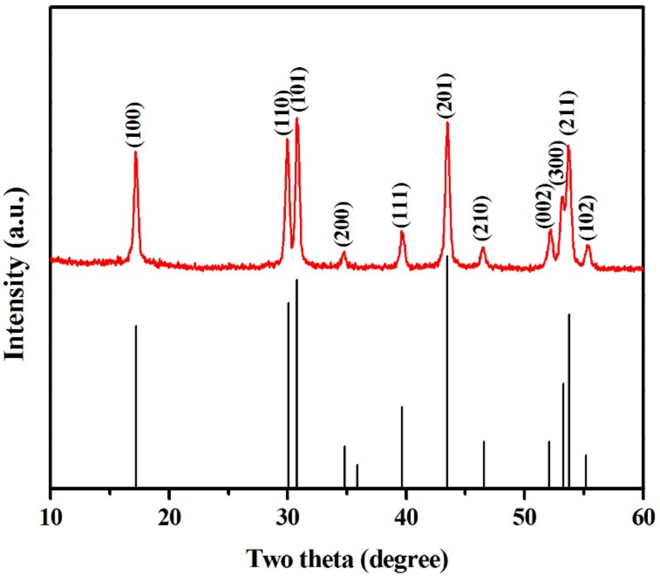

Fig. S2. Experimental powder X-ray diffraction (XRD) pattern for the $NaYF_4$: Yb^{3+}, Er^{3+} UCNPs (red) and the calculated line (black) pattern for the hexagonal $NaYF_4$ phase.

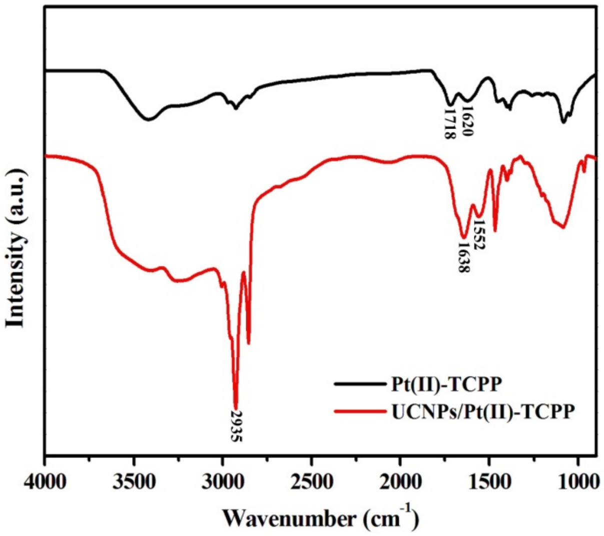

Fig. S3. FTIR absorption spectra of the UCNPs/Pt(II)-TCPP nanoconjugate (red line) and free Pt(II)-TCPP(black line).

For a free Pt(II)-TCPP, the absorption peak at 1718 cm^{-1} is associated with the conjugate C = O stretching vibration mode of the carboxyl group. After conjugating with UCNPs, the peak at 1718 cm^{-1} disappeared and two new peaks appeared at 1638 cm^{-1} and 1552 cm^{-1}, corresponding to the C = O stretching vibration and N-H bending vibration modes of secondary amide, respectively. The absorption peak at 2935 cm^{-1} is associated with the C- H stretching vibration from the PAAm.

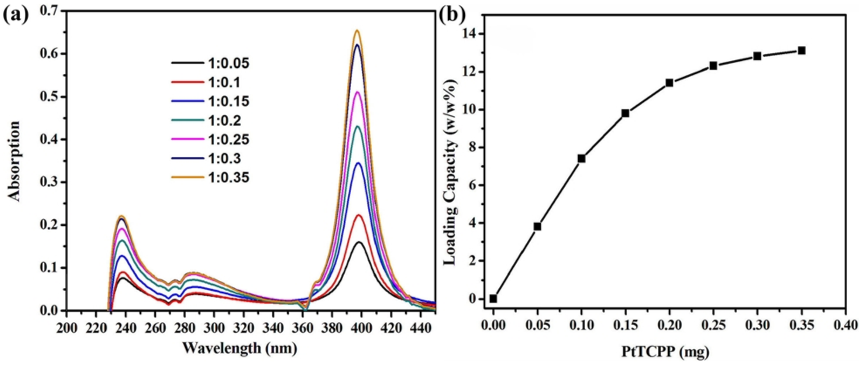

Fig. S4. (a) Absorption spectra and (b) Loading of various weights of Pt(II)-TCPP on UCNP.

In order to determine the loading capacity of Pt(II)-TCPP, NH_2-functionalized UCNPs (1 mg/ml in water solution) were covalently bound with various amounts of Pt(II)-TCPP. After removing free Pt(II)-TCPP by washing, UV-VIS absorption spectra of the UCNP/Pt(II)-TCPP nanophotosensitizer were recorded. The concentration of Pt(II)-TCPP was calculated by Beer-Lambert law $A = \varepsilon bc$, where A represents the absorption value; ε is the molar absorption coefficient of Pt(II)-TCPP at 400 nm in water solution; the optical path length b equals to 1 cm; c is the concentration. The Pt(II)-TCPP loading capacity = [amount of Pt(II)-TCPP in UCNPs (g)]/[amount of UCNP/Pt(II)-TCPP (g)] ×100. It can be seen that the absorption intensities increased with the amount of added Pt(II)-TCPP, and saturated at 13%(w/w).

Quantifying the number of Pt(II)-TCPP per UCNP:

(1) In this case, the Pt(II)-TCPP loading capacity is 13% (w/w). Namely, 1mg UCNP/Pt(II)-TCPP contains 0.13mg Pt(II)-TCPP.

(2) The number of UCNPs:

(a) The mass of single UCNP (M_{NP}) = $M_{w1} \cdot V / N_A \cdot V_{cell} = 2.388 \times 10^{-17}$g

M_{w1}: the formula weight of $NaYF_4$: 20%Yb^{3+}, 2%Er^{3+},$M_{w1} = 204$
V: the volume of single UCNP = $4\pi r^3/3$, r = 13nm (according to the TEM)
N_A: Avogadro constant 6.02×10^{23}
V_{cell}: the volume of unit cell 130.5Å^3

(b) The number of UCNPs = the amount of UCNPs / M_{NP}= 0.87 mg / 2.388×10^{-17}g = 3.64×10^{13}

(3) The number of Pt(II)-TCPP = M $\cdot N_A / M_{w2} = 7.96\times10^{16}$

M: the mass of Pt(II)-TCPP (namely 0.13mg)

N_A: Avogadro constant 6.02×10^{23}

M_{w2}: the formula weight of Pt(II)-TCPP, $M_{w2} = 983$

(4) The number of Pt(II)-TCPP per UCNP = The number of Pt(II)-TCPP / The number of UCNPs = $7.96\times10^{16} / 3.64\times10^{13} = 2.19\times10^{3}$

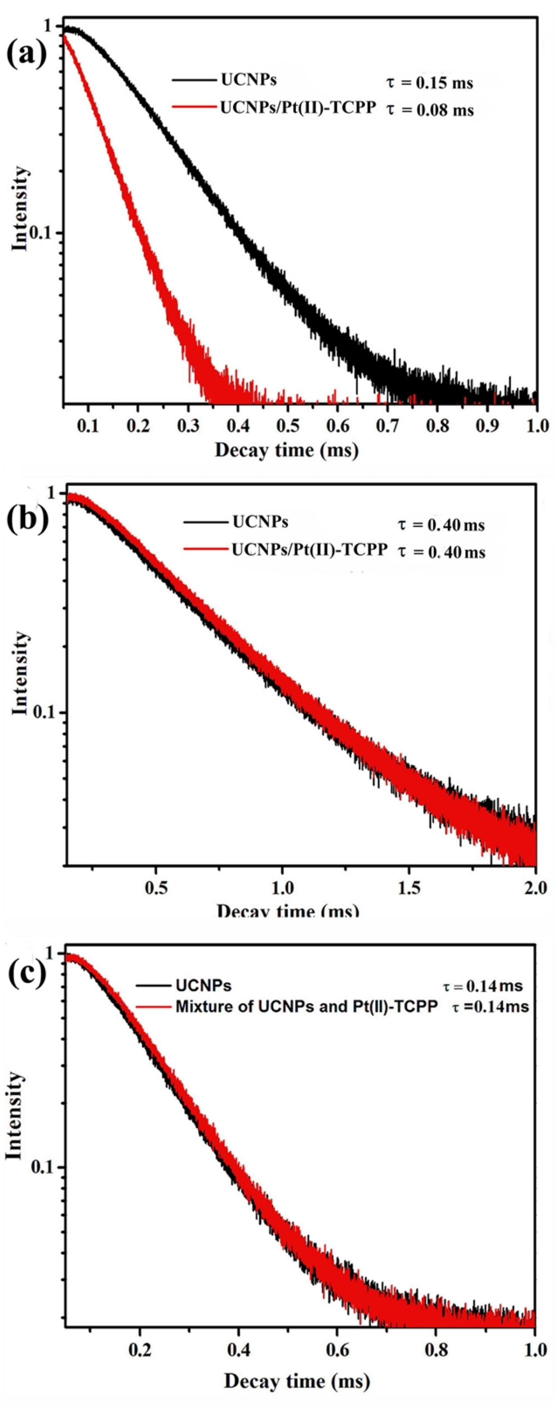

Fig. S5. Luminescence decay curves of upconversion emissions monitored at (a) 540 nm and (b) 650 nm for NH_2-functionalized UCNPs (suspension, 2 × 10^{-3} M) and covalent conjugated UCNPs/Pt(II)TCPP nanophotosensitizer (suspension, 2 × 10^{-3} M). (c) Luminescence decay curves of upconversion emissions monitored at 540 nm for NH_2-functionalized UCNPs only, and the mixture of NH_2-functionalized UCNPs and Pt(II)TCPP.

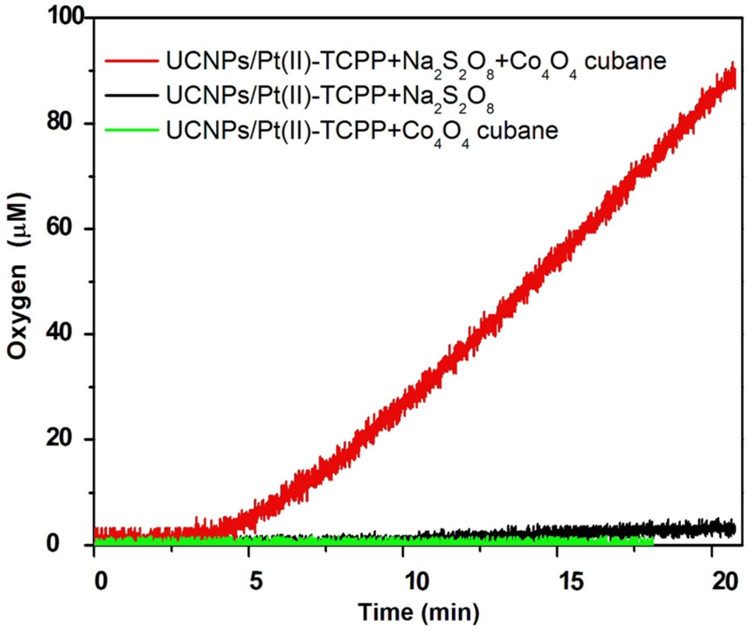

Fig. S6.(a) Photochemical oxygen evolution in 1.5 mL of a pH 7.0, 0.1 M phosphate buffer solution containing $Na_2S_2O_8$ (0.15 M), UCNPs/Pt(II)-TCPP (1.83×10^{-3} M) and catalyst Co_4O_4-cubane (1.5×10^{-4} M). The black line is the result of a control experiment without catalyst Co_4O_4-cubane. The green line is the result of a control experiment without $Na_2S_2O_8$. Illumination was started after ~3 min.

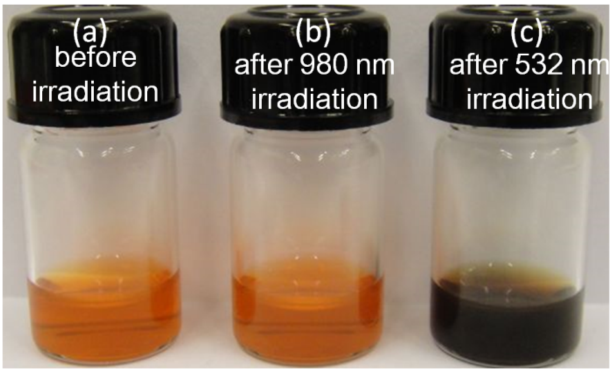

Fig. S7. Digital photos of 1.5 mL of a pH 7.0, 0.1 M phosphate buffer solution containing $Na_2S_2O_8$ (0.1 M), UCNPs/Pt(II)-TCPP (1.83×10^{-3} M) and catalysts Co_4O_4-cubane (1.5×10^{-4} M) sample solution (a) before irradiation, (b) after 980nm irradiation (300mW, 20minutes) and (c) after 532nm irradiation (100mW, 20minutes).

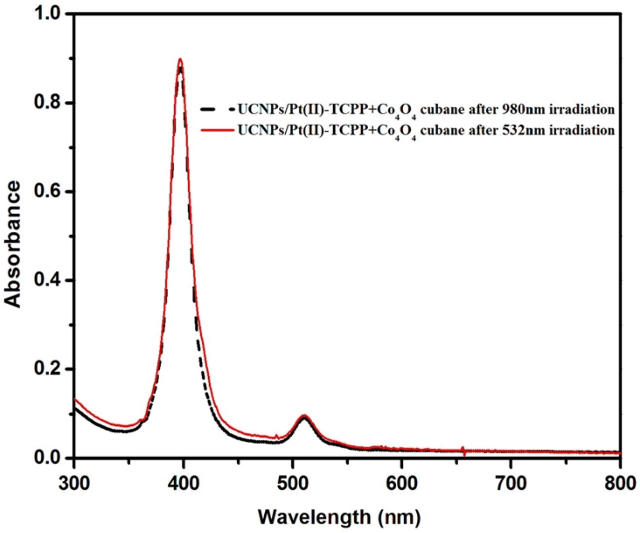

Fig. S8. Absorption spectra of UCNPs/Pt(II)-TCPP nanophotosensitizer solutions without addition of sacrificial electron acceptor ($Na_2S_2O_8$) after excitation at 980nm (black) and 532nm (red) respectively.