Science Advances
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Supplementary Materials for

Three-level spaser for next-generation luminescent nanoprobe

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Published 17 August 2018, *Sci. Adv.* **4**, eaat0292 (2018)
DOI: 10.1126/sciadv.aat0292

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Supplementary Text

Instruction of broadband time-resolved emission spectroscopy

Before analysis, the synthesized spaser nanoprobe solution was placed into a quartz cuvette. The ns pulse laser (λ = 488 nm) was irradiated on the quartz cuvette with a spot size of ~1 cm^2, while a spectrometer was placed on the vertical direction to monitor emission spectrum of the nanoprobe. In addition, a 500 nm long-pass filter was placed in front of the fiber collimator to eliminate the influence of scattering light from laser.

Time-resolved emission spectra of the nanoprobe were collected by using timing gate controlling technology. At time t = 0, ns pulse laser was irradiated on the sample, while a delayed (Δt) TTL signal was generated by using DG645 to trigger the spectrometer working. Then the emission spectrum of spaser nanoprobe at time Δt was acquired, at a broad band from 500 to 900 nm. Hence, the whole time-resolved emission spectra of the nanoprobe were obtained, if changing the delayed time (Δt) from DG645 in an order.

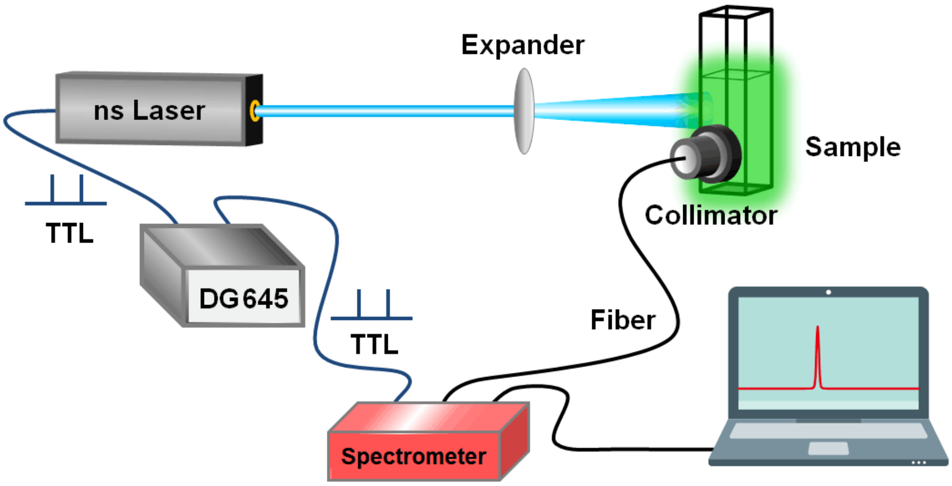

Fig. S1. Schematic diagram of broadband time-resolved emission spectroscopy system.

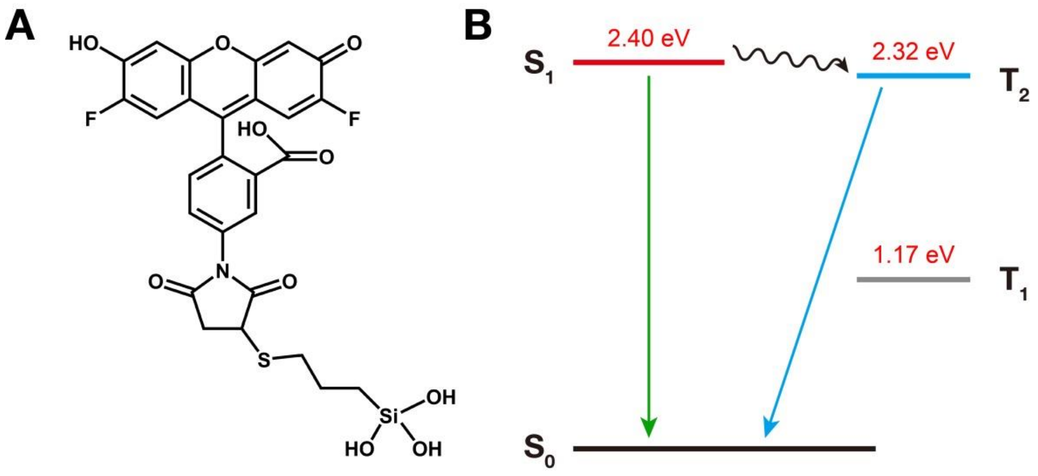

Fig. S2. Molecular modeling of the dye. (**A**) Molecular structure and (**B**) calculated energy diagram of the dye.

We calculated the energy level about the excited states of the used dye molecule by Gaussian 03 program. Based on B3LYP/6-31G level, the ground state and each excited state of the system were geometrically optimized, and the vertical excitation energy and vertical emission energy were calculated by TD-DFT method. All calculations take into account of the water environment through the PCM implicit solvation model. As the reviewer predicted, the energy gap between S_1 and T_1 is huge ($\Delta E_{(S1\text{-}T1)}$=1.23 eV), which is adverse to the occurrence of intersystem crossing. However, the energy gap between S_1 and T_2 is very small ($\Delta E_{(S1\text{-}T2)}$ = 0.08 eV), which is benefit for the intersystem crossing. Therefore, the triplet state electrons more likely to accumulate at T_2 state and transit to S_0 accompanying phosphorescent emission (calculated λ_{max}=534 nm), because the energy gap between T_1 and T_2 is as large as 1.15 eV, which would against the internal conversion. Moreover, the faster transition rate of T_2 ($T_2 \rightarrow S_0$, ~7 fold) than T_1 is favor of the phosphorescent emission from T_2 to S_0. Certainly, the phosphorescent emission of $T_1 \rightarrow S_0$ is still exists, but its emission wavelength (1059 nm) is not in the visible region and too weak to be detected. It is also important to note that such wavelength ($\lambda_{(T1\rightarrow S0)} \approx$ 1059 nm) is far away from the resonance band (~470−560 nm) of plasmon cavity.

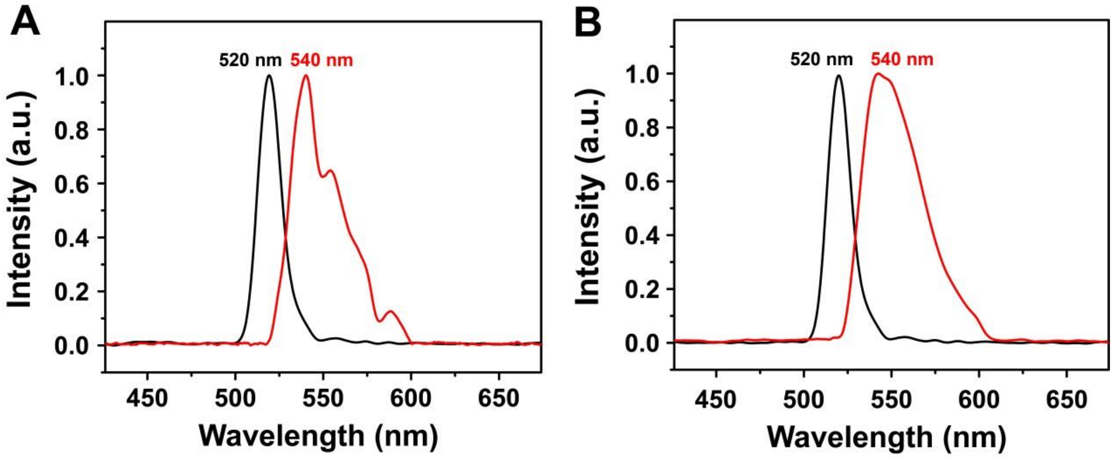

Fig. S3. Photoluminescent spectrum measurement. Fluorescence (black) and phosphorescence (red) emission spectra of dye solution (**A**) and dye-doped SiO_2 (**B**).

To measure the singlet-triplet energy gap, fluorescence and phosphorescence spectra of this dye were collected. Emission signals in the first 100 ns after pump was collected as fluorescence, and emission signals after 10 µs were collected as phosphorescence. As seen, the fluorescence spectrum with a maxium emission (λ_{max}) at 520 nm and the phosphorescence spectrum with a λ_{max} at 540 nm, suggesting a singlet-triplet energy gap of ~0.09 eV.

Taking together, theoretical calculation suggested a singlet-triplet energy gap ($\Delta E_{(S1-T2)}$) about ~0.08 eV, and the observed emission at λ_{max} = 540 nm was most like from transition of $T_2 \rightarrow S_0$, which is an exception of Kasha’s rule. This calculated result matched the experimental results very well.

All in all, based on the experimental results we observed and the calculation results, we believe the T_1 sate was not involved in the lasing mode selection and amplification processes, thus the gain medium of our current spaser is still a three-level system (S_0, T_2, S_1).

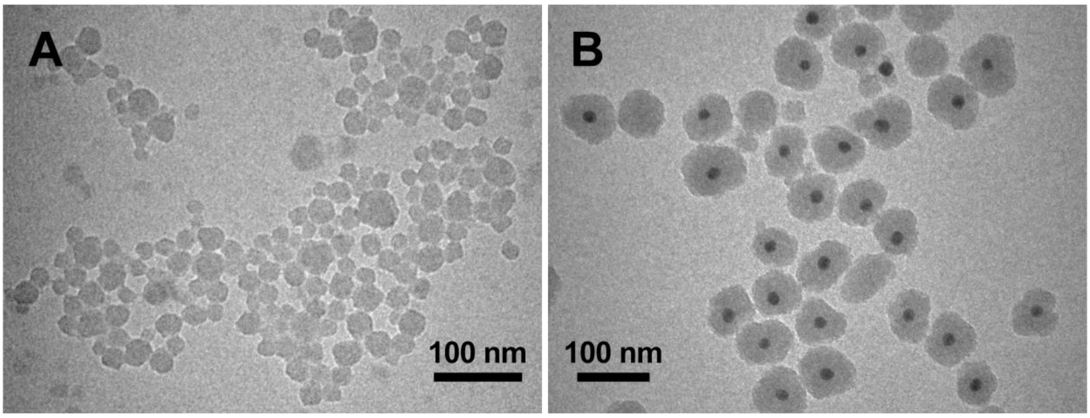

Fig. S4. Morphology characterization of the control samples. TEM images of dye-doped SiO_2 (**A**) and Au@SiO_2 (**B**).

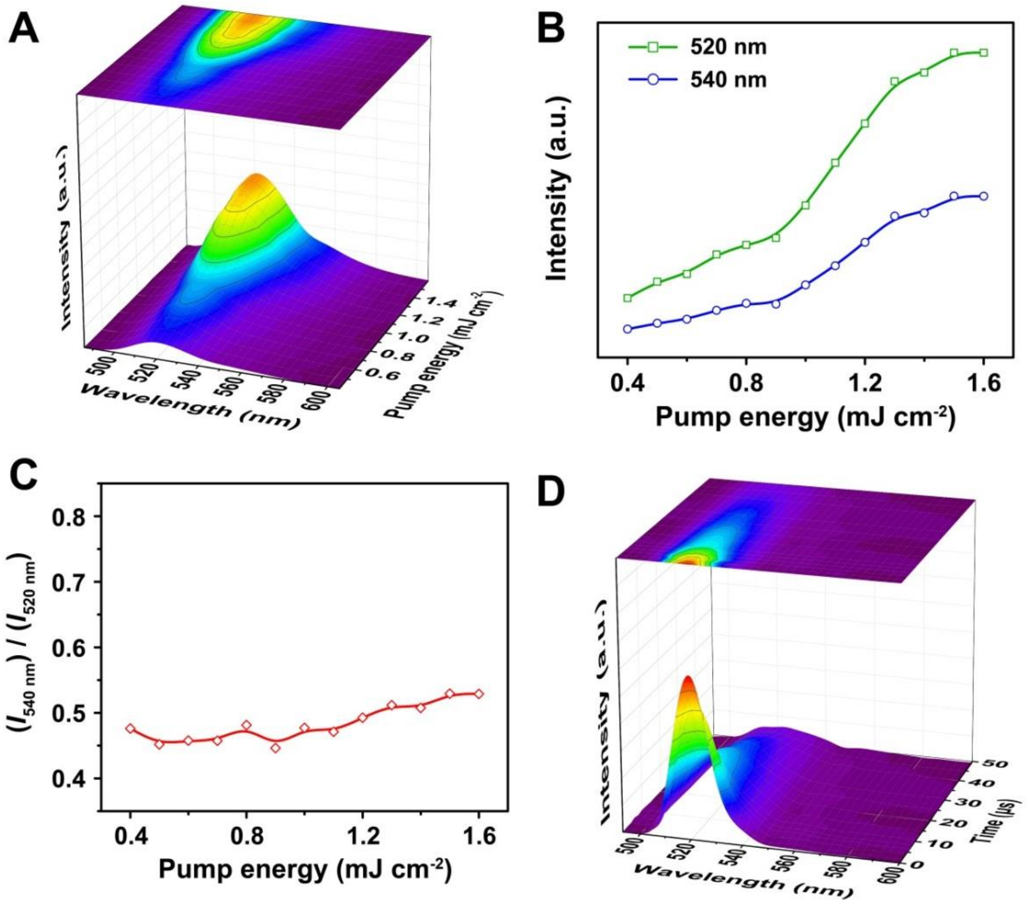

Fig. S5. Pump-dependent steady-state emission and time-resolved emission spectra of dye solution. (**A**) Emission spectra of the dye solution under pump energy from 0.4 to 1.6 mJ·cm^{-2}. Curves of emission intensity at 520 nm and 540 nm (**B**) and their ratio (**C**) with the changing of pump energy. (**D**) Time-resolved emission spectra of dye under the identical pump condition as used in pumping dsDs spasers.

Neither electrons accumulation in T_2 state nor promoted T_2 emission was observed in pump-dependent spectra of dye in solution, and no pump threshold appeared. The reason might be that, in solution, dye molecules were free of motion and the interaction between molecules was relative weak, even the concentration is high. However, when doping dye molecules into SiO_2, the molecular motion was confined and the interaction between molecules could be strong at high dope concentration.

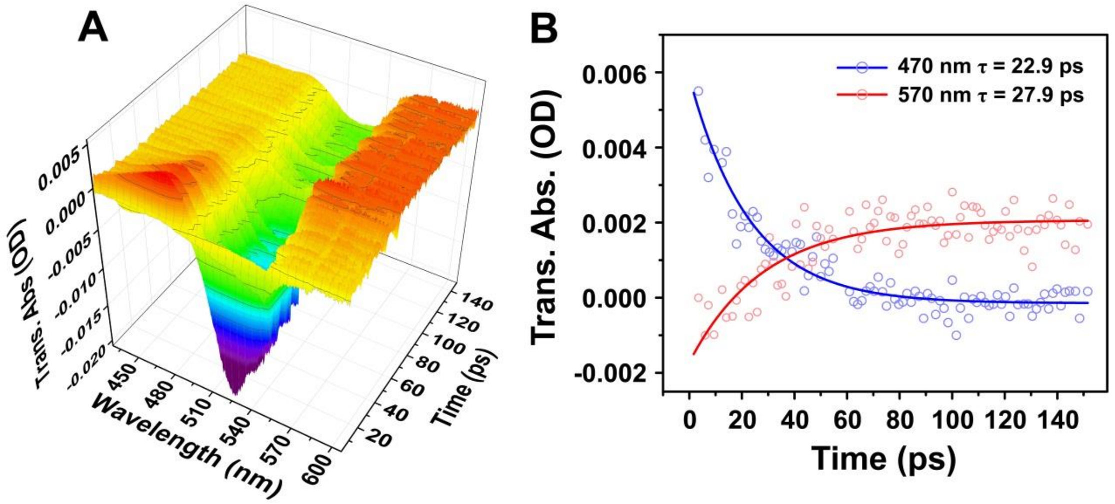

Fig. S6. Electron transition dynamic spectrum of dye solution. (**A**) Picosecond transient absorption spectra of dye solution. (**B**) Evolution of transient absorptive signature of $S_1 \rightarrow S_n$ (470 nm, $\tau = 22.9$ ps) and $T_2 \rightarrow T_n$ (570 nm, $\tau = 27.9$ ps) along with time. The dip around 490−530 nm could be attributed to the overlap of ground state absorption and fluorescence emission.

The transient absorption spectra of dye in solution was basically the same as dye-doped SiO_2. The decay of absorption band at 470 and 570 nm exhibited a slightly longer lifetime of ~22.9 ps and ~27.9 ps, respectively, compared to ~21.5 ps and ~25.3 ps in dye-doped SiO_2. This might be duo to the high localized concentration and much strong inter-molecule interaction in dye-doped SiO_2 than in solution.