

## Electronic Supplementary Information

### Plasmon induced self assembly of gold nanorods in polymer films

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#### **MATERIALS AND METHODS**

**Materials.** Gold (III) tetrachloroauric acid hydrate ( $\text{HAuCl}_4$ , 99.99%), Cetyltrimethyl ammonium bromide ( $\text{C}_{16}\text{TAB}$ , 96%), Sodium borohydride ( $\text{NaBH}_4$ , 99%), Silver nitrate ( $\text{AgNO}_3$ , >99%), tetraoctylammonium bromide (TOAB) and Ascorbic acid (99%) were purchased from Sigma-Aldrich and used without further purification. Aqueous solutions were prepared using  $18.2 \text{ M}\Omega\text{cm}^{-1}$  Milli-Q water obtained from a Millipore system equipped with a  $0.22 \mu\text{m}$  filter. SU-8 photoresist solution was purchased from MicroChem.

**Instrumentation.** SEM images were recorded using a JSM-7500F field emission scanning electron microscope from Jeol Ltd.

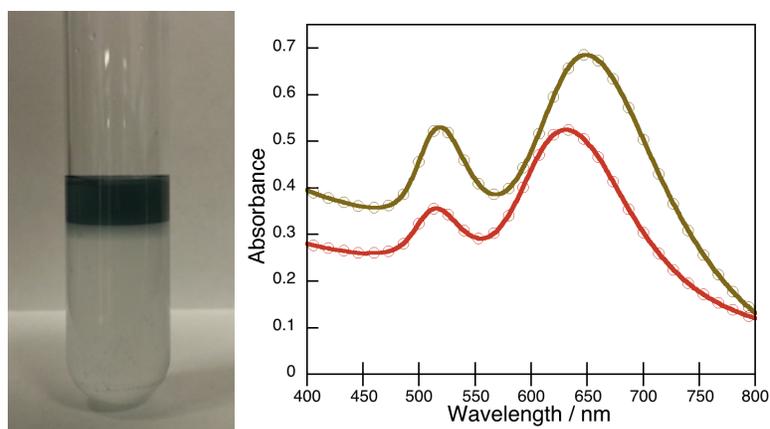
UV-vis spectra were taken using a Cary-100 UV-vis spectrophotometer.

Crosslinked and non-crosslinked films were irradiated using a Continuum Surelite SL-II-10 Nd:YAG pump laser with 355 nm third harmonic (~6 ns); 690 nm pulses were generated by a Continuum Optical Parametric Oscillator, model SLOPO Plus (~6 ns).

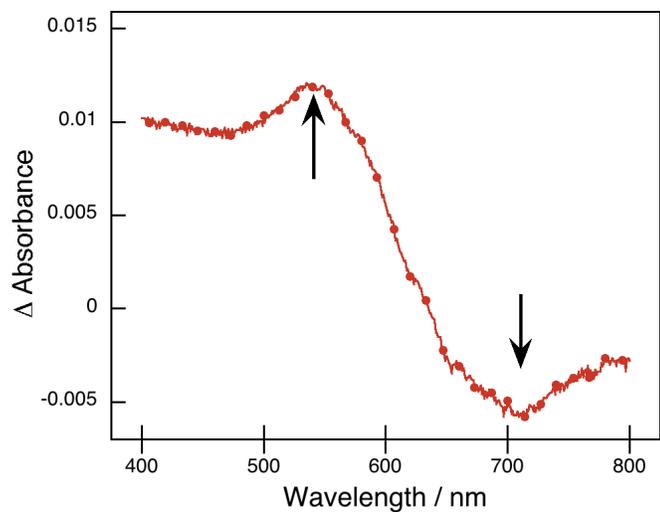
**Synthesis of AuNRs.** Au nanorods were synthesized based on a seed-mediated method reported by He *et al.*<sup>1</sup> Briefly, a seed solution was prepared by adding 100  $\mu$ L of HAuCl<sub>4</sub> (24 mM) to 7.5 mL of CTAB (0.1 M) and diluting to 9.4 mL. Next, 0.6 mL of an ice-cold NaBH<sub>4</sub> aqueous solution (0.01 M) was added while stirring for a couple of minutes. The solution was kept undisturbed for 45 min. Next, a growth solution was prepared by consecutively adding 2.04 mL of HAuCl<sub>4</sub> (24 mM), 2 mL of H<sub>2</sub>SO<sub>4</sub> (0.5 M), 0.4 mL of AgNO<sub>3</sub> (10 mM) and 0.8 mL of ascorbic acid (0.1 M) into a 100 mL CTAB solution (0.1 M). Finally, 240  $\mu$ L of seed solution were added into the growth solution while stirring and the mixture was kept undisturbed for 19 h. Excess of surfactant was removed by centrifugation (12000 rpm, 10 min) and further re-dispersion of the AuNR in 100 mL of water. AuNR were transferred from water into chloroform by extraction for further incorporation into the polymer matrix. Longer AuNR with an aspect ratio of 4.5 were prepared following a recently reported procedure.<sup>2</sup>

**Extraction of AuNRs into organic solvents.** AuNRs were transferred from water into chloroform by extraction. Briefly, 1 mL of mercaptosuccinic acid (10 mM, pH 8-9) was mixed with 1 mL of aqueous AuNR solution. Then, 0.5 mL of TOAB in chloroform (50 mM) was added and shaken vigorously during 3 minutes. Finally, the water phase was removed and the organic one was added into a desired amount of SU-8. Extraction of AuNR into other organic solvents such as toluene it is also possible (See Figure S1).

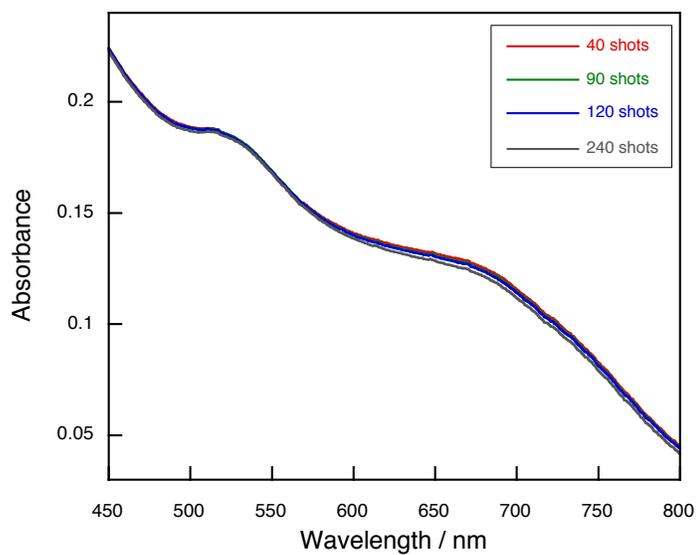
**Formation of Films.** Typically, 1 mL of SU-8 and 1.5 mL of AuNR (AR = 3) in chloroform solution were mixed in a test tube. After 12 hours, the solutions were casted on microscope slides to form a thin layer and prebaked at 65°C for 5 minutes and 95°C for 3 minutes. This procedure was repeated several times in order to achieve thicker non cross-linked films. Cross-linked films were obtained by a similar procedure by irradiation of each non cross-linked layer under 400 nm LED irradiation (~2.1 W) during 3 minutes.



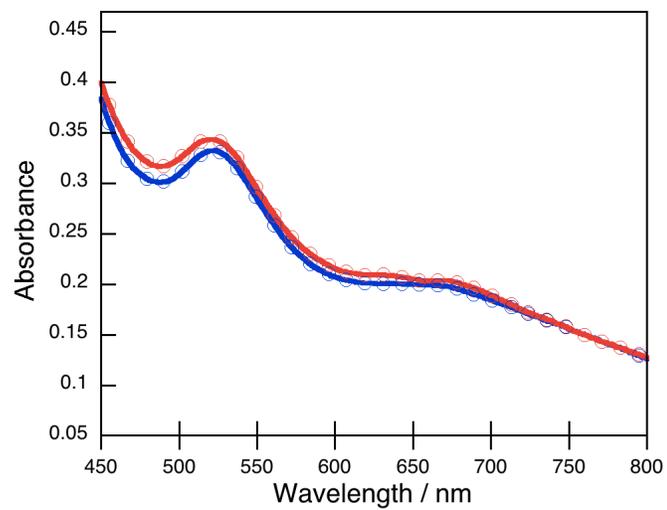
**Figure S1.** (left) Transference of AuNRs into organic solvents. Top layer: toluene; Bottom layer: water. (right) Absorption spectra of AuNRs solutions in organic and aqueous solvents. Slight red shift is observed due to changes in the environment. Red: water; Green: Toluene. Polymer SU-8, AR = 3.



**Figure S2.** Change in absorbance of a crosslinked film at each wavelength after 290 seconds of 690 nm irradiation. Polymer SU-8, AR = 3.

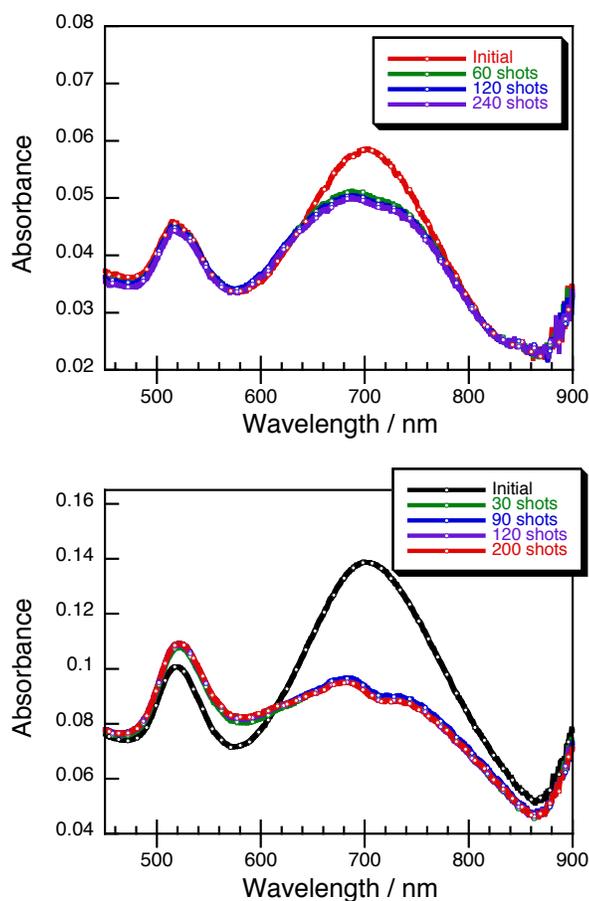


**Figure S3.** Absorption spectra at different irradiation times (532 nm). Initial film (red), 90 seconds (green), 120 seconds (blue) and 240 seconds (gray). Complete overlap of the spectra prevents detailed observation of individual traces. Polymer SU-8, AR = 3.



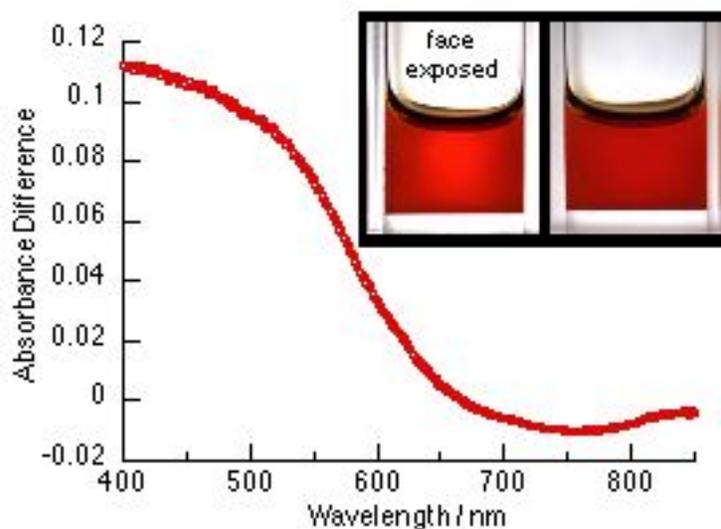
**Figure S4.** Absorption spectra of red-light oriented AuNRs in SU-8 film (blue) and the same film after 1h heating (red). Polymer SU-8, AR = 3. Notice a minor (but real) increase at 530 nm.

**Spectral changes observed in PMMA.** Spectral differences obtained in PMMA have been included in the main text (see Figure 2, lower panel). The spectral data (before subtraction) are shown in Figure S5. Orientation required higher energies than for polymer SU-8, probably a reflection of the higher T<sub>g</sub> for PMMA.



**Figure S5.** Absorption spectra of red-light oriented AuNR (AR = 3) in PMMA films exposed to 1 mJ (top) and 5 mJ (bottom) laser pulses at 690 nm. The number of laser pulses is given in each panel.

**Spectral changes observed in an SU-8 block.** Spectral differences were recorded on a 10 x 10 mm block of SU-8 polymer containing AuNR (AR = 3). The block was prepared by slow evaporation of the solvent at room temperature over a period of 2 days. The spectra were recorded in the two directions (90 degree rotation) and subtracted. Visual changes are present but less dramatic than in thin films. The opposite face to the exposed one (180 degree rotation) showed same modified characteristics indicating the studied phenomenon occurs in the bulk of the exposed irradiated area not just at the surface.



**Figure S6.** Absorption difference for a polymer 10 x 10 mm block made of SU-8 containing AuNR (AR = 3). The inset shows the face illuminated at 690 nm (left) and after 90 degree rotation of the cuvette the face that was not illuminated (right). The spectrum corresponds to the absorbance difference between the two cuvette faces (illuminated minus perpendicular).

## References

- (1) He, W.; Hou, S.; Mao, X.; Wu, X.; Ji, Y.; Liu, J.; Hu, X.; Zhang, K.; Wang, C.; Yang, Y.; Wang, Q., *Chem. Comm.* **2011**, *47*, 5482-5484.
- (2) Zheng, Z.; Tachikawa, T.; Majima, T., *J. Am. Chem. Soc.* **2014**, *136*, 6870-6873.