Supplementary Information

Different behaviour of molecules in dark SERS state on colloidal Ag nanoparticles estimated by truncated power law analysis of blinking SERS

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Surface coverage of the TC on the Ag surface. A stock aqueous solution of the anionic TC dyes (25 μM), a NaCl aqueous solution (100 mM), and the Ag colloidal suspension were mixed at a volume ratio of 1:1:2 at room temperature. The sample was centrifuged at 15000 rpm for 10 min, and then the supernatant was measured by a UV-Vis spectrometer. On the other hand, a stock aqueous solution of the TC dyes (25 μM), a NaCl aqueous solution (100 mM), and water were mixed at a volume ratio of 1:1:2 at room temperature; namely, the corresponding sample was prepared by using water instead of the Ag colloid. Figure S1 shows that a difference between the absorption band intensities of the sample with and without the Ag colloids was roughly 2/27 of the band intensity of the latter, which attributed to 6.25 μM of the TC dyes. Thus, it is estimated that the Ag adsorbs 0.46 μM of the TC dyes.

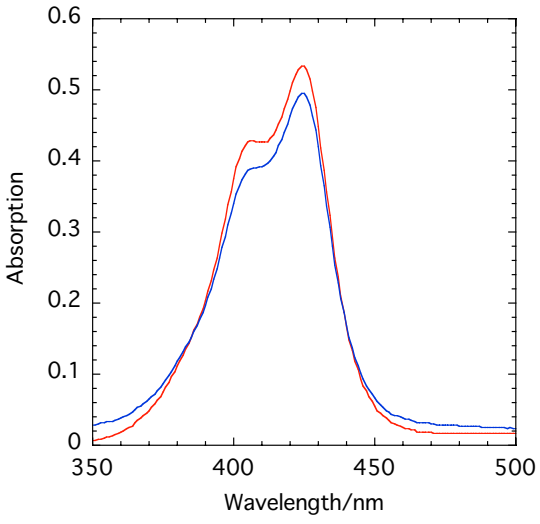

Figure S1 Absorption spectra of the TC dyes (6.25 μM) in a NaCl (25 mM) aqueous solution and the supernatant of the sample after centrifugation, which indicated by red and blue curves, respectively.

Effect of high concentration of NaCl on the Ag nanoaggregates. Figure S2 show microscope images of the Ag nanoaggregates by a dark-field illumination. Many white spots were observed and may be attributed to large-sized Ag aggregates, which are independent of LSPR. In the case of the various colored Ag nanoaggregate in 1 M NaCl solution, prominent change of their colors was not observed for 20 min, which is the same time as the observation of the blinking, unlike the previous report.[1]

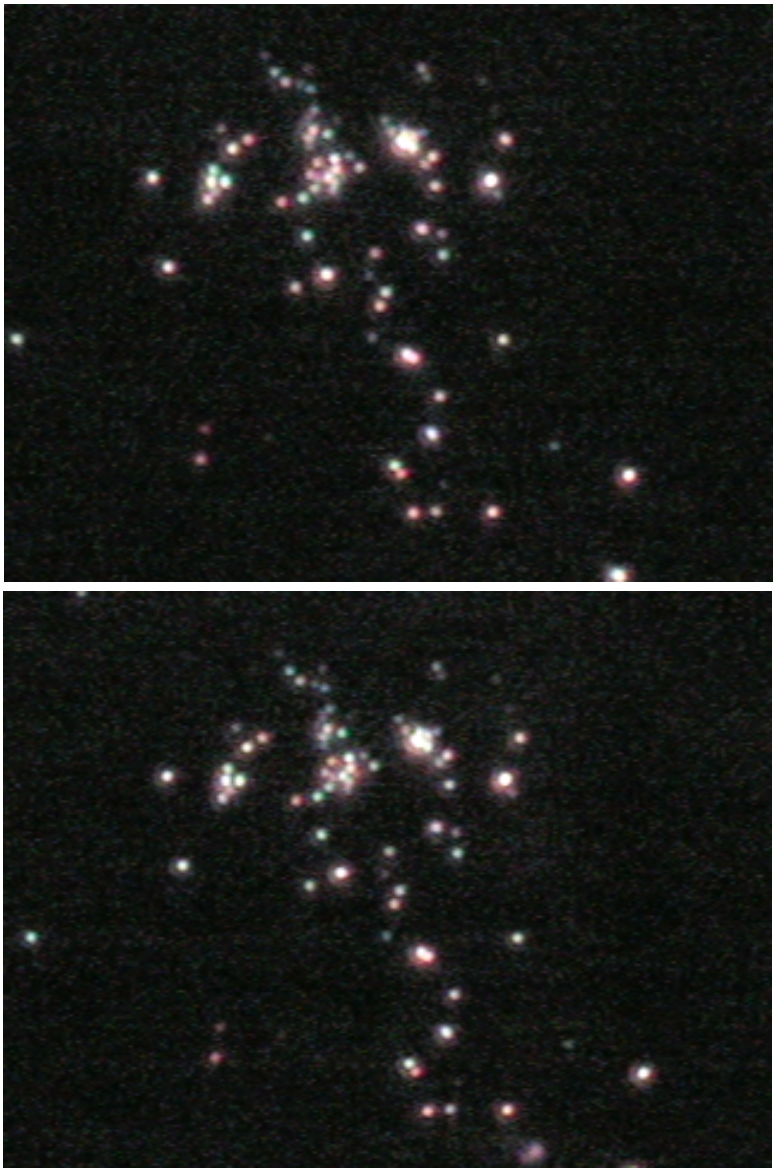

Figure S2 (a) Microscope image of the Ag nanoaggregates in 1 M NaCl aqueous solution by a dark-field illumination and (b) the image of the same area after 20 min. The images cover 50 × 40 μm^2.

Reference for Supplementary Information

1 K. Yoshida, T. Itoh, V. Biju, M. Ishikawa and Y. Ozaki, *Appl. Phys. Lett.,* 2009, **95**, 263104.