

Supplementary data

Experimental details

Chemicals

Potassium tetrachloroplatinate (K_2PtCl_4 , Riedel de Haen) was used to prepare the solution of Pt^{2+} . 1,6-Hexanedithiol ($HS(CH_2)_6SH$, HDT, Aldrich) was used as purchased. The water used was purified using a Milli-QTM Millipore system.

The preparation of HDT self-assembled monolayer on gold thin film.

Microscope slide glasses (1-inch \times 1-inch SF10) were immersed in a piranha solution ($H_2SO_4 : H_2O_2 = 7:3$ v/v) for the purification. The glass substrate were rinsed several times with the copious amount of DI water and ethanol and, then, dried. The 50-nm gold thin film was prepared by a thermal evaporation with a 5-nm Cr adhesion layer. The SAM of HDT on gold substrate was formed by the treatment with 1 mM HDT ethanolic solution for 4 hrs. The formation of HDT monolayer was monitored by in-situ SPR measurements. The gold substrate with the HDT monolayer was attached to an SF10 prism with index matching oil (Cargille Laboratories Inc., certified refractive index liquids, $n = 1.730 \pm 0.0005$). A Teflon cell was attached to the gold substrate. The 635-nm He-Ne diode laser (Power Technology Inc.) was p-polarized and focused with a lens through the prism onto the gold substrate. Both the prism and the gold substrate were mounted on a rotating plate to control the angle of the incident light. The reflectance was measured with a photo-power meter (Oriol). The changes in Pt^{2+} concentration after the adsorption of Pt^{2+} to a thiolated gold substrate in these experiments are negligible, because the adsorption surface area is limited (about 8×10^{-5} mm²).

The estimation of the dielectric constant and thickness of the full-adsorbed Pt^{2+} layer.

We considered the immersion of the HDT-gold substrate into 1 mM Pt^{2+} solution for 12 hr as the fully saturated status of the HDT-gold substrate with Pt^{2+} (the immersion time of 12 hr is expected to be enough for the saturation).

Calculation details

SPR angle shift for both cases (one is the fixed thickness and the other is the fixed dielectric constant) was calculated using the Fresnel equations (using SPR software: Winspall version 2.20, Max-Planck-Institute for Polymer Research, Mainz, Germany). Fig. 1 (upper figure) represents the simulation results of SPR angle shift. Normalized SPR angle shifts were obtained from the following equation.

$$\text{Normalized } \Delta\theta_{SPR} = \frac{\Delta\theta_{SPR}^{Instant}}{\Delta\theta_{SPR}^{Final}}$$

The maximum SPR angle shift was obtained from SPR measurements for the fully saturated HDT layer with Pt^{2+} .

For spherical inclusions, the effective medium dielectric constant can be calculated from the following equation

$$\frac{(\epsilon_{eff} - \epsilon_4)}{(\epsilon_{eff} + 2\epsilon_4)} = \beta f \text{ where } \beta = \frac{(\epsilon_3 - \epsilon_4)}{(\epsilon_3 + 2\epsilon_4)}$$

We assumed that the filling factor f of the adsorbed Pt^{2+} layer reaches the value $f \sim 1$, when the HDT layer was saturated with Pt^{2+} ion. (Strictly speaking, the filling factor f , being 0.74 at maximum in cubic or hexagonal close packed geometry for considering Pt^{2+} as a uniformly sized spheres)

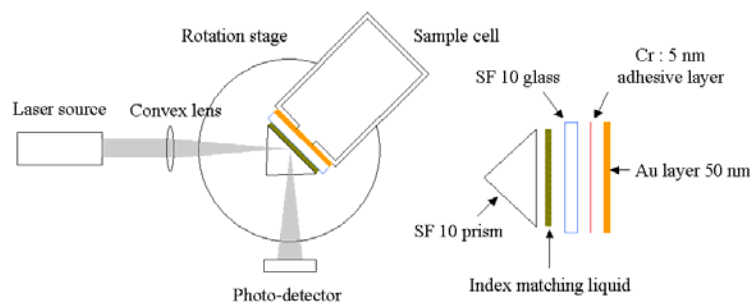


Fig. S1 The schematic configuration of surface plasmon resonance (SPR) measurements in the present study.

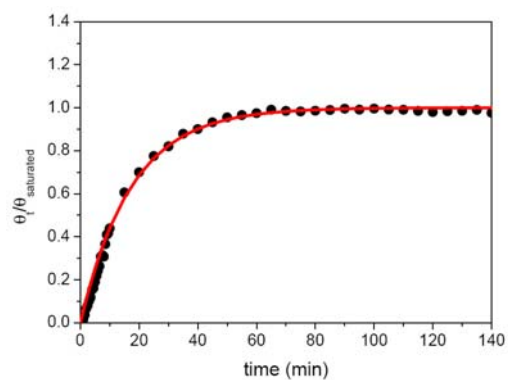


Fig. S2 SPR curve of 1,6-hexanedithiol on a gold substrate as a function of time.