

## Experimental Procedures and details

**Reagents.** 2-aminoethanethiolhydrochloride (AET, Sigma-Aldrich) was used as an adsorption-inducing chemical. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , Fisher Scientific) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , Fisher Scientific) were used to clean the glass slides on which chromium and gold films were subsequently evaporated. Hydrogen chloride (HCl, Fisher Scientific) and sodium hydroxide (NaOH, Mallinckrodt Chemicals) were used to control the pH of the solution.  $\text{H}_2\text{O}$  was purified to more 18 M $\Omega$  using a Milli-Q water system (Millipore). Copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ , Junsei), nickel nitrate ( $\text{Ni}(\text{NO}_3)_2$ , Junsei), and Zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ , Shinyo) were used to prepare metal ion solutions.

**SPR system.** The SPR measurements were performed using an in-house constructed instrument. Briefly, the setup was based on the Kretschmann configuration, in which a *p*-polarized laser beam ( $\lambda = 635$  nm) is focused through a prism onto a metal film placed on the prism. The Au substrate with an AET monolayer was attached to an SF10 prism with index matching oil (Cargille Laboratories Inc., certified refractive index liquids,  $n = 1.730 \pm 0.0005$ ). The 635-nm He-Ne diode laser (Power Technology Inc.) was *p*-polarized and focused with a lens through the prism onto the Au substrate. Both the prism and the Au substrate were mounted on a rotating plate to control the angle of the incident light. The reflectance was measured with a photo-power meter (Oriel). A Teflon cell was attached to the Au substrate to hold the solution. The cell had an O-ring (ID = 0.8 cm) in the middle through which the laser light contacted the solution.

**The preparation of AET SAM on an Au thin film.** The overall experimental procedures are summarized in Scheme 1. Glass microscope slides (1-inch  $\times$  1-inch SF10) were immersed in a piranha solution ( $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 7:3$  v/v) for purification (*caution*: piranha solution should be handled with extreme care). The glass substrate was rinsed several times with copious amounts of deionized water and ethanol and, then, dried. The 50-nm Au thin film was prepared by a thermal evaporation with a 5-nm Cr adhesion layer. The SAM of AET on the Au thin film was formed by treatment with a 1 mM AET ethanolic solution for 18 hrs. The formation of an AET monolayer was investigated by SPR measurements and auger electron spectroscopy (AES).

Prior to the detection of  $\text{Cu}^{2+}$  using AET SAM on the Au thin film, the initially formed AET SAM on the Au surface was treated with a NaOH (pH 11) solution for 2 min, in order to remove  $\text{H}^+$  on “nitrogen” atoms. To investigate the ionization behavior of AET SAM on the Au thin film, the time resolved SPR angle shift was measured using the fixed angle method which enabled the reflectance change,  $\Delta R$ , to be linearly correlated with the SPR angle shift,  $\Delta\theta_{\text{SPR}}$  ( $I\theta$ ). The fixed incident angle for measuring the reflectance was adjusted before the ionization of AET SAM. The reflectance data at a fixed incident angle were acquired by a computer in real time. Based on the previous results for the pH-dependent SPR response of carboxylic acid-terminated SAM, we found that changing the buffer solution had a significant effect on the SPR data (by significantly affecting the refractive index of medium 4), irrespective of the presence of the SAM layer in the multilayer structure. Therefore, instead of using a buffer solution, HCl and NaOH were used to control the pH of the ambient medium. Intrinsic optical effects of these latter solutions were also examined by SPR measurements.

**The SPR analysis of  $\text{Cu}^{2+}$  using AET modified Au thin film.** We utilized a six-phase, denoted as (012345) SPR system in the Kretschmann configuration using attenuated total reflection (ATR) (see schematic stratified structure in

Fig. S1). The different phases were labeled as follows: 0, a glass slide (SF10), optically coupled to a 90 ° ATR prism; 1, a thin binder layer of Cr (5 nm); 2, a layer of Au thin film (50 nm); 3, a amino-terminated self-assembled monolayer (SAM) of AET; 4, a layer of adsorbed Cu<sup>2+</sup>; 5, an ambient dielectric medium of air (for detection of Cu<sup>2+</sup>) and water (for investigating the ionization of AET SAM, in this case, the adsorbed Cu<sup>2+</sup> layer of 4 was absent). A batch technique was used to determine the detection ability of AET-Au thin film. The AET-Au surface was equilibrated with a Cu<sup>2+</sup> solution (pH 5) in the concentration range of 1×10<sup>-7</sup> M ~ 1×10<sup>-3</sup> M for 15 hrs at 22 °C. The same experiments were repeated three times. After the adsorption of Cu<sup>2+</sup>, the sensor surface (AET-Au thin film) was analyzed by SPR measurements. The same procedures were repeated for single metal ions (Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>) and solutions of multiple metal ions (Cu(NO<sub>3</sub>)<sub>2</sub>/Ni(NO<sub>3</sub>)<sub>2</sub>/Zn(NO<sub>3</sub>)<sub>2</sub>). The pH of all metal solutions was controlled to be pH 5 in order to avoid their precipitation by forming hydroxyl complexes, and all experiments were performed at 22 °C.

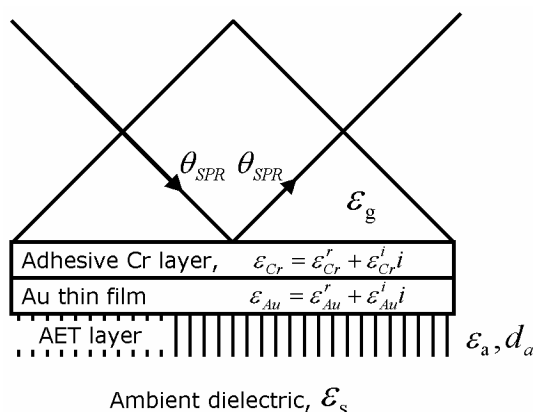


Fig. S1. Stratified structure (not drawn to scale) of an SPR system:  $\theta_{SPR}$ , surface plasmon resonance angle;  $\epsilon_g$ ,  $\epsilon_a$ , and  $\epsilon_s$ , dielectric constant of the glass prism, AET layer, and ambient, respectively;  $\epsilon'_m$  and  $\epsilon''_m$ , real and imaginary components of the complex dielectric constants of metal (Cr and Au);  $d_a$ , thickness of the AET layer.

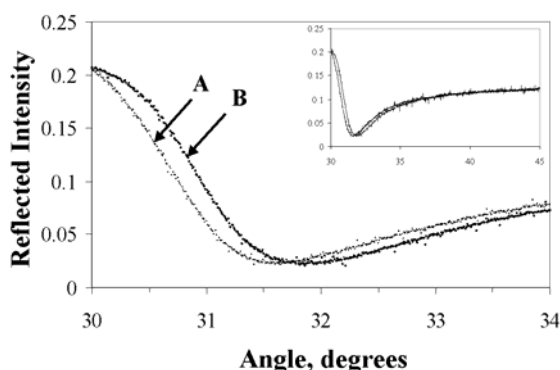


Fig. S2. Incident angle dependent SPR reflectivity (R) for (A) four-phase and (B) five-phase multilayer systems, using the ambient dielectrics of air. For each graph, every fourth point from the collected raw data is plotted to preserve the clarity of the contour plot. The four-phase system corresponds to an AET-free Au SPP substrate. In the five-phase case, the Au thin film is coated with a SAM of AET by immersing the Au thin film in a 1.0 mM ethanolic solution of AET.