Physical Chemistry Chemical Physics

Electronic Supplementary Information

for

Effect of Chemisorbed Thiophenols with Electron Donating Group on Surface-Enhanced Raman Scattering of Gold Nanorods

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<Table of Contents>

1. Supplementary Movies

Movies S1-S3: A movie to support the formation of possible aggregations in the presence of *p*-ATP by DF microscopic imaging. There is a tendency toward AuNR aggregates with intense scattering signals and slow movement of large, bright spots in the presence of *p*-ATP.

Movies S4-S6: A movie to show the motions of AuNRs in the presence of *p*-NTP in solution. This movie of AuNRs with *p*-NTP showed single nanoparticles or small aggregations, unlike *p*-ATP.

2. Experimental Section

2-1. Real-Time Surface-Enhanced Raman Spectroscopy

For real-time SERS sample preparation, 100 μL of the AuNR solution was transferred to a tube and centrifuged at 12,000 rpm for 10 min to remove the CTAB surfactant. The washed AuNR sample was resuspended in ethanol and sonicated for a few seconds for adequate dispersion. Immediately after the probe-molecule solutions of each concentration were added to the rinsed AuNR solution, the prepared samples were transferred to capillary tubes with 0.25 mm wall thickness and 100 mm length. In real-time experiments, 1 mM *p*-NTP and AuNRs in ethanol were mixed with the sample prepared by SERS methodology. Immediately after the two solutions were mixed, SERS measurements were conducted every 3 min until the Raman signals were saturated. Both ends of the sample capillary tube were sealed to prevent loss of solvent by evaporation.

2-2. Dark-Field Microscopic Imaging

We used a Nikon inverted microscope (ECLIPSE Ti-U, JAPAN) for dark-field (DF) scattering microscopy. In DF mode, we utilized a Nikon Plan Fluor 100× 0.5–1.3 oil iris objective and a Nikon DF condenser. We used an Andor iXon^{EM}+ CCD camera (iXon Ultra 897, UK) to obtain DF scattering images of the AuNPs. The collected images were analyzed with the Image J software.

2-3. Calculation of Optical Absorption Spectra of Gold Nanorods

We used Gans theory with the known dielectric function for gold to simulate the optical absorption spectra of randomly oriented AuNR colloids by varying the refractive index of

surrounding medium (*n*). According to Gans theory, the extinction coefficient γ of randomly oriented particles in the dipole approximation is given by Eq. (1):

$$\gamma = \frac{2\pi NV\varepsilon_m^{3/2}}{3\lambda}\sum_j \frac{(1/P_j^2)\varepsilon_2}{(\varepsilon_1 + \frac{1-P_j}{P_j}\varepsilon_m)^2 + \varepsilon_2^2} \quad (1)$$

N: the number of particles per unit volume

V: the volume of each particle

ε_m: the dielectric constant of the surrounding medium, is equal to n^2

λ: the wavelength of the interacting light

and : the real and complex part of the material dielectric function

P_j: the depolarization factors for the three axes *A*, *B*, *C* of the rod with *A*>*B*=*C*

$$P_A = \frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right) - 1\right] \quad (2)$$

$$P_B = P_C = \frac{1-P_A}{2} \quad (3)$$

$$e = \sqrt{1-\left(\frac{B}{A}\right)^2} \quad (4)$$

Eq. (1) for γ was plotted as a function of *n* while the aspect ratio (*A/B*) of AuNRs was fixed to a value of 3.4 same as the average aspect ratio of AuNRs (25.6 nm × 85.9 nm) used in this study.

3. Supplementary Figures

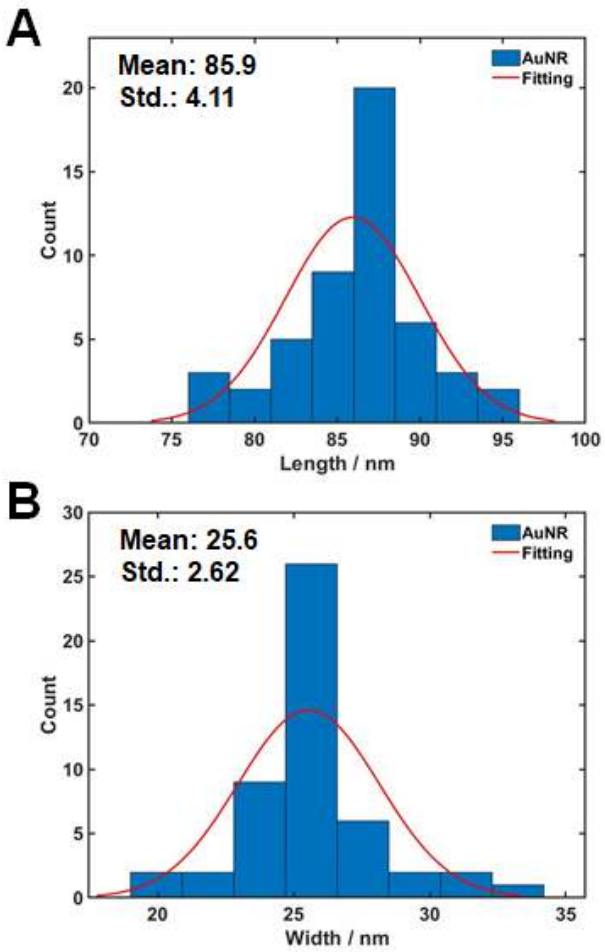

Fig. S1 Size distributions of AuNRs with gaussian fitting. The average length and width were determined to be 85.9 nm and 25.6 nm, respectively. Total 50 particles were counted from SEM images to build the histrograms.

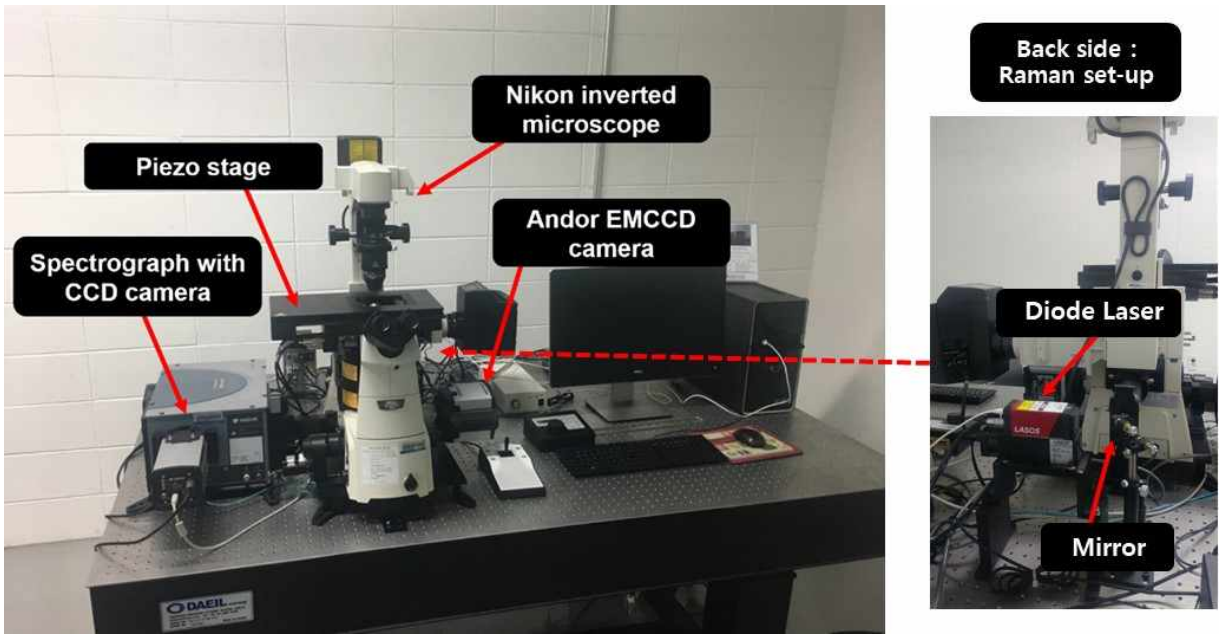

Fig. S2 A photograph showing the experimental setup for Raman spectroscopy and DF single particle scattering spectroscopy. The back side shows the laser source and beam paths for Raman measurement.

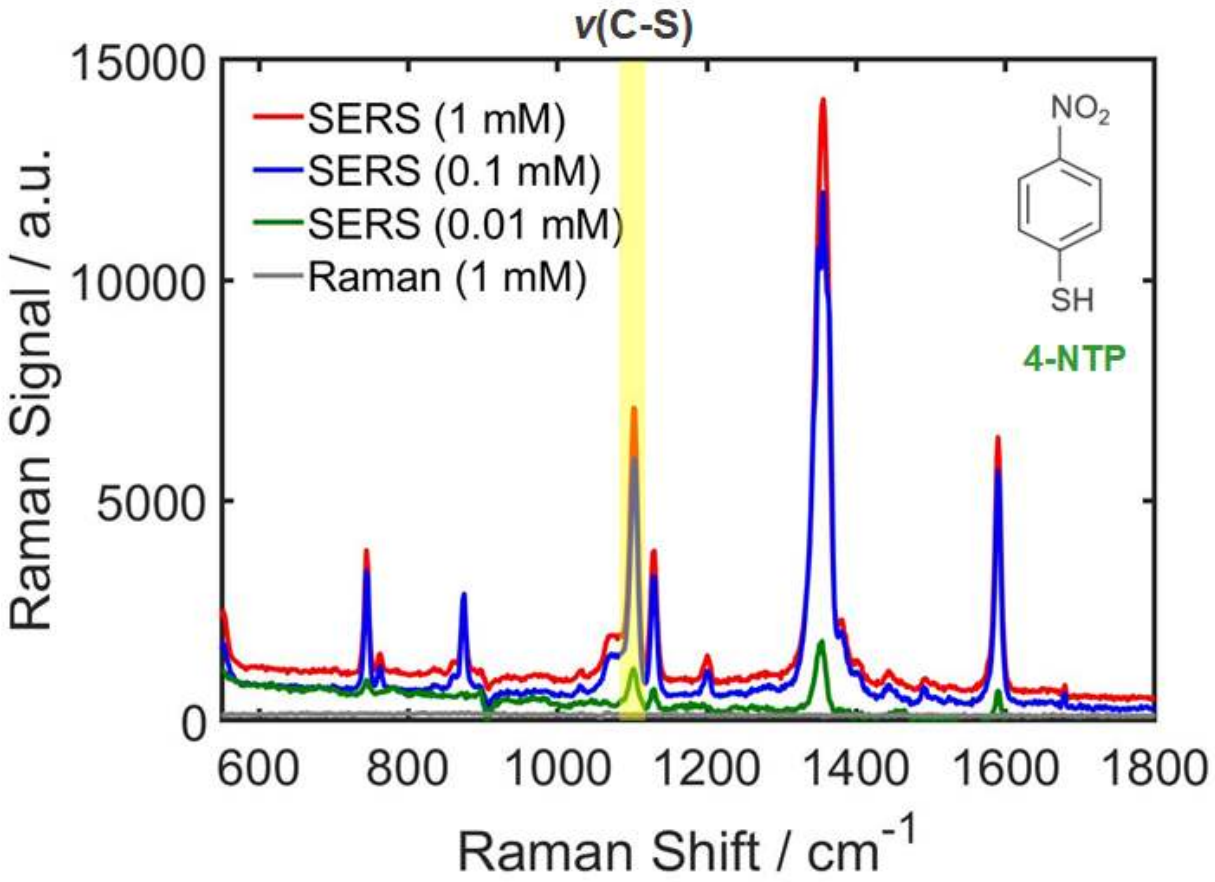

Fig. S3 Raman spectra of *p*-nitrothiophenol (*p*-NTP) at various concentrations (1 mM, 0.1 mM, 0.01 mM) and normal Raman spectrum at 1 mM.

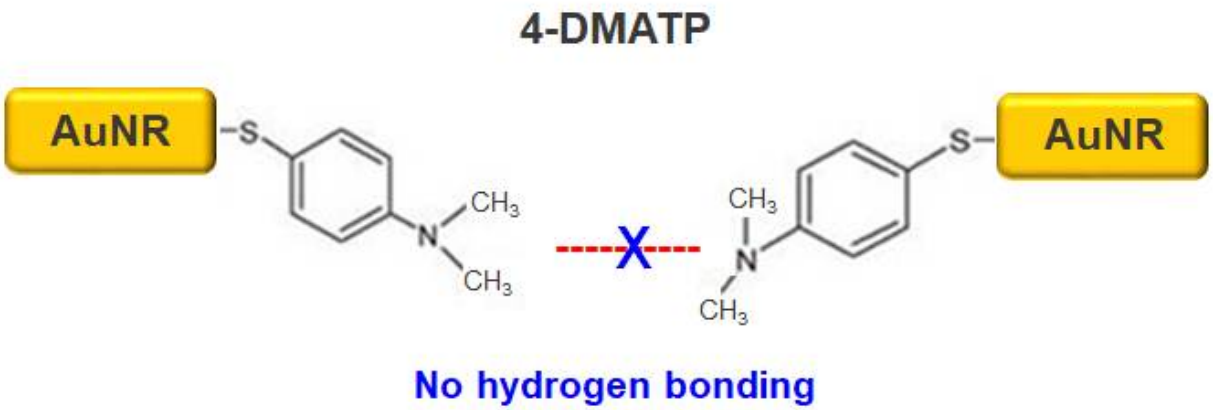

Fig. S4 Schematic to depict the impossibility of intermolecular interaction between probe molecules such as dimerization with hydrogen bonding in the presence of *p*-(dimethyl)aminothiophenol (*p*-DMATP).

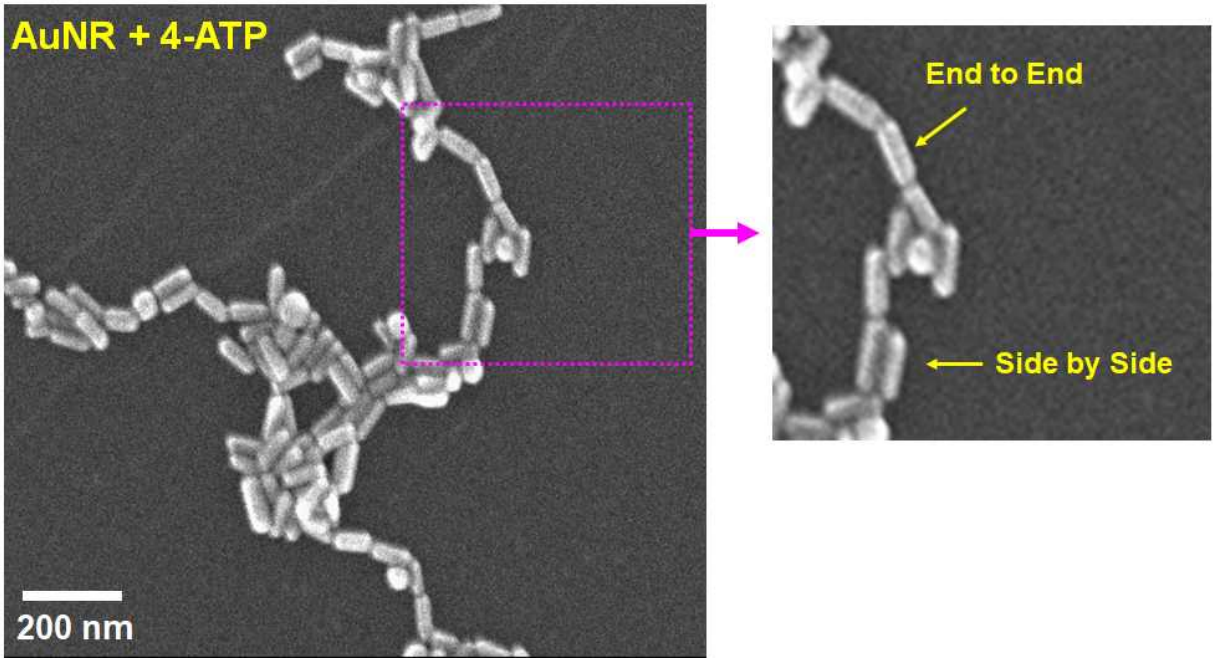

Fig. S5 SEM image of AuNRs in the presence of *p*-ATP. The formation of aggregates (both end-to-end interaction and side-by-side interaction) through intermolecular interaction among probe molecules in ethanol is confirmed.

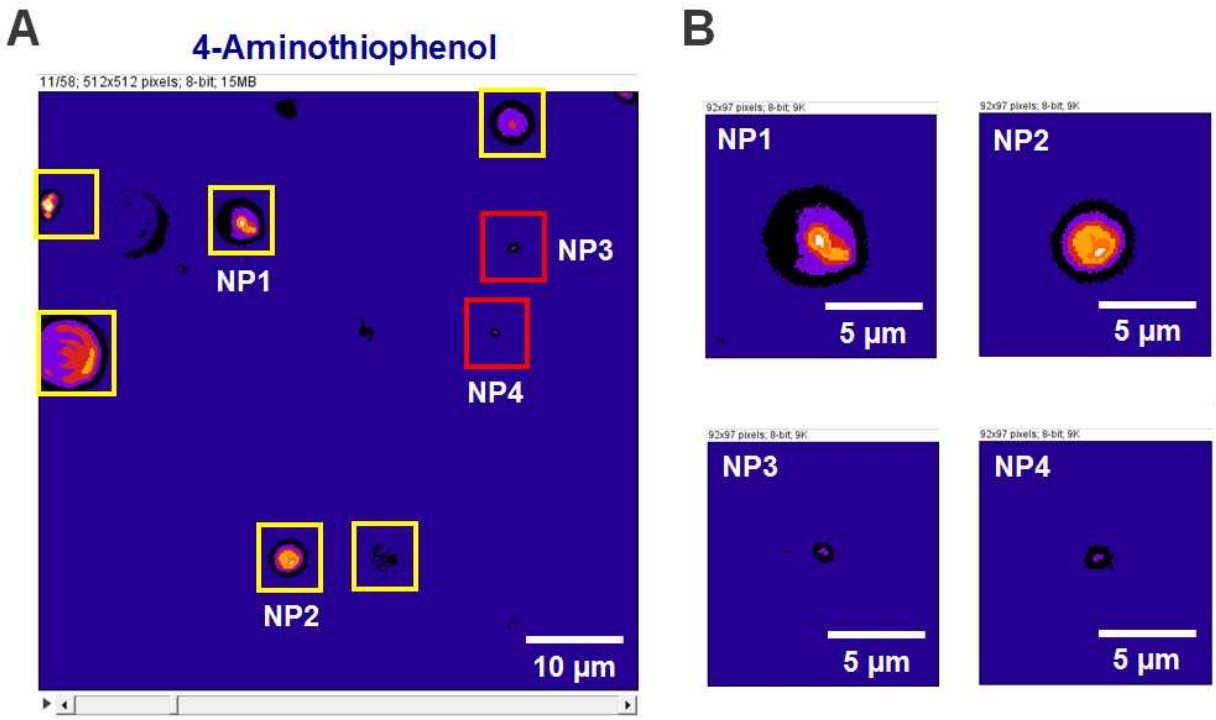

Fig. S6 (A) DF image to show the motion of AuNRs in the presence of *p*-NTP in solution. **(B)** Enlarged DF images of AuNRs selected and squared in (A). There is a tendency toward AuNR aggregates with intense scattering signals and slow movement of large, bright spots in the presence of *p*-ATP.

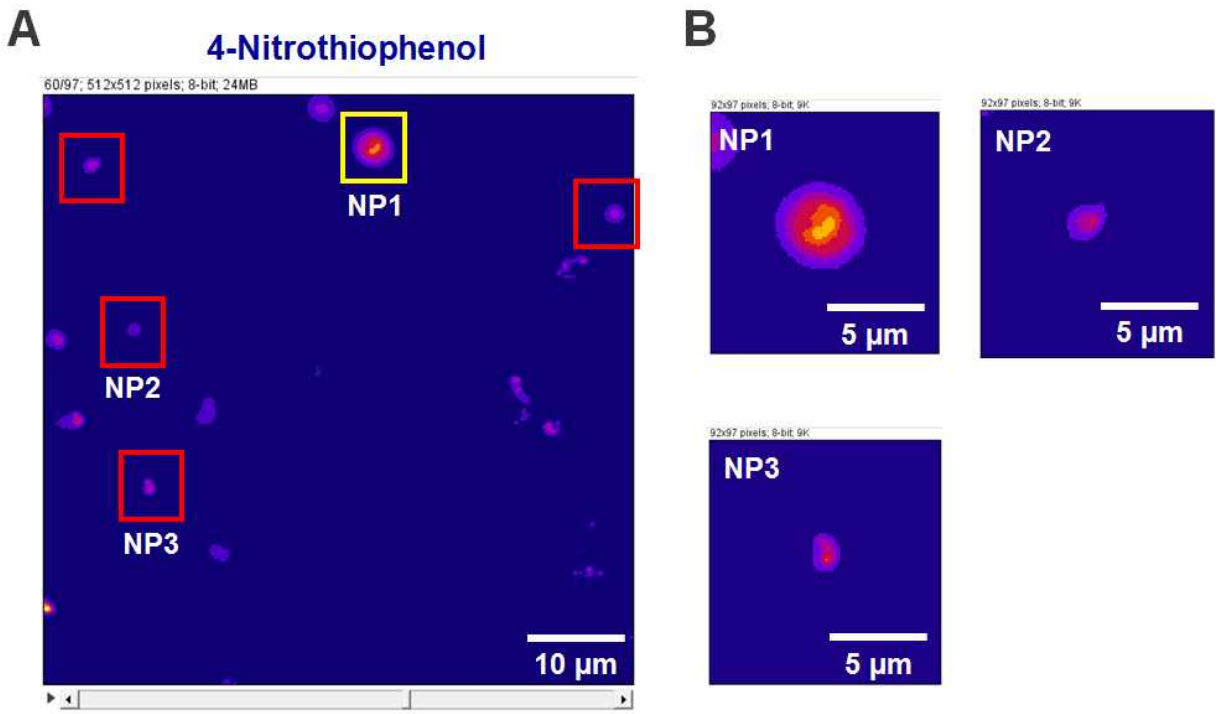

Fig. S7 (A) DF image to show the motion of AuNRs in the presence of *p*-NTP in solution. **(B)** Enlarged DF images of AuNRs selected and squared in (A). The AuNRs with *p*-NTP showed single nanoparticles or small aggregations, unlike *p*-ATP. The result supports the small possibility of intermolecular interaction due to the absence of hydrogen in the substituent group.

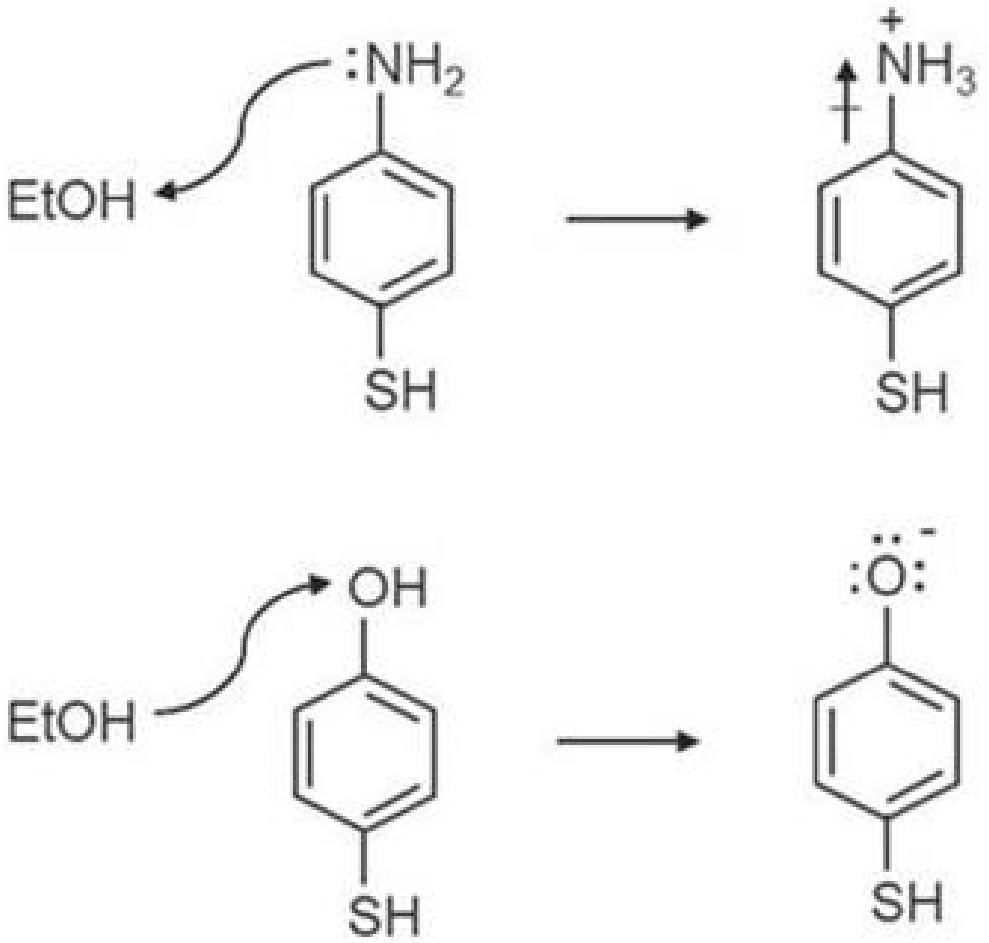

Fig. S8 The effect of ethanol solvent. When the lone pair of the amino group of *p*-ATP interacts with ethanol, the amino group ($-NH_2$) could become positively charged ($-NH_3^+$) by accepting hydrogen from ethanol; this form could temporarily become an EWG.

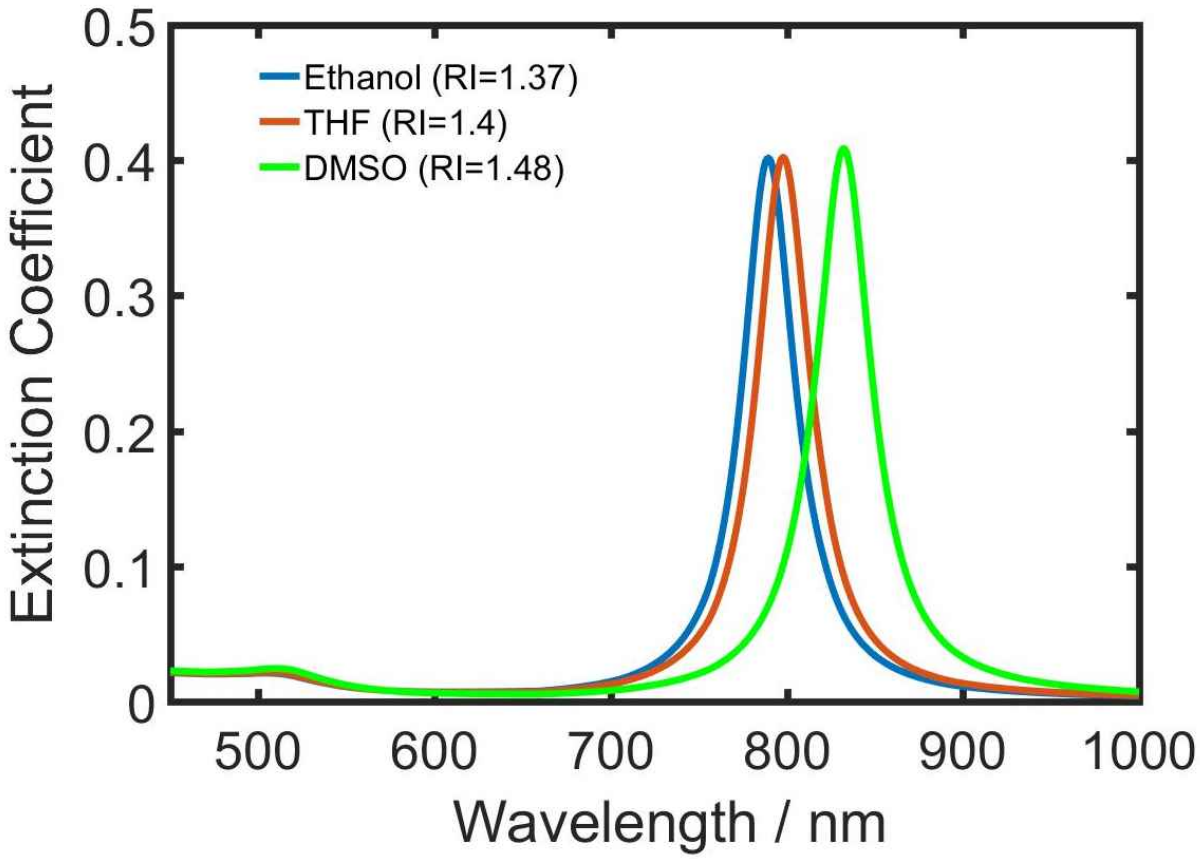

Fig. S9 The simulated LSPR absorption spectra of AuNRs at different RI media of ethanol (blue-curve), THF (red-curve), and DMSO (green-curve)