Electronic Supplementary Information

Tuning of Chemical Interface Damping in Single Gold Nanorods through pH-Dependent Host–Guest Interactions Using Cucurbit[6]uril

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Experimental Methods

Materials and Chemicals. Bis(3-aminopropyl) amine (BAPA, $C_6H_{17}N_3$, 98%) and cucurbit[6]uril hydrate ($C_{36}H_{36}N_{24}O_{12}\cdot xH_2O$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 35%) was purchased from DAEJUNG, and sodium hydroxide (NaOH, 98.0%) was purchased form SAMCHUN. CTAB-stabilized AuNRs (25 nm × 75 nm) was purchased from Nanopartz (Loveland, CO, USA).

Sample Preparation. Slide glass (76 mm × 26 mm × 1 mm, MARIENFELD) and cover glass (22 mm × 22 mm, 24 mm × 50 mm, BRAND) were ultrasonically pre-cleaned with ethanol, deionized (DI) water and isopropyl alcohol for 15 min each. First, for the sample, AuNRs solution was diluted with DI water for minimize interparticle LSPR coupling. The diluted AuNR solution was sonicated for 15 min at room temperature to prevent aggregation. The diluted solution onto a slide glass and aqueous solution allowed to dry. Subsequently, oxygen plasma cleaner (PDC-32G-2, Harrick Plasma, USA) was used to remove the CTAB surrounding the AuNRs.

Characterization of AuNRs. The morphology and size distribution of AuNRs were investigated using a scanning electron microscope (SEM; JSM-6500F, JEOL, Japan). The ensemble extinction spectrum of AuNRs was obtained using a UV-Vis spectrophotometer (UV-1800, SHIMADZU, Japan).

Single-Particle DF Microscopy and Spectroscopy. DF spectroscopic analysis was done by using microscope camera system at total-period analysis center for Ulsan chemical industry of

Korea Basic Science Institute (KBSI). To obtain the spectrum of single AuNR particles using a scattering-based DF microscope (ECLIPSE Ti-U, NIKON, Japan), we utilized an oil iris objective lens (N.A.= 0.7-1.4) connected to an Andor CCD camera (Newton DU920P-OE, UK) coupled with an Andor spectrometer (SHAMROCK 303i, SR-303I-A). Scattered light from a single particle was collected by the objective lens and transmitted to the entrance of the spectrometer. The scattered light was then dispersed through a grating (300 l/mm) inside the spectrometer and detected by the CCD camera (central wavelength:700 nm). Background spectra were measured in areas without nanoparticles. DF scattering images were obtained using an Andor EMCCD camera (iXon Ultra 897, UK). Image J software was used for image analysis, and data analysis was performed using Matlab and Origin programs.

Characterization of CB[6]-BAPA Complex. The complex was formed by reacting CB[6] with BAPA in H_2O. The formation and molecular weight of the complex were confirmed using time-of-flight mass spectrometry (TOF-MS, Accu TOF 4G+ DART, JEOL, USA) in central research facilities of UNIST, South Korea.

Supplementary Figures

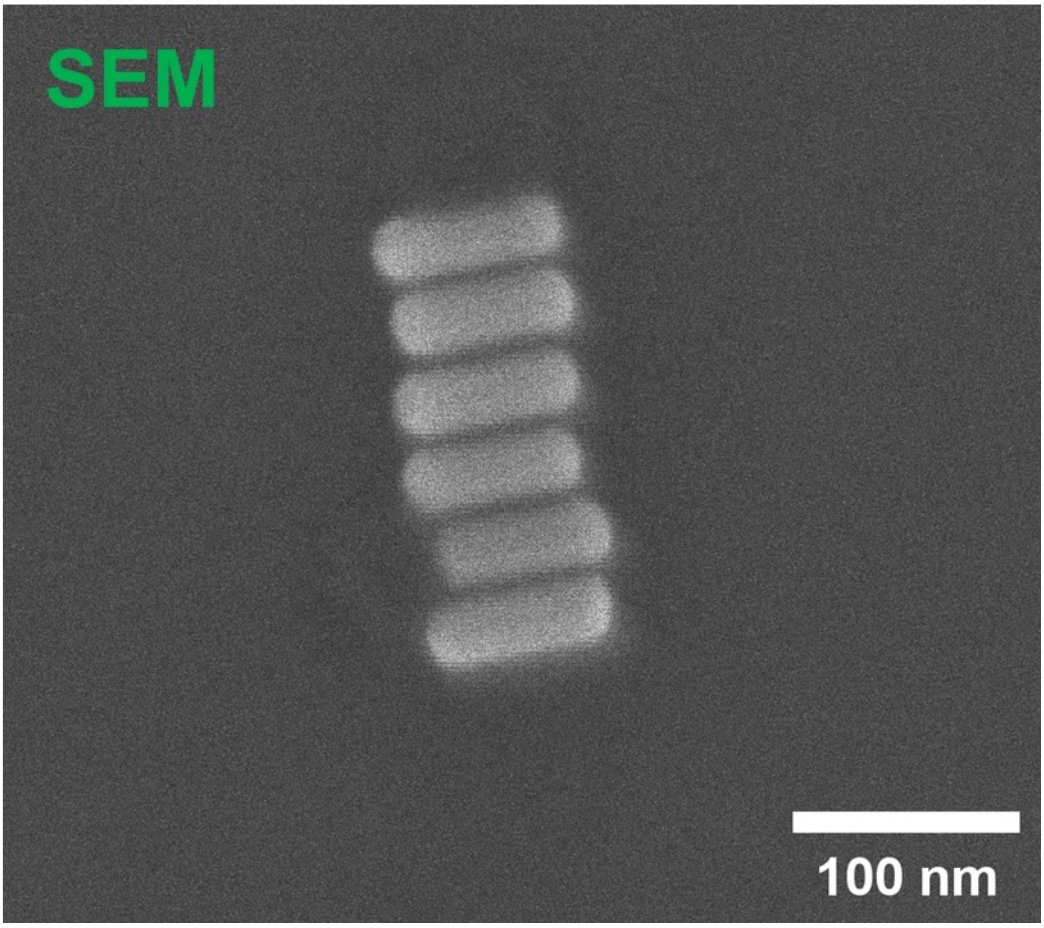


Fig. S1 SEM image of CTAB-capped AuNRs used in this study

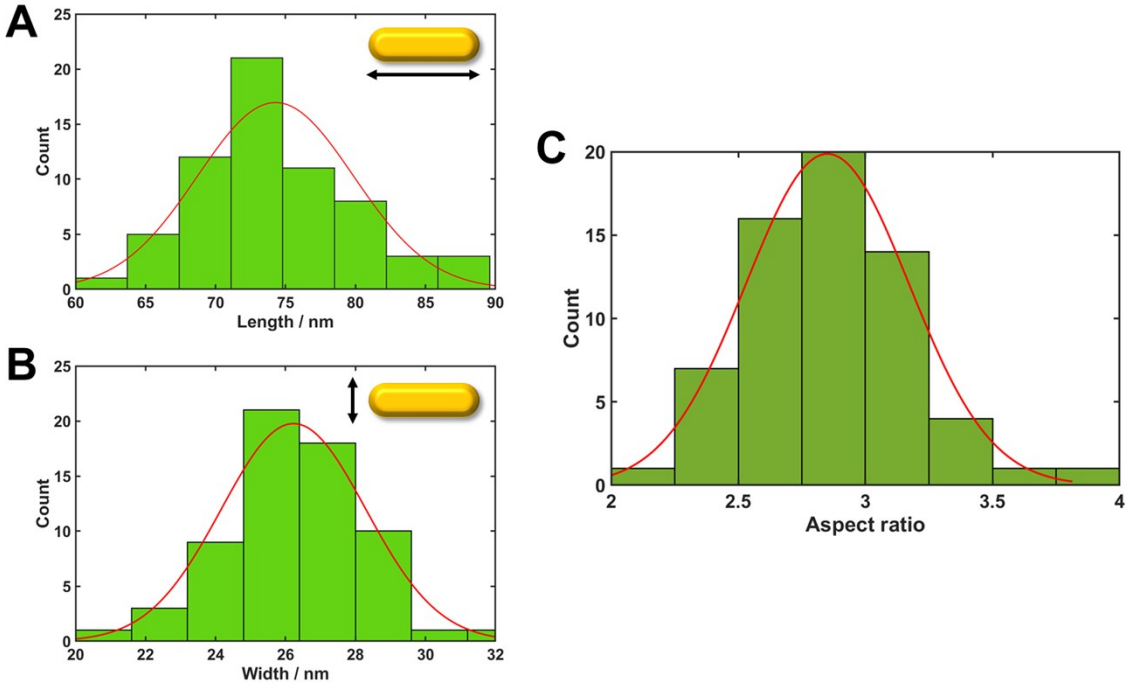


Fig. S2 Histograms to show the average length **(A)**, width **(B)** and aspect ratio **(C)** of single AuNRs used in this study. Their length, width, and aspect ratio were determined to be 23.23 (±2.07) nm, 74.29 (±5.57) nm, and 2.85 (±0.32), respectively.

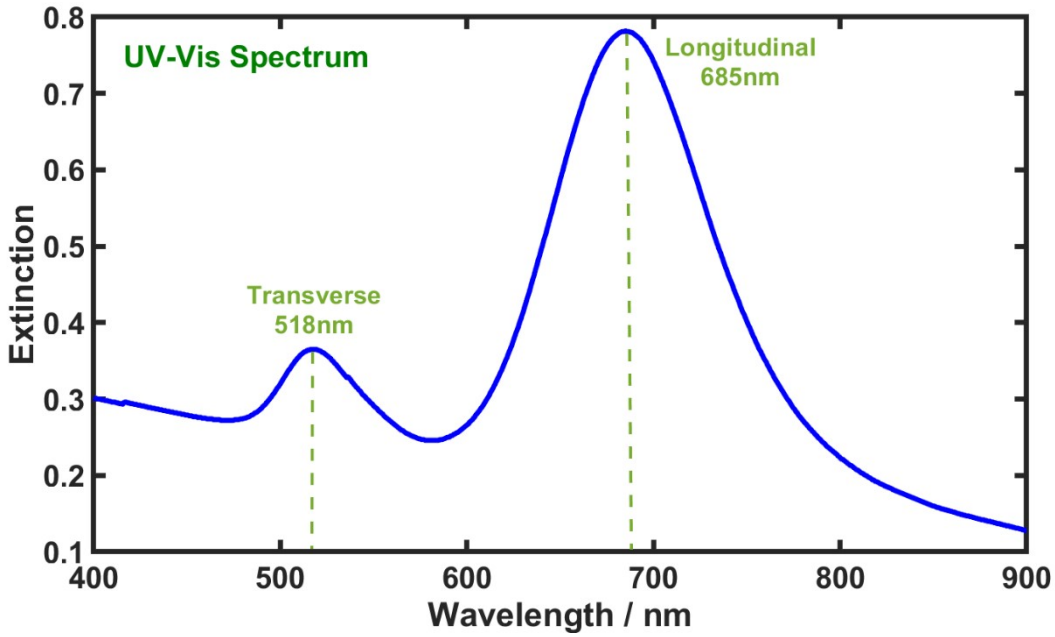


Fig. S3 UV-Vis extinction spectrum of AuNRs dispersed in water. Two transverse and longitudinal LSPR peaks are observed at approximately 518 nm and 685 nm, respectively.

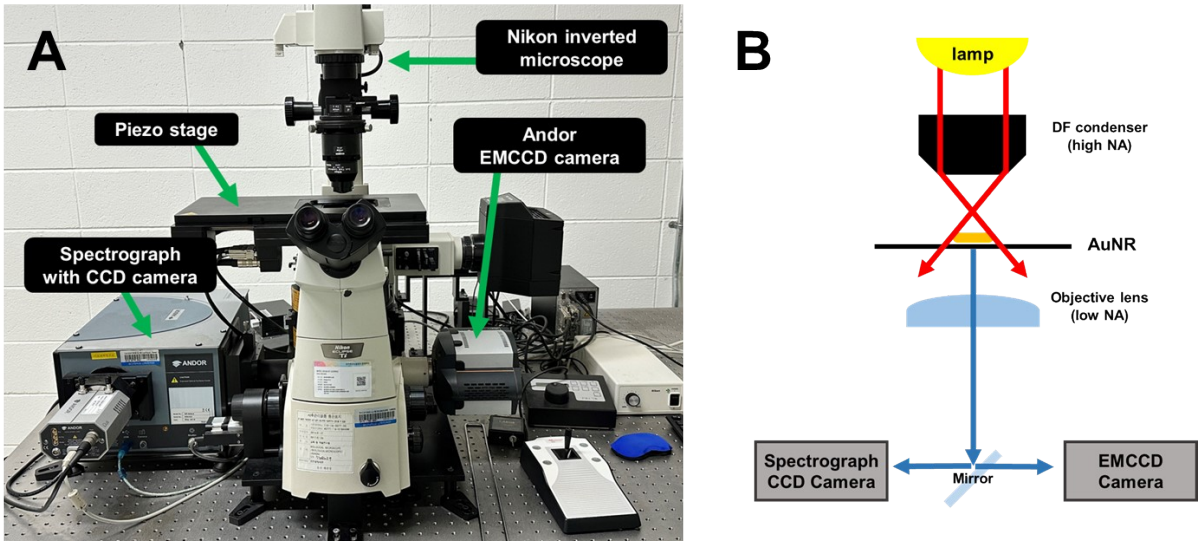


Fig. S4 (A) A photograph showing the experimental setup of single-particle microscopy and spectroscopy. **(B)** Schematic illustrating the working principle of scattering-based DF microscopy and spectroscopy

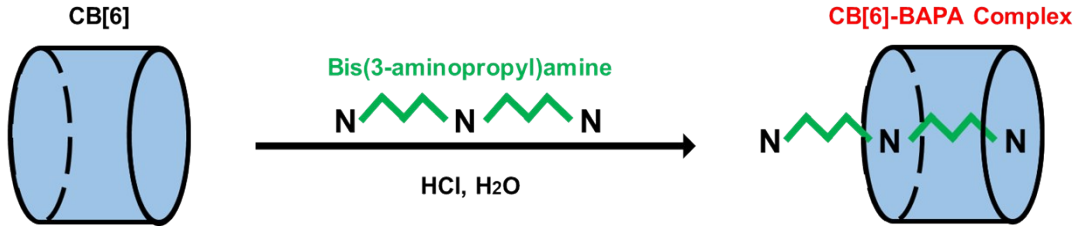


Fig. S5 Schematic representing the process of forming the CB[6]-BAPA complex.

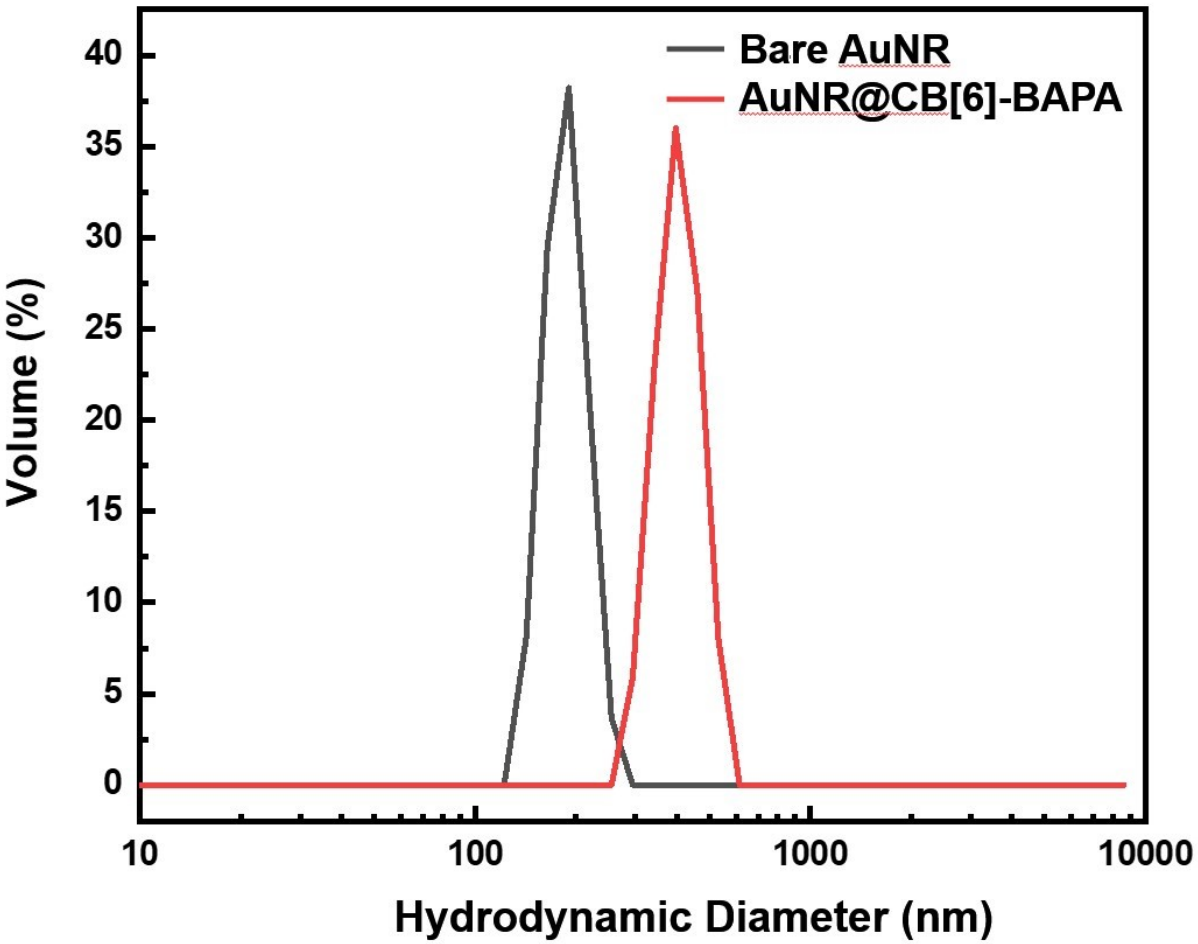


Fig. S6 Dynamic light scattering measurements of bare AuNRs (black curve) and AuNRs@CB[6]-BAPA (red curve).

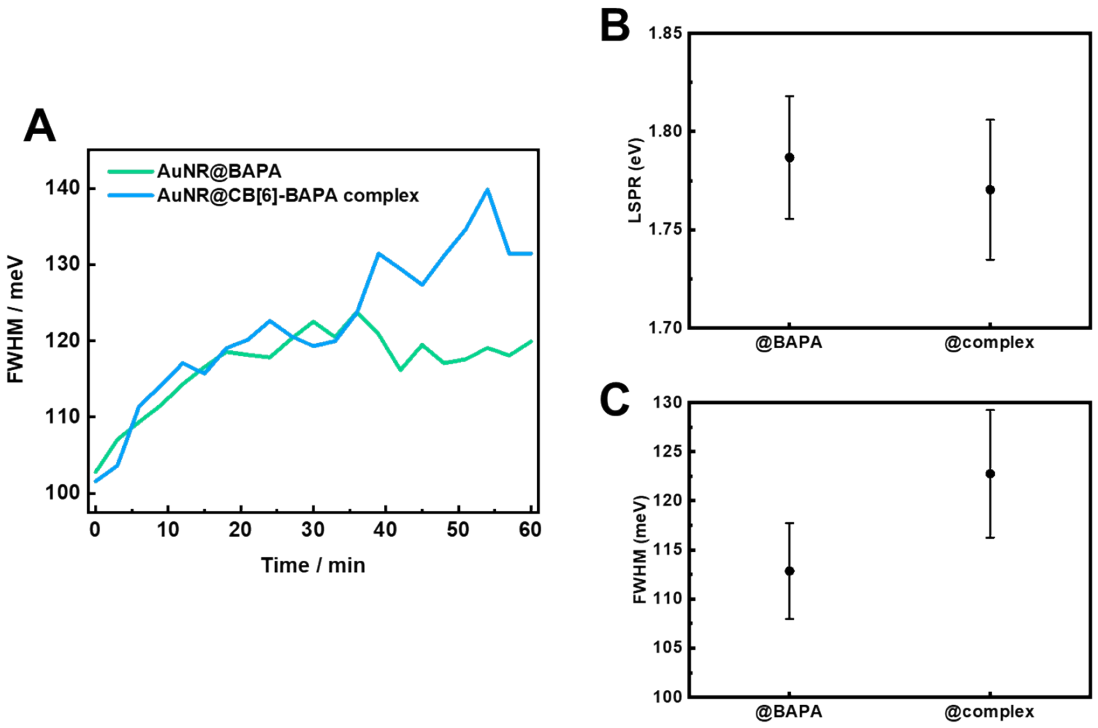
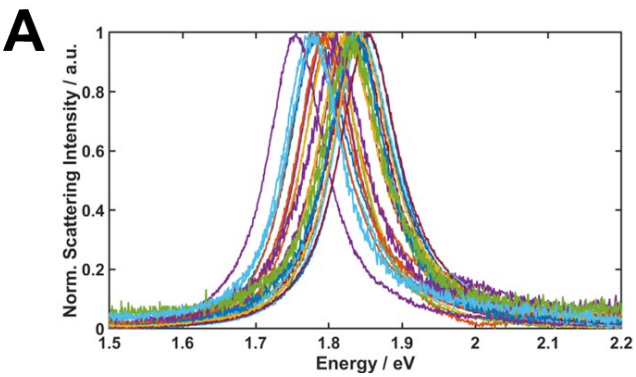
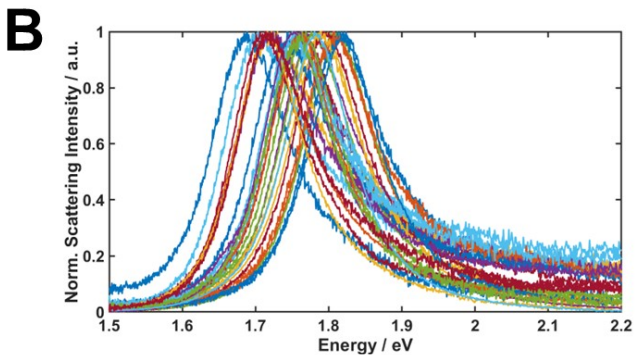


Fig. S7 (A) Changes in FWHM over time when BAPA and CB[6]-BAPA complex are attached to single AuNRs. **(B, C)** Comparison of LSPR wavelength and FWHM in BAPA attached to AuNR and CB[6]-BAPA complex attached to AuNR.



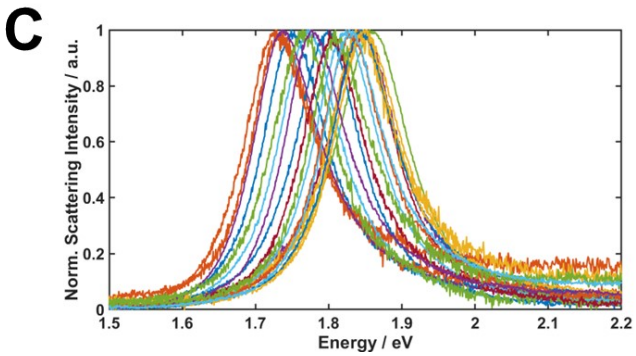
Bare

LSPR (eV)	FWHM (meV)
1.81330665	96.90606522



@Complex

LSPR (eV)	FWHM (meV)
1.770400786	122.7530714



w; NaOH

LSPR (eV)	FWHM (meV)
1.805669	109.87475

Fig. S8 (A) Single particle scattering spectra of AuNRs and their corresponding average values. **(B)** Single particle scattering spectra of AuNRs attached with CB[6]-BAPA complex and their corresponding average values. **(C)** Single particle scattering spectra and corresponding average values for AuNRs attached with CB[6]-BAPA when immersed in NaOH solution.

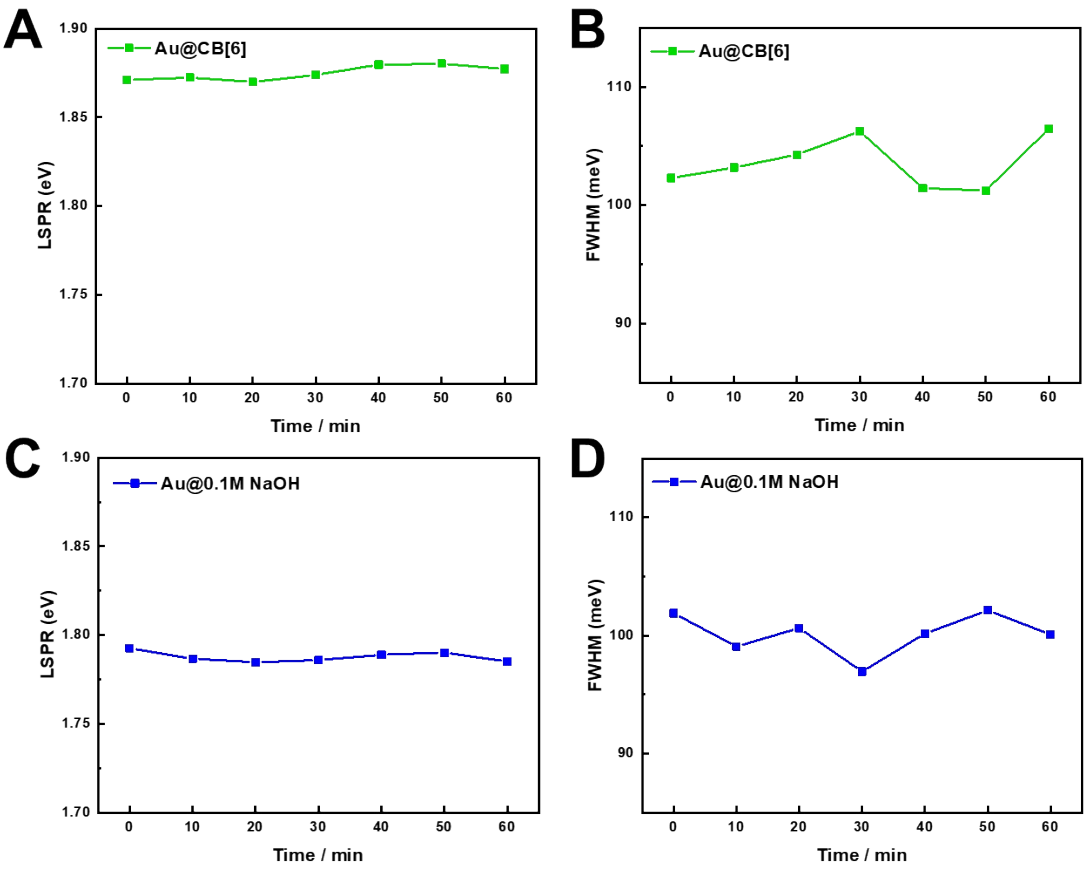


Fig. S9 (A, B) Time-dependent variations of (A) LSPR energy and (B) FWHM of a single AuNR upon addition of CB[6]. **(C, D)** Time-dependent variation of (C) LSPR energy and (D) FWHM of a single AuNR in NaOH solution (0.1 M).