

Experimental

The Ag dimer arrays were prepared by an angle-resolved nanosphere lithography technique (AR-NSL) using repeated vapor depositions onto the polystyrene (PS) particle (Polysciences Inc.; diameters = 350 nm) monolayer prepared on a glass substrate. Aqueous PS particle suspension was concentrated to 8 and 10 wt.%, and then diluted by ethanol (60 and 50 %). As well as previously documented drop-coating method, we adapted the other method using PS monolayers prepared on liquid-gas interfaces to improve the quality of the array.^{3, 20} The PS solutions (20 μ L) were dropped on convex surface of a watch glass immersed in Milli-Q water. Thin water layer on the glass surface leads to uniform spreading of PS beads on the air-water interface. After the spreading of PS beads to water surface, the layer was packed tight in the course of nature. The change in the surface tension of the water around the PS layer results in the formation of well-ordered monolayers with low density of defects, dislocations, and vacancies on the liquid-water interface. The prepared monolayer with high quality was then lifted off from the water surface using cleaned glass substrate. The metal was deposited onto the PS monolayer prepared on the glass substrate. After the first metal deposition, the second metal was deposited with different angles. Then, the PS mask was removed by sonication in Milli-Q water for 10-30 s. Extinction spectrum of the metal dimer array in the visible-near infrared region were recorded utilizing a multi-channel spectrometer (MCPD-2000, Ohtsuka Electronics). The structure of the dimer on the glass substrate was inspected by an atomic force microscope (AFM, Nanoscope-IIIa, Digital Instruments) in air.

A home-made polarized Raman microprobe spectrometer was specially modified for NIR laser light ($\lambda_{ex} = 785$ nm). Raman measurements were carried out at the backscattering configuration collecting the scattering photons with the parallel and the perpendicular polarization directions simultaneously (Figure S1). The expanded NIR beam is focused onto the sample using a water-immersion objective lens with 100x magnification and a numerical aperture of 1.0. The estimated spot size of irradiation ca. 1 μ m,

with tunable output intensity was in the range between $10 \mu\text{W}$ and 20mW . All of Raman measurements were carried out in-situ by immersion of the SERS active substrates into aqueous solutions containing target molecule (4,4'-bipyridine; reagent grade, Wako Co. Ltd.) with controlled concentration ($1 \mu\text{M} - 1 \text{mM}$). The measurement on a single crystal (Figure S2) was carried out in air by controlling the excitation polarization direction to the crystal axis determined by XRD.

The dimer structure consists of the different size Ag triangle. The size is 50nm , 100nm at each side of triangle, and the height is 25nm , 30nm . Gap size are estimated by comparison of the calculation of reference S1 at the Supporting Information. From the extinction spectra at Fig. 2(b), the polarized excitation along the long axis leads to the appearance of a peak at longer wavelength (around 800nm). This agrees well with the theoretically calculated spectra of "tip-to-side" Ag triangular dimers whose distances are a few nanometers. So the AR-NSL dimers has a few nanometers gap distance. The spot size irradiated to substrate is estimated $\sim 1 \mu\text{m}$, and this area include about 9-10 dimers. A blown-up image are shown in reference S2.

The stability of the metal structure was checked by the polarized Rayleigh scattering light measurement. Completely the same polarized properties were obtained before and after the light irradiation, indicating that the metal dimer structure is stable regardless of the light irradiation.

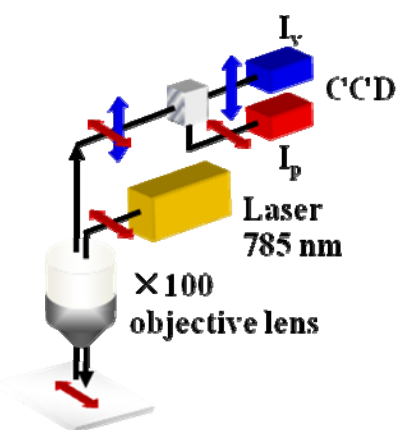


Figure S1. Schematic presentation of a polarized Raman microprobe spectrometer

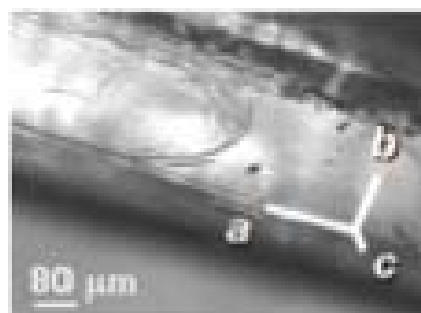


Figure S2. Photograph of a 4,4'-bipyridine single crystal.

Density functional theory (DFT) calculations were carried out by the use of the Gaussian 03, revision E.01, at the B3LYP level of DFT with 6-31G** basis sets. Calculation were carried out without the contribution of the resonance of 4,4'-bipyridine molecule. , Raman intensity was estimated using $I \propto \nu_s^4 (e_s \alpha e_i)^2$

where ν_s is the wavenumber of the Raman scattering and e_s, e_i are the unit vector along the scattering and incident electric field and α is the polarization tensor.

Calculated modes were shown as the animations; 770 and 870 cm^{-1} assigned to the out-of-plane ring and C-H deformation (Figure S3(a), (b)); 1240 cm^{-1} assigned to in-plane C-H bending mode (Figure S3(c)); 1300 cm^{-1} assigned to the inter-ring stretching mode (Figure S3(d)).

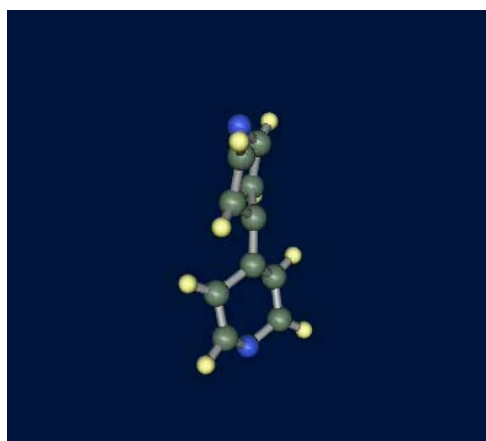


Figure S3 (a) mode at 770 cm^{-1} assigned to the out-of-plane ring deformation



Figure S3 (b) mode at 870 cm^{-1} assigned to the out-of-plane C-H deformation

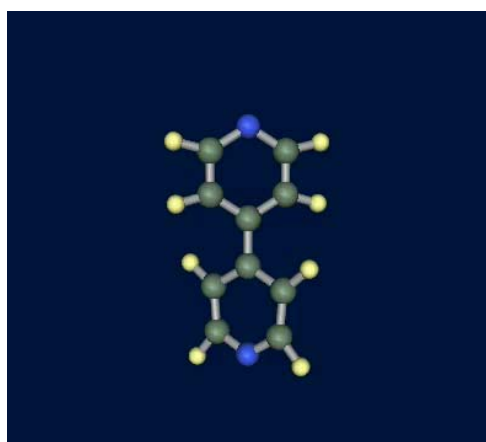


Figure S3 (c) mode at 1230 cm^{-1} assigned to the C-H bending.

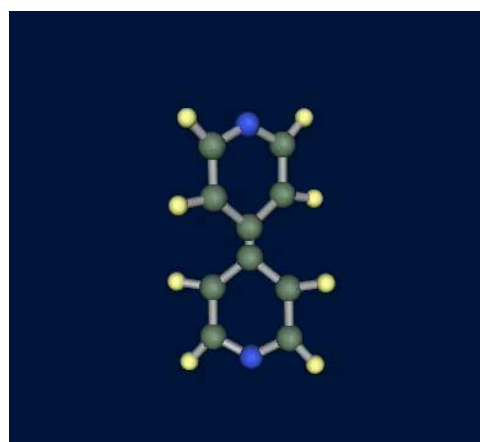


Figure S3 (d) mode at 1300 cm^{-1} assigned to the inter-ring stretching.

Reference

- 1 E. Hao, G. C. Schatz, *J. Chem. Phys.*, 2004, **120**, 357.
- 2 Y. Sawai, B. Takimoto, H. Nabika, K. Ajito, K. Murakoshi, *Faraday Discuss.*, 2006, **132**, 179.