Supporting Information

Directional Fluorescence Emission Mediated by Chemically-Prepared Plasmonic Nanowire Junctions

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S1. Sample preparation

Protocol for synthesis of coupled silver nanowire dimer

The serially coupled AgNW dimers were synthesized using an established method.[1,2] This is based on well-known method of polyol reduction of silver nitrate ($AgNO_3$).[3] First, 3 ml 0.0854 M solution of $AgNO_3$ in ethylene glycol and 3 ml 0.3416 M solution of polyvinyl-pyrrolidone (PVP) in ethylene glycol were prepared separately. These two solutions were very slowly (0.2 ml/min) injected into the 5ml of ethylene glycol, preheated at 160^0C. The whole mixture was then stirred for one hour at 160^0C. This solution contained nanowires along with nanoparticles. These nanoparticles were removed by centrifuging in deionized water and discarding supernatants. After sonication of the sample, we obtained a large fraction of nanowire dimers, as well as isolated nanowires of various lengths. Figure 1a is an optical image and figure 1b is scanning electron microscope image of the Ag NW dimer used for fluorescence study.

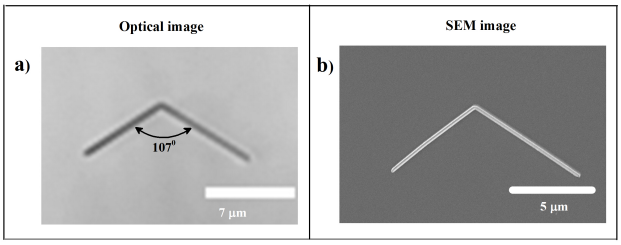

Figure S1: a) Optical image of a serially coupled Ag NW dimer used for the study. b) SEM image of the same nanowire.

Sample preparation for optical measurements:

Ethylene glycol and PVP on the nanowires were removed by washing it twice in acetone and 6 times in ethanol. Then the wires were dispersed in mili-Q water. 10μl of this suspension is spin-coated on a glass microslide. Many AgNW dimers along with isolated nanowires were seen by an optical microscope on the prepared microslide. For fluorescence optical studies

a mixture of polyvinyl alcohol (PVA) and nile blue-A was spin coated on the microslide containing AgNW dimer to create a very thin film (30nm) of dye doped PVA on AgNW.

S2. Unidirectional fluorescence emission from coupled nanowire junction

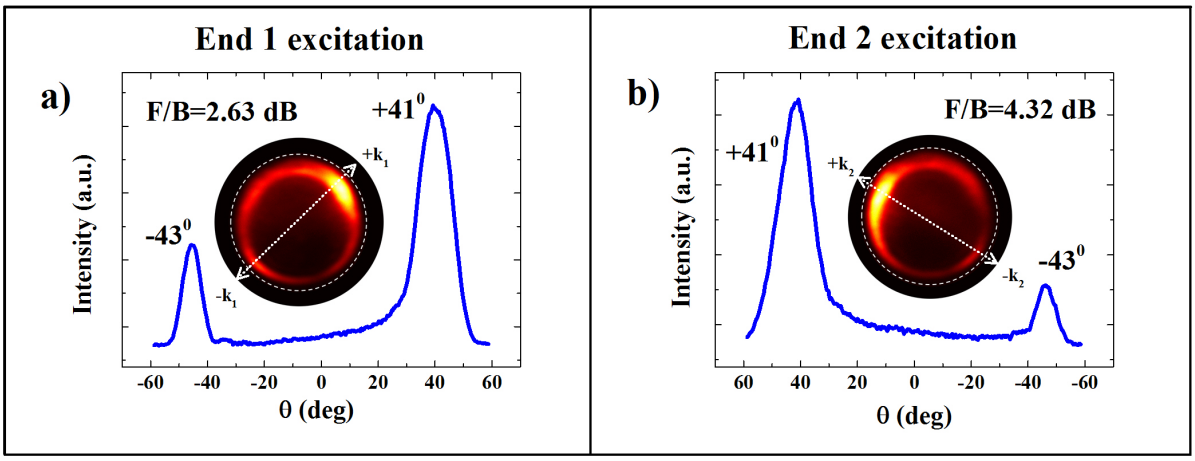

Figure S2: Degree of unidirectional emission. a) I vs θ plot in case end1 excitation. b) I vs θ for end 2 excitation. Intensity variation was taken along the white dotted line in inset BFP image for respective cases. This line represents the orientation of the excited wire.

In case of single end excitation, unidirectional fluorescence emission was observed (Also see in figure 1 of the main article). Here the intensity I variation along radial direction θ has been plotted along the axis of the excited wire. Figure S3a represents the case of end 1 excitation. In this case, we observed a emission peak at $\theta = +41^0$ in the forward direction, whereas a much weaker peak was observed in the backward direction at $\theta = -43^0$. The forward to backward ratio of this emission in dB was calculated to be 2.63dB. When the other end was excited as shown is figure S3b. the unidirectional emission along k_2 direction had an forward to backward scattering ratio of 4.32 dB.

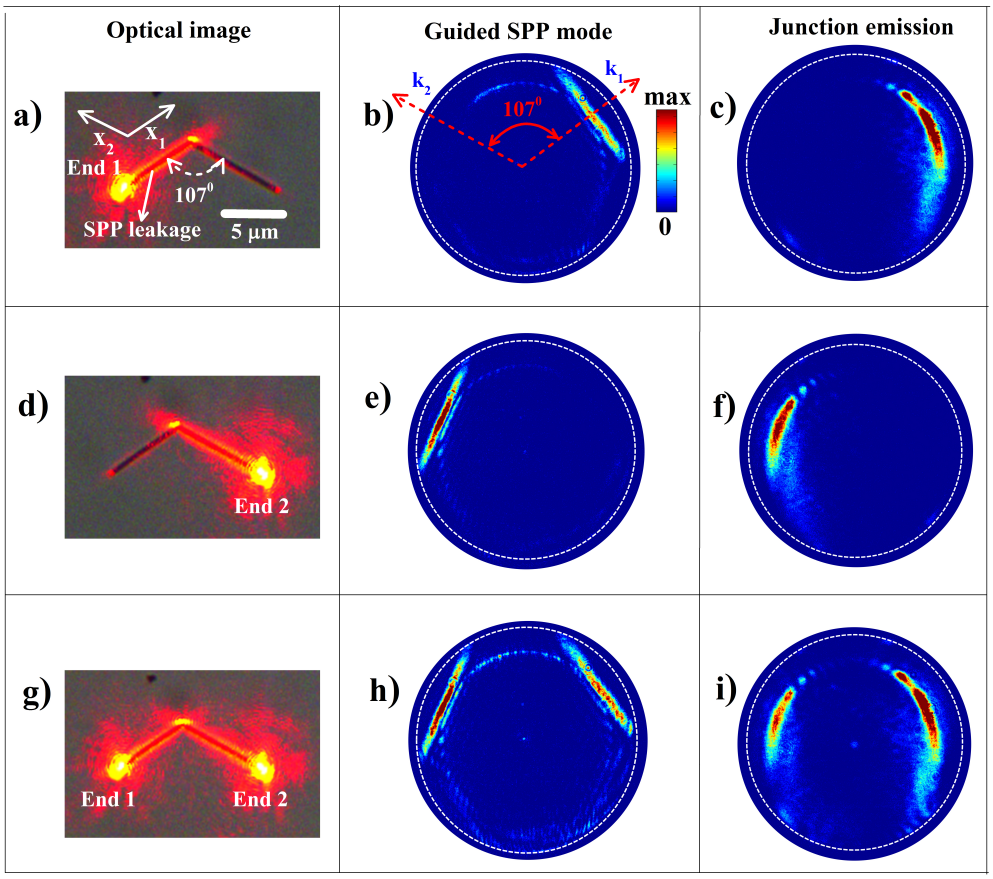

Figure S3: Characterization of plasmon propagation through the nanowire system. a) Optical image of SPP propagation due to laser excitation at end 1. b) BFP image of the guided SPP mode c) BFP image of emission from the junction. c),d),e) are corresponding data for end 2 excitation and end 1 + end 2 excitation of the system.

S3: Characterization of leaky plasmon modes in the Ag NW dimer

As we discussed in the main text that the experimental observations are governed by two process. Out of which process I represents the excitation of fluorescent molecules deposited on the wire. This excitation is happened due to the interaction between molecules and the propagating SPP modes generated in the wires due to focused illumination of the free ends. To understand this, we characterized the guided SPP modes present in the system[4]. For this experiment we used an Ag NW dimer of dimensions similar to the one shown in figure

2 in the main article. This time the wire was not coated with nile blue and no Rayleigh rejection filter was used in the detection path. When end 1 of the dimer was excited, leaky plasmon mode was observed along the excited wire and weak leakage along the other was also detected (see figure S4a). Presence of underlying high refractive index medium is the reason behind this leakage radiation. By monitoring this leaky SPP in the BFP, we observed a bright line across the plane perpendicular to the axis k_1 at $k_1/k_2 = 1.05$, where $k_0 = 2\pi/\lambda_0$ is the free space wave number (see figure S4b). Very weak signal was observed along $-k_1$ which indicated very low reflection from the junction. This implies that the excited wire behaved as one dimensional waveguide[5] where SPPs are being guided towards the junction while being confined in the direction perpendicular to x_1. Very weak signal along $-k_2$ direction in the BFP image in figure S4b further implies that very small part of the energy is being coupled to the SPP modes in the other wire. Therefore, maximum energy is being decoupled at the junction and efficiently scattered along the forward direction of the axis of the excited nanowire (see figure S4c) to conserve the energy and momentum of propagating SPPs. Illumination of end 2 of the dimer (see figure S4d) and projection of leaky SPPs in the BFP of the objective also showed a guided mode perpendicular to $+k_2$ direction (figure S4e). Monitored emission from the junction in BFP was again unidirectional along the axis of the excited wire(figure S4f). When the both the ends were excited propagating SPP modes directed towards the junction were generated in the both wires (see figure S4g-i).

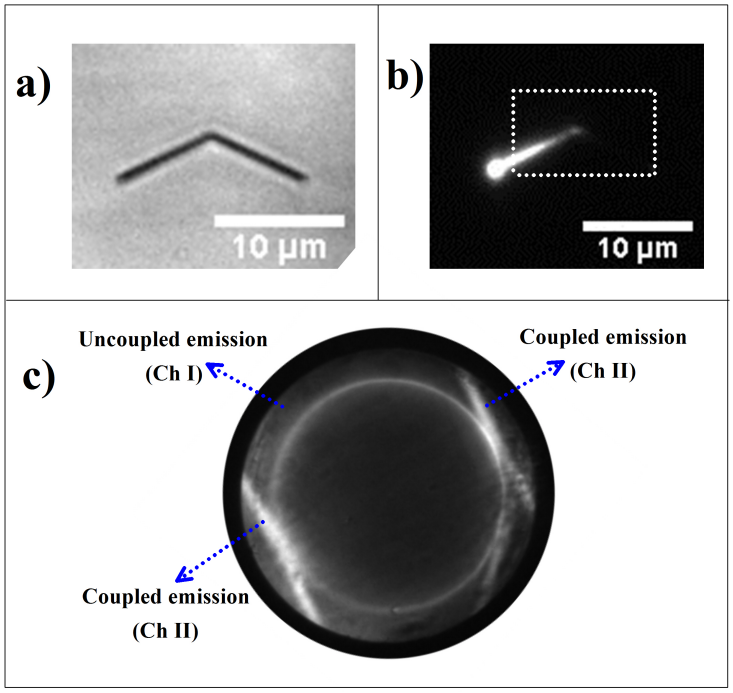

Figure S4: Plasmon coupled emission of molecules coated along the nanowire dimer: a) Optical image of the wire used for the experiment. b)Fluorescence optical image of single end excitation and c)corresponding BFP image.

S4. Plasmon coupled emission from molecule coated on the wire.

To find out how the emission from the molecules coated on the wire is being influenced due to the presence of the plasmonic nanowires (process *II* in figure 3 of the main article) we performed the following experiment. Here we not only examined the fluorescence emission from the junction but also from the molecules caoted along the entire Ag NW dimer. Optical image of the wire we used for this experiment is shown in figure S5a. Figure S5b shows the fluorescence image of the dimer when one of the ends was excited. The area enclosed by the white dotted rectangle signifies the area that was projected in the back-focal plane of the microscope objective lens. Interestingly, here we observed two guided SPP modes in both the direction forward and backward along the excited wire along with an isotropic fluorescence background (figure S5c). The background of isotropic emission was obtained

due to molecular emission that was not coupled to the plasmon modes of the nanowire dimer. This radiative decay channel is labelled as Channel *I* in figure 3a in main article. The guided modes were obtained because of the plasmon coupled emission of the molecules coated on the Ag NW dimer. As indicated in the main text, the molecular emission that coupled to the plasmon modes of the system gave rise to prapagating SPPs in both directions along the excited nanowire. The leakage of these guided SPP modes into the under-lying glass substrate allowed us detect them. This emission channel was labelled as Channel *II* in figure 3 of main article.

Apart from this, we also observed weak guided SPP modes along the orientation of the other wire. This can be considered as the signature of SPP tunnelling into the adjoined wire from the excited nanowire through the junction.

These observations further supported that the plasmon coupled emission of the molecules coated on the Ag NW dimer is the main reason behind observing such directional fluorescence from the junction.

S5: Propagation lengths of the SPP modes in a serially coupled NW dimer

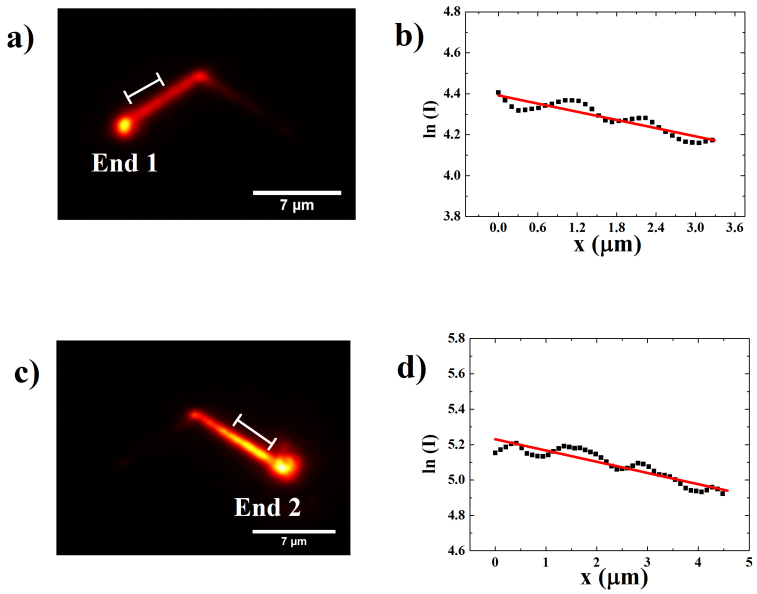

Figure S5: Plasmon propagation length calculation: a)Fluorescence image of a coupled wire when end 1 was excited. b)$ln(I)$ vs distance (x) plot for the wire along the white line shown in the fluorescence image. c) Fluorescence image of the wire when end 2 was illuminated. d)Corresponding $ln(I)$ vs x plot.

To calculate propagation length of SP modes excited in the coupled wire dimer we performed the following experiment.[6] First we coated the dimers with a fluorescent dye, Nile blue-A and captured fluorescence optical images of the Ag NW dimer for single end excitations (see figure S6 a and c). The intensity of the fluorescence was measured at different points along the white line shown in the optical images. Generally propagating SP mode intensity decays with distance at a rate given by $I = I_0 exp(-\frac{x}{L})$. Where x is the distance and L is the propagation length. We plotted measured intensities (I) as function of distances (x) in figure S6 b and d. The slope of the linear fit of the $ln(I)$ vs x plot gives plasmon propagation length for the particular excited nanowire. In this case for excitation shown

in figure S6a, the wire had propagation length of $16\mu m$ and for excitation shown in figure S6c, the wire had a propagation length of $14\mu m$. The wires we prepared had a propagation length ranging from $7\mu m$ to $17\mu m$ which is in agreement to what is already reported in case of silver nanowires.

S6: Influence of the mutual phase of the excitation laser at the ends of the nanowire on SPP interference at the junction

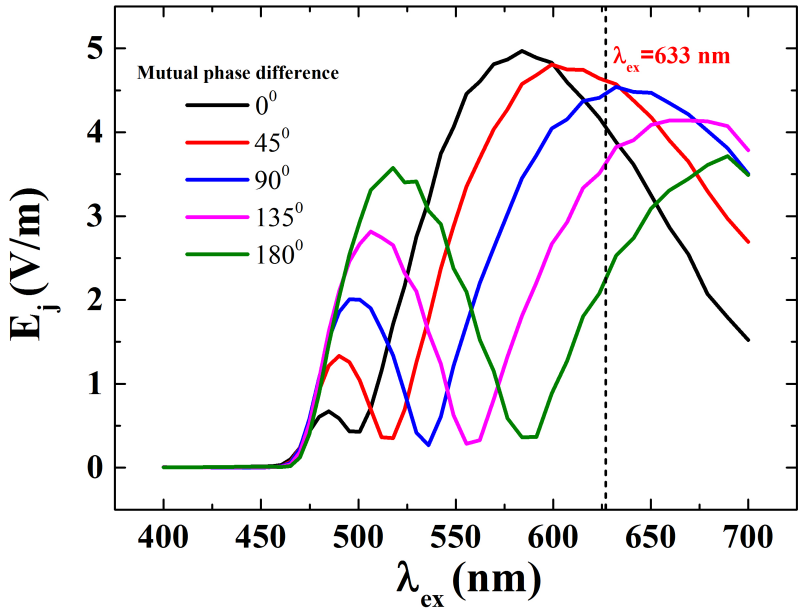

Figure S6: Variation of junction electric field E_j with excitation wavelength λ_{ex} as a function of mutual phase of the excitation beams at the ends of the nanowire dimer.

References

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