Supporting Information for:

Tuning Nanoscale Plasmon-Exciton Coupling *via* Chemical Interface Damping

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S1. Synthesis of gold nanorods

Chemical used:

Gold (III) chloride trihydrate (HAuCl₄.3H₂O), Hexadecyltrimethylammonium bromide (CTAB), 5-bromosalicylic acid (5-BSA), Silver nitrate (AgNO₃), L-Ascorbic acid (AA), Hydroquinone (HQ), Sodium borohydride (NaBH₄), 4-Nitrothiophenol (4-NTP) were purchased from Sigma-Aldrich. H₂SO₄ and H₂O₂ were purchased from Thermo Fisher and Merc, respectively. Cy78 dye was bought from Few Chemicals. No purification was performed further for any chemicals. HPLC grade water and MeOH were used throughout for synthesis and optical measurements.

Synthesis of NR1 and NR2:

For this paper, NR1 and NR2 were synthesized following the previously reported two-step method by Ye *et. al.*¹ In the first step, a seed solution was prepared by mixing 5 mL of 0.5 mM HAuCl₄ with 5 mL of 0.2 M CTAB solution. 0.6 mL of 0.01 M NaBH₄ diluted to 1 mL, and under vigorous stirring conditions was injected into the Au (III) and CTAB mixture. After that, it was stirred for 2 minutes at 1200 rpm and kept undisturbed for 2 hours in the dark for further use (used for both NR1 and NR2).

For the growth of the nanorods, 0.18 g CTAB and 0.022 g 5-bromosalicylic acid (5-BSA) were mixed and dissolved into 5 mL of warm water in a culture tube. After cooling it to 30°C, 165 μ L 4 mM AgNO₃ solution was added and kept in the dark for another 15 minutes at 30°C. Then, 5 mL of 1 mM HAuCl₄ solution was added to it. After 15 minutes of slow stirring (400 rpm) at 30°C, 40 μ L of 0.064 M ascorbic acid (AA) was injected and again stirred gently until the solution became colorless. To it, then, the previously prepared 16 μ L seed solution was added and kept for 12 hours at 30°C undisturbed in the dark.

In the growth step of NR2, all the chemicals were mixed the same as that for NR1, Except AgNO₃ and seed solution. Instead of 165 μ L 4 mM AgNO₃ solution and 16 μ L seed solution, 185 μ L 4 mM AgNO₃ solution and 8 μ L seed solution were added, respectively.

Synthesis of NR3:

The bigger Au NR sample, NR3 was synthesized following the one pot synthesis method reported by Zhang *et.* $al.^2$ In a glass vial, 40 µL of 0.01 M AgNO₃ was added to 3.8 mL of 0.2 M CTAB solution, followed by the addition of 304 µL of 0.01 M aqueous HAuCl₄ solution. After

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that, 400 μ L of 0.1 M hydroquinone solution were added and stirred gently until the dark yellow color disappeared. Then 0.013 μ L of freshly prepared ice cold 0.001 M NaBH₄ was added. Finally, the total volume of the reaction mixture was made to 7.6 mL by addition of water. The resultant mixture was kept in the dark, undisturbed for 12 hours at 30°C.

S2. Characterization of the gold nanorods:

The dimensions of the gold nanorods were estimated with the help of transmission electron microscopy (TEM) using a FEI-Tecnai G2 12 Twin 120 KV transmission electron microscope. The length (l) and diameter (d) of a large number of nanorods were analyzed using image-J software, and average values were calculated form those measurements. Fig. S1 shows the statistical distributions of the l and d for the three NR samples measured from the TEM images.



Fig. S1: Statistical distribution histograms of three synthesized nanorod samples measured using TEM images. The left panel corresponds to the diameter distribution measurements of (a) NR1, (c) NR2, and (e) NR3. The right panel shows the distribution of lengths of (b) NR1, (d) NR2, and (f) NR3. Red lines depict the normal distribution of the data set in each plot.

Sample	Diameter (nm)	Length (nm)	Avg. volume (nm ³)	Aspect ratio (AR)
NR1	12.3 <u>+</u> 1.6	30.8 <u>+</u> 5.7	3658	2.50
NR2	21.5 <u>+</u> 2.1	54.1 <u>+</u> 5.8	19631	2.51
NR3	40.4 <u>±</u> 1.5	101.2 ± 6.8	129662	2.50

Table S1: Average diameter (d), length (l) and volume (V) of different gold nanorod samples.

S3. Ensemble-level extinction spectra of NR samples before and after surface modification:



Fig. S2: Ensemble-level extinction spectra of Au nanorods prior to any surface modification (a-c: black lines) and after incubating for 8 hours with 4-NTP (d-f: red lines). The left panel (a and d), middle panel (b and e), and right panel (c and f) correspond to the NR1, NR2, and NR3, respectively.

S4. Determination of linewidth in ensemble-level extinction spectra using multi-peak fitting:

We used Origin 9.1 software to extract the linewidth of the ensemble-level extinction spectra of gold nanorods, before and after surface modification by 4-NTP. We used three peaks corresponding to (i) interband transition, (ii) transverse LSPR mode, and (iii) longitudinal LSPR mode of the nanorods.³ Note that here we are interested in the longitudinal mode and how it changes due to the 4-NTP modification of the Au NR surface⁴. Hence, the linewidth of a NR sample corresponds to the extracted linewidth of the longitudinal mode.



Fig. S3: Multi peak fitting analyses of the extinction spectra to extract the LSPR linewidth of (a) NR1, (b) NR2, and (c) NR3 are shown.

S5. Sample preparation for SERS measurements and results:

1 mL of the NR1 sample was centrifuged twice to remove the maximum amount of CTAB. 0.040 μ L methanolic 4-NTP was added to that and kept for 6-8 hours. After that, the solution was centrifuged, and the excess 4-NTP in the supernatant was removed. In the residue portion, 50 μ L water was added and a concentrated solution was prepared. This solution was drop-casted on a silicon wafer, previously cleaned with piranha solution (solution of H₂SO₄ and H₂O₂ in 3:1 ratio), and dried under vacuum. After drying, SERS signals from different parts of the sample were collected using WiTec CRM 200 Raman spectrometer equipped with a piezoscanner and a 100 × microscope objective (NA = 0.9). A continuous laser having 532 nm wavelength was used for excitation. The exposure time was 2 seconds while integration time was 10 sec As shown in Fig. S4, the characteristic peaks of 4-NTP were found (Raman signal of only 4-NTP on a silicon wafer is shown in the inset of Fig. S4) ^{5,6}. This data suggests the formation of strong bond between the gold surface and the thiol group of 4-NTP through favorable soft-soft interaction, which facilitates the direct transfer of hot electrons to the LUMO of adsorbed 4-NTP molecules.⁴



Fig. S4: SERS signal of 4-NTP functionalized Au nanorod (NR1). Clearly, the characteristic peaks of 4-NTP are visible: i.e., C-H stretching mode (1084 cm⁻¹), C-S stretching mode (1100 cm⁻¹), N–O bond stretching (symmetric) in –NO₂ group (1343 cm⁻¹) and C-C stretching mode (1571 cm⁻¹). Raman spectra of only 4-NTP on the silicon wafer is given in the inset.

S6. Preparation of plexciton hybrids:

For this study, two types of plexcitons were made following previously know protocol³:

(i) 2 mL of each synthesized nanorods was centrifuged (12,000 rpm 12 mins for NR1; 10,000 rpm 12 minutes for NR2; and 8,000 rpm 12 minutes for NR3) and redispersed in 1.7 mL water again. To it, 300 μ L aqueous 1 mM monomeric Cy78 solution was added. The resultant solution was kept in the dark for 24 hours. After that, the solutions were centrifuged again to remove the excess dye present, leaving the plexcitonic hybrids as residue. The residue was then redispersed in water for further experiments.

(ii) To investigate the impact of CID on plasmon-exciton coupling, the surface of the nanorods were modified with 4-NTP by addition of 0.080 μ L 1 mM 4-NTP solution (in methanol) beforehand to each set of centrifuged NR samples (1.7 mL) prior to the dye addition. After 6-

8 hours of 4-NTP addition, 300 µL aqueous 1 mM Cy78 monomeric solution was added and kept in the dark for 24 hours. Then the excess dye and unbound 4-NTP molecules were removed by centrifuging the mixtures again. Similarly, the obtained residue was redispersed in water for further experiments.

S7. Sample preparation for single-particle dark-field scattering and data acquisition:

Sample preparation:

Here we measured the Full Width at Half Maxima (FWHM) of the longitudinal LSPR mode obtained from the single-particle dark-field spectra of the gold nanorods. In this paper, we measured LSPR spectral linewidths (Γ_{scat}) of the same nanorod in three cases: (i) CTAB capped, (ii) "surface cleaned", i.e., washed by methanol, and (iii) surface modified with 4-NTP. For that, we immobilized gold nanorods on a glass slide and changed the adsorbate on the surface of the gold nanorods flowing desired chemicals according to our experimental requirements. Glass slides were cleaned using methanol and piranha solution. Then the glass slides were washed with distilled water, followed by deionized water and then immersed in a 1% v/v methanolic solution of (3-Mercaptopropyl)trimethoxy silane (MPTMS) for an hour. On the top of the MPTMS coated glass slides, dilute solution of washed Au nanorods was drop-casted and kept for 6 hours. Then the following steps were performed to obtain the single-particle level dark-field scattering spectra.

(i) The glass slide was then washed with deionized water for 3-4 minutes with a slow flow of water. This step ensures the removal of the loosely bound gold nanorods with excess CTAB from the glass-slide. We proceeded to take the single-particle dark-field spectra using the slide. For each spectral acquisition, the position of the stage (XYZ-coordinates) of the microscope was noted as well as the image with 'marker' pattern was recorded so that we can locate those exact nanorods for acquiring their spectra on demand afterwards. Also, this allows us to carry out SEM measurements of those particles which are studied using single particle spectroscopy (correlated electron microscopy and optical spectroscopy measurements).

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(ii) Then the glass slide was washed with methanol to remove the maximum amount of CTAB from the Au nanorod surface. After drying, it was attached to the microscope, and the spectra of the same nanorods were recorded again with the help of the known position of the stage of the microscope (and the recorded pattern).

(iii) To modify the Au NR surfaces with 4-NTP molecules, 1 mM methanolic 4-NTP solution was allowed to flow over the gold nanorods for some time and then washed with MeOH. This step was repeated 3-4 times to ensure the maximum amount of 4-NTP attachment on the surface. After that the dark-field scattering spectra of the same nanorods were recorded once again.

S8. Effective path length of electrons (l_{eff}) deciding contribution of different damping channels to overall plasmon decay:

The average distance an electron travels to reach the surface of the nanorods is called the effective path length of electrons (l_{eff}). The value of l_{eff} can be calculated from the volume (V) and total surface area (S) of the nanorods as $l_{eff} = 4V/S$.^{7,8} Generally, excited plasmon decays through four decay channels: (i) bulk damping (Γ^{Bulk}), (ii) radiation damping (Γ^{Rad}), (iii) electron-surface scattering damping (Γ^{Surf}), and (iv) chemical interface damping (Γ^{CID}). Following the previous reports, we can write the homogeneous linewidth (Γ^{Homo}) as a function of l_{eff} , as, ^{9,10}

$$\Gamma^{Homo} = \Gamma^{Bulk} + h\kappa V/\pi + \frac{A_{Surf}v_F}{l_{eff}} + \frac{A_{CID}v_F}{l_{eff}} \dots (S1)$$

$$\Gamma^{Homo} = \Gamma^{Bulk} + h\kappa V/\pi + \frac{v_F}{l_{eff}} (A_{Surf} + A_{CID}) \dots (S2)$$

In this study, we used nanorods of different dimensions but identical aspect ratio $(\frac{length}{diameter} \approx 2.5)$ which suggests the, $l_{eff} = \frac{5d}{6}$ and $V = \frac{5\pi d^3}{8}$ (where *d* is the diameter, *l* is the length, and *V* is the volume of the nanorod). These simplify equation S2 to

$$\Gamma^{Homo} = \Gamma_{Scat} = \Gamma^{Bulk} + 5h\kappa d^3/8 + \frac{6v_F}{5} (A_{Surf} + A_{CID}).....(S3)$$

The linewidth of a nanorod immobilized on a glass slide, obtained from single-particle darkfield scattering measurements (Γ_{scat}) is free from any broadening effects due to the size distribution of the sample and any kind of heterogeneous line broadening effect, so we can consider that the single particle scattering spectral linewidth, Γ_{Scat} to be essentially equal to Γ^{Homo} , i.e.,

$$\Gamma^{Homo} = \Gamma_{Scat} = \Gamma^{Bulk} + 5h\kappa d^3/8 + \frac{6\nu_F}{5} \left(A_{Surf} + A_{CID}\right).....(S4)$$

We used equation S4 to fit our measured homogenous linewidths acquired from dark-field scattering experiments shown in Fig. 4b of the main text. The value of Γ^{Bulk} is assumed to be constant in range of the 1-2 eV LSPR position, which is equal to ~72 meV.⁹ For Γ^{Rad} , the value $\kappa = 4.0 \times 10^{-7}$ fs⁻¹ nm⁻³ was used (reported by Sönnichsen *et al.*).¹¹ Using these values of these constants and our experimental data, the plot of Γ_{Scat} vs $1/l_{eff}$ constructed according to equation S4. Note that before surface modification of nanorods with 4-NTP, the contribution of CID to overall homogenous linewidth is insignificant, which allows us to consider $A_{CID} = 0$. This helps us to determine the value of A_{Surf} which is estimated to be 0.21. After addition of 4-NTP the linewidth gets increased, and the value of $(A_{Surf} + A_{CID})$ is found to be 0.38. Thus, the value of A_{CID} is 0.17 in the present case. In these calculations, the value of v_F was taken to be 1.4 mm/fs.¹²

S9. Fitting of UPB and LPB energies according to coupled oscillator model and estimation of Rabi splitting:

Generally, plasmon-exciton coupling is described classically by the coupled oscillator model, according to which the energy of UPB (ω_{UPB}) and LPB (ω_{LPB}) can be simplified as ^{13,14}

$$\omega_{UPB} = \frac{(\omega_p + \omega_e)}{2} + \frac{1}{2} \sqrt[4]{(\omega_p - \omega_e)^2 (\gamma_p - \gamma_e)^2} + \left[4g^2 + (\omega_p - \omega_e)^2 - \frac{(\gamma_p - \gamma_e)^2}{4}\right]^2 \dots (S5)$$

And

$$\omega_{LPB} = \frac{(\omega_p + \omega_e)}{2} - \frac{1}{2} \sqrt[4]{(\omega_p - \omega_e)^2 (\gamma_p - \gamma_e)^2} + \left[4g^2 + (\omega_p - \omega_e)^2 - \frac{(\gamma_p - \gamma_e)^2}{4}\right]^2 \dots (S6)$$

(Where, ω_{UPB} is frequency of UPB, ω_{LPB} frequency of LPB is, ω_p is LSPR frequency, ω_e is exciton resonance frequency, γ_p is LSPR linewidth, γ_e is linewidth of the excitonic resonance, and g is coupling constant)

We fitted the UPB and LPB energy values obtained from single-particle dark-field scattering spectra of individual plexciton Au NR-plexciton hybrids (for all six plexciton hybrid samples) to equations S5 and S6 as a function of plasmon energy (ω_P) which clearly show the avoided crossing behavior. At zero detuning (i.e., when $\omega_P = \omega_e$) the energy difference between the fitted lines corresponding to UPB and LPB gives the Rabi splitting ($\hbar\Omega_{Rabi}$).

From equation S4 and S5, we can calculate the energy difference between UPB and LPB as

$$\Delta \omega = \hbar \Omega = \sqrt[4]{(\omega_p - \omega_e)^2 (\gamma_p - \gamma_e)^2 + \left[4g^2 + (\omega_p - \omega_e)^2 - \frac{(\gamma_p - \gamma_e)^2}{4}\right]^2} \dots (S7)$$

At zero detuning $(\omega_P = \omega_e)$ equation S7 reduces to $\hbar\Omega_{\omega_p=\omega_e} = \sqrt{4g^2 - \frac{(\gamma_p - \gamma_e)^2}{4}}$ (S8), which is essentially the Rabi splitting $(\hbar\Omega_{Rabi})$. Equation S7 is also used to calculate the coupling constant (g) from the single-particle dark-field scattering measurement.



Fig. S5: Anti-crossing behavior of upper and lower plexcitonic branches as a function of LSPR detuning frequency, as obtained from single-particle spectra of plexcitonic hybrids of (a) NR1,

(b) NR2, and (c) NR3 before surface modification; and (d) NR1, (e) NR2, and (f) NR3 after surface modification by 4-NTP. The black and red lines correspond to the fit of the UPB and LPB energies to the coupled harmonic oscillator model. The magenta and dark cyan lines correspond to the exciton and plasmon resonances, respectively. At zero detuning (magenta and dark cyan lines cross each other), the energy gap between red and black lines (corresponding to UPB and LPB energies) gives the Rabi splitting value ($\hbar\Omega_{Rabi}$).

S10. Observation of higher Rabi splitting in ensemble-level extinction spectra as compared to single-particle dark-field scattering measurement:

For wet chemically synthesized nanoparticle systems at ensemble-level, we always deal with samples that inevitably have size heterogeneity of a certain degree (however small or large that may be). Thus, an ensemble of Au nanorods in solution will also have a certain degree of heterogeneity in the LSPR positions, and the overall ensemble-level LSPR spectra will be a weighted sum of all the possible LSPRs owing to the slight size dispersion. Clearly, the overall ensemble-level plexciton mode splitting is simply an incoherent sum of mode splitting arising from both on-resonance and off-resonance (when LSPR is either red- or blue-detuned with respect to the exciton resonance) plasmon-exciton coupling. The contribution from off-resonance LSPRs lead to an overall mode splitting in ensemble-level spectra that is larger than what is observed for purely on-resonant coupling, as we encounter in single-particle level measurements.¹⁵

S11. Competing roles of plasmon mode volume (V_{mode}) and plasmon dephasing on plasmon-exciton coupling:

The plasmon-exciton coupling strength depends mainly on the interplay between: (i) plasmon-exciton energy exchange and (ii) decay rate of excited plasmon. The plasmon-exciton energy exchange rate increases as the mode volume decreases as $\gamma_{e \to p} \propto \sqrt{1/V_{\text{mode}}}$ ¹³ (where, $\gamma_{e \to p}$ is the energy exchange rate between exciton and plasmon and V_{mode} is the plasmon mode-volume). Considering the effect of V_{mode} on coupling, NR1-plexciton is

anticipated to demonstrate higher Rabi splitting than NR2-plexciton.³ Conversely, in terms of plasmon dephasing, NR2-plexciton is expected to exhibit increased Rabi splitting because of faster plasmon decay of NR1 through the electron-surface dephasing channel (Γ^{Surf}) having a smaller effective path length (l_{eff})⁹. However, in our experiments, higher Rabi splitting value for NR1-plexciton was observed when the Au nanorods surface was not modified with 4-NTP. This clearly indicates that in absence of CID, the plasmon mode-volume plays a dominant role over the plasmon decay rates in governing the plasmon-exciton coupling.

Interestingly, post-surface modification, the CID channel is introduced additionally to the already existing plasmon decay channels (Γ^{Bulk} , Γ^{Rad} , and Γ^{Surf}) for the Au nanorods. This additional decay channel reduces the plasmon-exciton coupling further. The reduction in Rabi splitting due to the incorporation of CID is more pronounced for NR1-plexciton than for NR2-plexciton. It is intriguing to observe that following surface modification with 4-NTP, the Rabi splitting value of NR2-plexciton surpasses that of NR1-plexciton. This observation provides clear evidence that when CID channel is operative, plasmon dephasing emerges as the dominant factor, superseding the influence of plasmon mode volume (V_{mode}).

S12. Determination of number of J-aggregate interacting with Nanorod after and prior to the surface modification with 4-NTP

As mentioned in the main text, the reduction of Rabi splitting values can be attributed to the faster plasmon dephasing or the formation of a smaller number of excitons (J-aggregates of Cy78) on Au NR surface due to hindrance created after 4-NTP modification. To verify, we prepared two plexcitonic hybrid samples following the usual steps, adding 300 μ L 1 mM monomeric solution of Cy78: (i) one with surface modified NR1 (with 4-NTP), and (ii) another with exact same amount of NR1 without any surface modification. After that, we separated the supernatant from both solutions by centrifugation after 24 hours, which contains unbound J-aggregates as well as monomers of Cy78. All the J-aggregates were converted to monomers by the addition of 500 μ L of MeOH. The concentration of Cy78 in both supernatant solutions were calculated, using the molar extinction coefficient of the Cy78 monomeric system in methanol (Fig. S6). Interestingly, we found similar concentrations of monomeric Cy78 in both the cases. The calculated concentrations of Cy78 monomer in the supernatants

were 0.088 mM and 0.086 mM corresponding to the plexcitonic hybrid of 4-NTP-modified NR1 and surface unmodified NR1, respectively. This experiment indicates similar numbers of Cy78 monomer involved in plexciton hybrid formation in both surface -modified and unmodified cases. The comparable number of interacting J-aggregates (excitons) in both scenarios implies that the reduction in Rabi splitting (coupling strength) is primarily due to the introduction of the CID channel and not due to a different number of attached excitons.



Fig. S6: Absorption spectra of monomeric Cy78 obtained from the supernatant solutions of NR1 (with surface modified and unmodified NR1)-plexciton hybrid after centrifugation. Similar concentrations of Cy78 monomers were observed in both the plexcitons (i.e., surface unmodified NR1 and surface modified NR1-plexciton). This result suggests involvement of similar number of excitonic units (J-aggregates of Cy78) in plexciton hybrid formation.

S13. Comparative CID effect of CTAB and 4-NTP

As we mentioned earlier, the CID arises due to the direct transfer of hot electrons from the nanoparticle to LUMO of the adsorbate molecules on the surface depending on the way the adsorbate molecules are attached to the metal^{4,16}. In CID process, the presence of closely and strongly interacting adsorbate molecules, i.e., hybridization on the interface, induces the direct generation of hot electrons in the available lowest unoccupied molecular orbitals (LUMO) acceptors of the adsorbate. Adsorbate molecules with free thiol group are preferred for inducing CID because thiol molecules bind to gold via efficient soft-soft covalent bonding, leading to significant orbital mixing between the gold and sulfur atoms.^{4,10} On the hand, the CTAB molecules are predominantly physiosorbed on the gold surface and thus the necessary

surface-adsorbate hybrid states are not formed in case of CTAB. Hence, the direct transfer of electrons is almost negligible in the case of CTAB, leading to very small change in damping process via CID. In our experiments too, we see a minimal change in LSPR linewidth due to removal of CTAB layers from the Au-nanorod surfaces in single particle darkfield measurements (Figure S7). For NR1 (which is most responsive toward the change on the surface), we observed a decrease of 2.07 \pm 1.6 meV in LSPR linewidth due to removal of CTAB, which is very less.

In comparison, 4-NTP molecules attach to the gold surface very strongly via sulfur-gold interaction. Such strong binding facilitates the formation of surface-adsorbate hybrid states for direct transfer of excited electrons and show very strong CID effect (Figure S7). This results supports the previous observation that *para*-substituted thiophenols molecules show excellent CID inducing properties^{4,10}.

We would like to make an additional note here that the present work deals with the nanorod's longitudinal modes and the corresponding linewidth changes. It is well known that the density of the CTAB bilayer is very less at the tips because of the small radius of curvature.¹⁷ This further reduces the ability of CTABs to induce any noticeable CID in the longitudinal LSPR mode of the nanorods.



Fig. S7: Change in LSPR linewidth obtained from single particle dark field scattering measurements ($\Delta\Gamma_{Scat}$) of immobilized NR1 due to change in the gold-surrounding medium interface. First bar represents the change in LSPR due to removal of CTAB from the surface and the second bar represents the change in LSPR linewidth due to surface modification with 4-NTP.

S14. Investigating the role of near-field enhancement in plasmon-exciton coupling

We carried out numerical simulation (using FDTD technique) to calculate the electric field distribution of all three nanorods. Very similar values of maximum electric field enhancement $(|E_{max}|/|E_0|)$ were observed for all the Au-nanorods (see the Fig. S8). Therefore, the effect of near-field enhancement factor on plasmon-exciton coupling will be very similar for all three Au-nanorods used in this study. Now, the scenario does not change when we consider the change in surrounding RI due to surface medication.



Fig. S8: Numerically calculated E-field distribution of (a) NR1, (b) NR2, and (c) NR3, at their corresponding LSPR maxima.

Brief details of numerical simulation method:

Numerically the near-field enhancement of Au nanorods were calculated by finite difference time domain (FDTD) method using a commercially available "Ansys Lumerical FDTD 2023 R2.2" software. A detailed description of the calculation of optical and electronic properties of the plasmonic and plexcitonic nanostructures were presented elsewhere^{3,18}. The dimensional parameters of the gold-nanorods for numerical simulations were taken from the TEM analyses. The special electric field distribution was calculated with by placing one twodimensional monitor in XY plane. Preoptimized mesh accuracy of 5 was used for the simulation. The cubic override mesh of 2 nm \times 2 nm \times 2 nm dimensions were used for the optical cross-section calculations. On the other hand, for near-field enhancement calculations a finer mesh of dimensions 0.5 nm \times 0.5 nm \times 0.5 nm dimensions was employed. The frequency dependent dielectric functions values for gold were taken from data set provided by Johnson and Cristy in 1972¹⁹. For the plexciton hybrid the exciton was models as a Lorentzian material^{20,21} as

$$\varepsilon_j(\omega) = \varepsilon_{\infty} + \frac{f\omega_e^2}{(\omega_e^2 - \omega^2 - i\gamma_e\omega)}$$
(S9)

Where, ε_{∞} is the high-frequency component of the J-aggregate dielectric function, ω_e is the exciton transition energy, γ_e is the spectral linewidth of exciton transition and f is the reduced oscillator strength. The values of ε_{∞} , ω_e , γ_e and f used in the simulations were 1.33, 1.907 eV, 94 meV and 0.03 respectively.

S15. Incident light polarization dependence of Rabi splitting

In the present case, the plasmon-exciton coupling strength does not depend on the incident light polarization. Neither the LSPR frequencies (longitudinal as well as transverse) of the Au nanorods, nor the J-band position of the exciton forming dye (Cy78) is polarization dependent (only the intensities vary). Also, by design, we are using only the longitudinal LSPR for coupling with exciton resonance (a constant parameter) of the J aggregate. Hence, we expect the Rabi splitting would also be independent of polarization of incident light. As a matter of fact, the polarization insensitivity of plasmon-exciton coupling (Rabi splitting) when considering nanorods and J-aggregates have already been documented by other groups²⁰. Nevertheless, we performed numerical simulations (using FDTD technique) of an Au-nanorod's plexcitonic hybrid under varying excitation polarization and monitored the wavelength dependent absorption and scattering cross-section of a plexciton hybrid. We found no change in Rabi splitting for different polarization angles (see Figure S9 below). Only the intensity was found to decrease with the polarization angle, which is expected as the intensity of the LSPR of nanorod changes as a function of polarization.



Fig. S9: Numerically calculated polarization-resolved absorption cross-sections (σ_{abs}) of an Au-nanorod's plexciton hybrid (dimension 20 nm × 50 nm). θ represents the angle between nanorod's long axis and the electric field polarization of the incident light. Black, red, blue, and green lines correspond to the σ_{abs} of same nanorod-plexciton hybrid at $\theta = 0^{0}$, 15⁰, 30⁰, and 45⁰.

S16. References:

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