Supporting Information for

Room-Temperature Strong Coupling of CdSe Nanoplatelets and Plasmonic Hole Arrays

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S1. Sample Fabrication

Materials. Four-inch diameter, single-side-polished, single-crystalline Si(100) wafers with <0.4 nm rootmean-square (RMS) roughness and thicknesses of either 500 or 1000 μ m were purchased from Silicon Valley Microelectronics or Silicon Quest and diced into 2 × 2 cm² or 1.5 × 1.5 cm² square pieces. Octadecyltrichlorosilane (ODTS, 96%) was purchased from Merck KGaA. Bicyclohexyl (99%, D79403), carbon tetrachloride (CCl₄, 99.5%, 289116), chloroform (99.8%, 132950), and sulfuric acid (H₂SO₄, 95– 98%, 258105) were purchased from Sigma. Hydrogen peroxide (H₂O₂, 30%, AnalaR Normapur) was purchased from VWR. Nitric Acid (65% HNO₃) was purchased from Fisher Chemical. 18.2 MΩ deionized water (DI) was obtained from a MilliQ Advantage A10 water-purification system. Silver (Ag, 99.999%) pellets were purchased from Kurt Lesker. Tungsten dimple boats (49 × 12 × 0.4 mm³) were purchased from Umicore. Acetone (Technic France, Micropur VLSI Grade), isopropanol (IPA, Technic France, Micropur VLSI Grade), CSAR 62 resist (AR-P 6200.09, Allresist GmbH), developer for CSAR 62 resist (AR 600-546, Allresist GmbH), and buffered oxide etch (BOE, hydrogen fluoride : ammonium fluoride 1:7, Technic France, Micropur VLSI Grade) were provided by the Binnig and Rohrer Nanotechnology Center (BRNC) at IBM Zurich.

Fabrication of hole-array template. A schematic of the fabrication process is shown in Figure S1. $2 \times 2 \text{ cm}^2 \text{ Si}(100)$ chips were first cleaned using acetone, isopropanol, and O₂ plasma (PVA-TePla, GIGAbatch 310M, 600 W, 5 min). After a prebake (hotplate, 180 °C, 10 min), the chips were coated with a 280 nm thick layer of AR-P 6200.09 (spin coater, 2000 revolutions per minute) and then soft-baked (hotplate, 150 °C, 5 min). Hole-array patterns were defined using electron-beam lithography (Vistec, NFL 5) and then developed in AR 600-546 for 1 min followed by rinsing in isopropanol and drying with a N₂ gun. Holes were etched into the Si chips using HBr-based inductive-coupled plasma etch (Oxford Instruments, PlasmaPro 100 Cobra, 80 W). The resist was removed by sonication in acetone and isopropanol for 2 min each, followed by O₂ plasma ashing (PVA TePla, GIGAbatch 310M, 600 W, 5 min). After dipping in BOE, the chip was cleaned for 10 min in a piranha solution (1:1 mixture of H₂SO₄ and H₂O₂; Caution: This solution reacts violently with solvents and other organic material). In a final step, the chip was thoroughly rinsed in DI water and then dried with a N₂ gun.

Deposition of Ag films. A thermal evaporator (Kurt J. Lesker, Nano36) was used for the Ag-film deposition. Deposition of a 250 nm thick Ag film onto hole-array templates was performed with Ag pellets evaporated from a tungsten dimple boat at high rates (>25 Å/s) and low residual gas pressures $(3 \times 10^{-7} \text{ mbar})$.^{S1} Hole-array templates can be reused by first removing the Ag films mechanically using Scotch tape, then chemically treating with nitric acid (HNO₃, 10 min), rinsing in DI water, sonicating in isopropanol for 5 min, and finally drying with a N₂ gun.

Preparation of NPL films. A schematic of the fabrication process is shown in Figure S1. First, unpatterned 1.5×1.5 cm² Si(001) chips were functionalized with ODTS self-assembled monolayers following a recipe by Lessel et al.^{S2} In short, Si chips and Teflon beakers were cleaned in a piranha solution (1:1 mixture of H₂SO₄ and H₂O₂; Caution: This solution reacts violently with solvents and other

organic material) for 10 min and rinsed in DI water. In the Teflon beaker with screw cap, 150 μ L of ODTS, 300 μ L of CCl₄, and 10 mL of bicyclohexyl were mixed. Moisture-sensitive ODTS was first added to the Teflon beaker inside a N₂ glovebox. Further processing steps were performed under ambient, but the Teflon beaker was kept closed whenever possible. A separate bowl of DI water was heated on a hotplate (hotplate temperature set to 170 °C), and a Si chip, which had previously been cleaned as above and dried with a N₂ gun, was quickly passed over the water vapor. Immediately after the shimmering film of condensed water visually disappeared, the sample was placed into the Teflon beaker for 15 min. Next, to remove unbound ODTS, the chips were thoroughly rinsed with chloroform and subsequently sonicated in a chloroform bath for 2 min. Chips were placed back in the Teflon container with ODTS and then rinsed and sonicated two more times to complete the process.

These functionalized Si chips were used as substrates to drop cast CdSe nanoplatelets of various concentrations. The CdSe NPL dispersions for drop casting were prepared using a 9:1 (v/v) mixture of hexane and octane and their concentration was determined by using an ultraviolet-visible spectrometer (Varian, 50 Scan) to measure the optical density (OD) at the heavy-hole transition. Prior to drop casting, all NPL dispersions were passed through a 0.2 μ m polytetrafluoroethylene (PTFE) syringe filter (VWR, 13 mm diameter). Finally, NPL films of different thickness were prepared by drop casting 20 μ L of NPL dispersions with concentrations corresponding to OD 10, 20, 30, 40, 60, and 80 at the heavy-hole transition for a 1 cm path length onto the functionalized Si chips. Slow and homogeneous drying of the NPL films was ensured by covering the Si chips with a petri dish immediately after drop casting.

Assembly of Ag-hole-array NPL samples. To place the NPL film onto the Ag hole array the film was removed from the Si chip using template stripping. Specifically, a glass slide was first adhered to the dried NPL film using a drop of epoxy (Norland Products, NOR 63). The epoxy was cured for 7 min using a 365 nm ultraviolet lamp. The NPL/epoxy/glass stack was then separated from the Si chip by placing a razor blade between the chip and the glass slide. A flat but flexible NPL film stabilized by an epoxy

backing layer was obtained by further cleaving the epoxy–glass interface with a razor blade. Finally, the NPL film was placed onto the hole array by gently pressing the NPL/epoxy stack onto the Ag film patterned with hole arrays. Formation of air bubbles between the Ag film and the NPL layer did occur but rarely coincided with the location of the hole-array patterns.

S2. Optical Measurements

Reflection measurements. The Ag-hole-array samples were mounted on an inverted microscope (Nikon, Eclipse Ti-U) using a 50× air objective [Nikon, TU Plan Fluor; numerical aperture (NA) of 0.8] for samples without NPLs and a 60× water-immersion (WI) objective (Nikon, Plan Apo VC; NA 1.2) for samples containing NPL and epoxy layers. The epoxy layer had a thickness comparable to a glass coverslip and thus allowed experiments with immersion objectives. A broadband halogen lamp was used as the light source for the reflection measurements. The reflected light was collected with the same objective. Flat Ag and flat Ag covered with NPLs and epoxy, respectively, served as the reference for the reflection measurements. The tube lens of the microscope (L_1 in Figure 1e in the main text) forms a real image of the sample on the plane labeled as "Image" in Figure 1e in the main text. To project the Fourier image onto the entrance slit of the imaging spectrograph (Andor, Shamrock 303i; 150 lines/mm grating blazed at 50 nm) an achromatic lens (L₂ in Figure 1e in the main text) with focal length $f_2 = 200$ mm was then used to collimate the real image from L_1 . A Fourier transform of the image was formed 200 mm behind the collimating lens L₂. A two-lens imaging system (with achromats L₃ and L₄ in Figure 1e in the main text, with focal lengths $f_3 = f_4 = 200$ mm) was used to project the Fourier image onto the entrance slit of the spectrograph. We switched between collecting the Fourier image and the real image by removing L₃. Dispersion relations were obtained by spectrally dispersing the Fourier image. The dispersion relation could be probed along arbitrary directions in the Brillouin zone by physically rotating the sample. All images were recorded using an Andor Zyla 4.2 PLUS sCMOS.

Photoluminescence measurements. For photoluminescence measurements, the same set-up used in reflection measurements was employed, except that the halogen lamp was replaced with a 385 nm light-emitting diode (Thorlabs, M385LP1) to excite the NPLs. Further, a broadband polarizer (Thorlabs, LPVISE100-A) was placed before the final imaging lens to record either TE- or TM-polarized emission.

S3. Atomic Force Microscopy

Height determination of NPL films. Atomic force microscopy (AFM, Bruker, FastScan) was used to determine the thickness of drop-cast NPL films. After template stripping the NPL film, a step edge formed at the border between the stripped film and the remaining NPLs on the Si chip. This step edge was used to measure the thickness of the NPL film. Uniform interference colors were observed from each NPL film, indicating that we obtained homogeneous film thicknesses over the whole chip. Figure S2 shows AFM images and the corresponding height distributions of films drop casted from dispersions with various concentrations (see section S1 above). The thicknesses of the different NPL films referenced in the main text resulted from the peak values of the height distributions.

S4. Surface Plasmon Polaritons (SPPs)

Linewidth of SPPs supported on a Ag hole array with air as a dielectric. The linewidth of surface plasmon polaritons supported on a Ag hole array is extracted from the angle-resolved reflectance map shown in Figure 1f in the main text. Cross-sections through the reflectance map at different in-plane momenta $k_{\parallel} = 0,1,2,3 \ \mu m^{-1}$ are plotted in Figure S3. The linewidth of the [±1,0] plasmon branch is determined by fitting a sum of Lorentzian oscillators to the spectra. The resulting full-width-at-half-maximum values are ~ 30 meV (exact values are highlighted in Figure S3) and do not significantly vary as a function of in-plane momentum.

Retrieving the fundamental SPP dispersion from hole-array dispersions. As mentioned in the main text, the periodic structure of the Ag hole array provides in-plane momentum to incident photons. SPPs with wave vector \vec{k}_{SPP} are then launched on the metal surface when

$$\left|\vec{k}_{||} + i\vec{G}_{x} + j\vec{G}_{y}\right| = \left|\vec{k}_{\text{SPP}}\right| = \frac{\omega}{c} \sqrt{\frac{\varepsilon_{\text{m}}(\omega)\varepsilon_{\text{d}}(\omega)}{\varepsilon_{\text{m}}(\omega) + \varepsilon_{\text{d}}(\omega)}}$$
(S1)

where \vec{k}_{\parallel} is the in-plane wave-vector component of the incident photon, $\vec{G}_x = (2\pi/a, 0)$ and $\vec{G}_y = (0,2\pi/a)$ are the reciprocal lattice vectors of the square periodic structure, and $i, j = 0, \pm 1, \pm 2, ...$ are integers. An angle-resolved reflectance measurement determines the energy *E* and in-plane momentum \vec{k}_{\parallel} of free-space light that couples to SPPs [cf. Figure 1f in the main text showing $E(k_{\parallel})$]. Successful coupling manifests in a dip in reflection. Now, as (for the lowest-energy branches of the hole-array dispersion, $[\pm 1,0]$ and $[0,\pm 1]$) we know the amount of momentum that was provided by the grating $|\vec{G}_{x,y}| = 2\pi/a$ and as energy is conserved when a photon couples to a plasmon, we are able to retrieve the fundamental SPP dispersion $E(k_{SPP})$ through eq S1. The appropriate grating momentum has to be added to the in-plane wave-vector component of the incident photon: $E(k_{SPP}) = E(|\vec{k}_{\parallel} + i\vec{G}_x + j\vec{G}_y|)$. For the case of the $[\pm 1,0]$ plasmon branch viewed along the *x*-direction $[\vec{k}_{\parallel} = (k_{\parallel}, 0)]$, one simply adds $2\pi/a$ to the hole-array dispersion: $E(k_{SPP}) = E(-k_{\parallel} + 2\pi/a)$.

To illustrate the validity of this procedure, we show in Figure S4a–f angle-resolved reflectance measurements of Ag hole arrays with six different hole spacings *a* and air on top. We indicate the reflectance minima and thus the hole-array bands using colored data points. Each minimum has a distinct in-plane momentum and energy value $E(k_{\parallel})$. After adding the appropriate grating momentum $2\pi/a$ to the in-plane momentum value of the minima, Figure S4g is obtained. The data points originating from the linear [±1,0] branches perfectly align on a single dispersion line. This reconstructed SPP dispersion line $E(k_{\text{SPP}})$ agrees very well with the theoretical dispersion given by eq S1 with $\varepsilon_d = 1$ and the metal dielectric function provided by McPeak et al.^{S1} However, the data points originating from the parabolic

 $[0, \pm 1]$ bands do not fall on top of each other. A different momentum substitution would be needed to end up on the plasmon dispersion, namely: $E(k_{\text{SPP}}) = E\left(\sqrt{k_{||}^2 + (2\pi/a)^2}\right)$.

S5. Plasmon–Exciton Strong-Coupling Measurements

Correction of angle-resolved reflectance maps using measurements of NPL films on flat Ag. Angleresolved reflectance maps of NPLs on Ag hole arrays (cf. Figure 2a in the main text) are always composed of three measurements. First, a background image (BG) is taken without illumination that accounts for the dark signal on the detector. Second, we take a reference measurement (RF) of white light reflected on a flat Ag film covered with NPLs. Usually, this reference is obtained right next to the hole-array structure measured afterward, such that the NPL film thickness is the same for both measurements. Last, we measure the light reflected by a hole array covered with NPLs (SIG). The final reflectance map (R) is obtained through R = (SIG-BG)/(RF-BG). Such a correction by reference measurements is commonly done in the literature^{S3,S4} to improve clarity of the data. For completeness, we additionally provide in Figure S5a,b reflectance maps of NPL films on hole arrays and on flat Ag, respectively, both corrected by a reference measurement on flat Ag without NPLs (i.e., a different correction than done in the main text). In Figure S5a, b we can clearly see the undispersed absorption features from uncoupled NPLs. If we divide the reflectance map of Figure S5a by the map in Figure S5b we obtain the data shown in Figure S5c. This is effectively the same data treatment as performed for all measurements presented in the main text and Figure S6, but now with explicit intermediate steps (Figure S5a,b) shown for clarity. As can be seen in Figure S5c, our data treatment effectively removes absorption features due to uncoupled NPLs.

Angle-resolved reflectance maps of Ag hole arrays covered with NPL films of various thicknesses.

Figure S6 shows angle-resolved reflectance maps of Ag hole arrays with NPL films of thicknesses ranging from 32 to 275 nm. A clear increase of the Rabi splitting at the HH transition can be seen when the film thickness is increased from d = 32 to 79 nm (cf. Figure S6a and S6b). No clear change in the Rabi splitting

is visible for films thicker than d = 121 nm, indicating a saturation of the splitting. The low reflectance feature appearing in Figure S6d-f at $E \sim 2.35$ eV and $k_{\parallel} \sim 14 \ \mu\text{m}^{-1}$ is assumed to be a waveguide mode supported in NPL films of a certain minimum thickness.

S6. Transition Dipole Moment of CdSe NPLs

Calculation of the transition dipole moment of CdSe NPLs. The Rabi splitting $\hbar \Omega_R$ for *N* dipoles is given by:^{S5}

$$\hbar\Omega_{\rm R} = \mu \sqrt{\frac{N}{V} \frac{2\hbar\omega}{\varepsilon_0 n_{\rm eff}^2}} \tag{S2}$$

where μ is the transition dipole moment, N the number of dipoles, V the electromagnetic mode volume, $\hbar\omega$ the dipole transition energy, and $n_{\rm eff}$ the effective refractive index inside the mode volume. We use the expression given in eq S2 to estimate the transition dipole moment of the HH transition of CdSe NPLs based on an experimentally determined Rabi splitting (approaching $\hbar\Omega_{R,HH}=124~meV$ for thick NPL films, see Figure 3d in the main text). If the NPL film thickness is much larger than the transverse SPP confinement length $d \gg \delta_{\text{SPP}, z}$ (see eq S10), the whole SPP mode volume is filled with a homogeneous NPL density N/V. This NPL number density is given by $N/V = \phi/V_{\text{NPL}}$ where ϕ is the packing fraction inside the NPL film (i.e. the fraction of volume occupied by semiconductor material) and $V_{\rm NPL}$ is the volume of an individual NPL. $V_{\rm NPL}$ is estimated to be 363 nm³ based on the lateral NPL size of 18.5 \times 15.7 nm² extracted from transmission electron microscopy images (averaged over 61 NPLs) and their atomically precise thickness of 1.25 nm. If we assume a packing density of approximately 10% we obtain a number density $N/V = 0.00028 \text{ nm}^{-3}$. This relatively low packing density accounts for voids between NPLs (e.g. ligands) and imperfect alignment between transition dipoles and the electric field. The effective refractive index of a film of NPLs n_{eff} (equal to n_{NPL} ; see eq S8) is given by our Lorentz model and has a value of 1.83 at the HH transition (2.399 eV).

Based on the above assumptions we obtain an estimated value of 2×10^{-28} Cm for the transition dipole moment of the NPLs. This value is an order of magnitude larger than a value obtained by time-resolved Stark spectroscopy.^{S6} The transition dipole moment obtained by using the same method as presented here but with NPLs coupled to an optical field yields a value of 2×10^{-27} Cm.^{S7}

S7. Modeling

Coupled-mode model for plasmon–plasmon coupling. To model the dispersion relation of surface plasmon polaritons (SPPs) on a square Ag hole array with pitch a = 500 nm (Figure 1f in the main text) we used an SPP-coupling model based on the one introduced by van Exter et al.^{S8} We adapted it to include higher-energy SPP bands. We also considered coupling between all of the bands, enabled by the hole-array structure. The energies of the coupled SPP bands were found by finding the eigenvalues of the matrix:

$$M = \begin{bmatrix} \omega_{00}^{(0)} & \beta & \beta & \beta & \beta & \kappa & \kappa & \kappa & \kappa \\ \beta & \omega_{10}^{(0)} & \kappa & \gamma & \kappa & \beta & \sigma & \sigma & \beta \\ \beta & \kappa & \omega_{01}^{(0)} & \kappa & \gamma & \beta & \beta & \sigma & \sigma \\ \beta & \gamma & \kappa & \omega_{10}^{(0)} & \kappa & \sigma & \beta & \beta & \sigma \\ \beta & \kappa & \gamma & \kappa & \omega_{01}^{(0)} & \sigma & \sigma & \beta & \beta \\ \kappa & \beta & \beta & \sigma & \sigma & \omega_{11}^{(0)} & \gamma & \lambda & \gamma \\ \kappa & \sigma & \beta & \beta & \beta & \lambda & \gamma & \omega_{11}^{(0)} & \gamma \\ \kappa & \beta & \sigma & \sigma & \beta & \gamma & \lambda & \gamma & \omega_{11}^{(0)} \end{bmatrix}$$
(S3)

Here $\omega_{ij}^{(0)}$ is the energy of the uncoupled SPP band with index *ij* (denoting the momentum provided by the hole-array structure):

$$\omega_{ij}^{(0)} = \omega_{\text{SPP}}^{(0)}(|\vec{k}_{||} + \vec{G}_{ij}|)$$
(S3)

where $\omega_{\text{SPP}}^{(0)}(k)$ is the SPP dispersion relation on a flat Ag/air interface (with no adjustable parameters; we used the dielectric function for Ag from McPeak et al.^{S1}), and $\vec{G}_{ij} = i\vec{G}_x + j\vec{G}_y$ is the momentum provided by the hole array (with $\vec{G}_{x,y}$ the reciprocal lattice vectors and *i*, *j* integers; $\vec{1}$ denotes -1). The parameters β , γ , κ , λ , and σ are the SPP scattering rates along the \vec{G}_{10} , \vec{G}_{20} , \vec{G}_{11} , \vec{G}_{22} , and \vec{G}_{21} vectors in reciprocal space, respectively. We make the approximation that the scattering rates are frequency-independent.

The coupled SPP dispersion in the $\Gamma - X$ direction is obtained by solving the eigenvalues of M for parallel wave vectors $\vec{k}_{||} = (k_{||}, 0)$ with $k_{||}$ between 0 and π/a . The optimal values for the five scattering rates are found by least-squares minimizing the deviation between the model and the experimental SPP dispersion (Figure 1f in the main text). We find as optimal values $\beta = 0$ meV, $\gamma = 38$ meV, $\kappa = 35$ meV, $\lambda = 255$ meV, and $\sigma = 130$ meV.

Coupled-mode model for exciton–plasmon coupling. The polariton dispersion relation in a three-layer Ag/NPL/epoxy stack can be described by evaluating the eigenvalues $[E_{LP}(k), E_{MP}(k), E_{UP}(k)]$ of the momentum-dependent Hamiltonian:^{S9}

$$H(k)\vec{\Psi}_{LP,MP,UP}(k) = E_{LP,MP,UP}(k)\vec{\Psi}_{LP,MP,UP}(k)$$
(S4)
with $H(k) = \begin{bmatrix} E_{SPP}(k) & g_{HH} & g_{LH} \\ g_{HH} & E_{HH} & 0 \\ g_{LH} & 0 & E_{LH} \end{bmatrix}$

where $E_{SPP}(k)$ is the uncoupled dispersion relation of SPPs at a metal/dielectric interface, E_{HH} and E_{LH} are the energies of the heavy- and light-hole transitions in CdSe NPLs, and g_{HH} and g_{LH} are the coupling constants between heavy- and light-hole transitions, respectively, and the SPPs. When we experimentally vary the thickness of the NPL layer, this affects the coupling constants g as well as the uncoupled SPP dispersion E_{SPP} . The heavy- and light-hole transition energies E_{HH} and E_{LH} of the NPLs are independent of layer thickness.

The SPP dispersion relation at a metal/dielectric interface expressed as $E_{\text{SPP}}(k) = \hbar \omega_{\text{SPP}}(k)$ can be obtained by numerically solving the closed-form SPP dispersion relation $k_{\text{SPP}}(\omega)$ for frequency ω :^{S10}

$$k_{\rm SPP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_{\rm d}(\omega)\varepsilon_{\rm m}(\omega)}{\varepsilon_{\rm d}(\omega) + \varepsilon_{\rm m}(\omega)}} \tag{S5}$$

where $\varepsilon_{\rm m}(\omega)$ is the dielectric function of the metal, which for Ag we take from McPeak et al.,^{S1} and $\varepsilon_{\rm d}(\omega)$ is that of the dielectric. We choose a frequency-dependent Cauchy model containing two fitting parameters $A_{\rm d}$ and $B_{\rm d}$ to account for the varying background dielectric environment as a function of NPL film thickness:^{S11}

$$\varepsilon_{\rm d}(\omega) = (A_{\rm d} + B_{\rm d}\omega^2)^2 \tag{S6}$$

By simultaneously least-squares minimizing the difference between the experimental polariton dispersion relations of Ag/NPL/epoxy stacks with six different NPL-layer thicknesses and the eigenvalues of eq S4, we obtain values for $E_{\rm HH}$ and $E_{\rm LH}$ that are independent of film thickness and a set of $A_{\rm d,i}$, $B_{\rm d,i}$, $g_{\rm HH,i}$, and $g_{\rm LH,i}$ for each NPL-layer thickness. The parameters resulting from the fit are given in Table S1; $E_{\rm HH} = 2.407$ eV and $E_{\rm LH} = 2.567$ eV.

Based on the parameters given in Table S1, a set of eigenvalues $[E_{LP}(k), E_{MP}(k), E_{UP}(k)]$ describing the polariton dispersion and a set of associated eigenvectors $[\overline{\Psi}_{LP}(k), \overline{\Psi}_{MP}(k), \overline{\Psi}_{UP}(k)]$ describing the composition of each polariton branch can be evaluated (see eq S4). The squared components of each eigenvector $\overline{\Psi}_i(k)$ are called the mixing coefficients (or Hopfield coefficients), and they describe the relative contribution of SPP, HH, and LH to the composition of each polariton branch.

Linear-dispersion model. In our experiments, we probe the dispersion of surface plasmon polaritons (SPPs) in three-layer stacks, i.e. Ag/NPL/epoxy. The intermediate layer of NPLs has a variable thickness up to d = 275 nm. We took the frequency-dependent dielectric constant $\varepsilon_{Ag}(\omega) = n_{Ag}^2(\omega)$ measured by McPeak et al.^{S1} for Ag, and assumed a Cauchy model with parameters A_{epoxy} and B_{epoxy} for the refractive index of our epoxy layer:

$$n_{\rm epoxy}(\omega) = A_{\rm epoxy} + B_{\rm epoxy}\omega^2$$
(S7)

For the dielectric constant of the NPL layer we used a Cauchy background^{S11} plus two Lorentzians describing coupling to the heavy- and light-hole excitons:

$$\varepsilon_{\rm NPL}(\omega) = n_{\rm NPL}^2(\omega) = (A_{\rm NPL} + B_{\rm NPL}\omega^2)^2 + \frac{f_{\rm HH}}{\omega_{\rm HH}^2 - \omega^2 - i\gamma_{\rm HH}\omega} + \frac{f_{\rm LH}}{\omega_{\rm LH}^2 - \omega^2 - i\gamma_{\rm LH}\omega}$$
(S8)

where A_{NPL} and B_{NPL} are fit parameters describing the Cauchy background due to various high-energy electronic transitions in the NPL film, $f_{\text{HH,LH}}$ are the oscillator strengths of the exciton transitions (heavy-hole and light-hole), $\omega_{\text{HH,LH}}$ are the resonance frequencies, and $\gamma_{\text{HH,LH}}$ are the damping rates.

At the interface between a semi-infinite metal and a semi-infinite dielectric, a geometry that is simpler than in our experiments, the dispersion of SPPs is given by:

$$k_{\rm SPP}^0 = k_0 \sqrt{\frac{\varepsilon_{\rm d} \varepsilon_{\rm m}}{\varepsilon_{\rm d} + \varepsilon_{\rm m}}} \tag{S9}$$

with $\varepsilon_{\rm m}$ the dielectric constant of the metal, $\varepsilon_{\rm d}$ that of the dielectric, and k_0 the free-space wave vector. The superscript (0) denotes the two-layer geometry. A SPP in this geometry is confined to the metal/dielectric interface and the intensity decays exponentially away from the interface. The transverse confinement length of the SPP intensity into the dielectric material is

$$\delta^{(0)} = 1/2 \operatorname{Im}\left(k_0 \sqrt{\frac{\varepsilon_d^2}{\varepsilon_d + \varepsilon_m}}\right)$$
(S10)

Figure S7 plots the wave vector (Figure S7a) and the transverse confinement (Figure S7b) of SPPs on the metal/dielectric interface between two semi-infinite layers, for Ag/NPL (orange) and Ag/epoxy (blue).

The SPP dispersion in our three-layer stacks depends on the NPL layer thickness d, and follows a more complicated expression than eq S9. Nevertheless, it should reduce to eq S9 in the limits of a very thick or a very thin NPL layer. For a thick NPL layer of $d/\delta^{(0)} \gg 1$, the SPP mode does not extend far enough away from the Ag interface to reach the epoxy layer. Hence, the SPP dispersion should be given by eq S9 with $\varepsilon_d = \varepsilon_{NPL}$. Conversely, for a vanishingly thin NPL layer of $d/\delta^{(0)} \ll 1$, the SPP mode resides mostly in the epoxy layer, so the dispersion can be approximated by eq S9 with $\varepsilon_d = \varepsilon_{epoxy}$. In our experiments the NPL layer has an intermediate thickness of $d/\delta^{(0)} \approx 1$. The simple expression eq S9 is therefore not sufficient to describe the SPP dispersion in terms of the properties of the NPL layer. We should then include the finite NPL-layer thickness. This can be done by considering the three-layer geometry explicitly and setting up boundary conditions that connect the layers.^{S12} To then obtain the dispersion relation, one has to numerically solve the complex SPP wave vector k_{SPP} from the equation

$$\cos(k_{z2}d)\left(1+\frac{k_{z1}\varepsilon_3}{k_{z3}\varepsilon_1}\right) - \mathrm{i}\sin(k_{z2}d)\left(\frac{k_{z1}\varepsilon_2}{k_{z2}\varepsilon_1}+\frac{k_{z2}\varepsilon_3}{k_{z3}\varepsilon_2}\right) = 0$$
(S11)

with $k_{zi} = \sqrt{\varepsilon_i k_0^2 - k_{\text{SPP}}^2}$.

Alternatively, one can treat the presence of the epoxy layer as a perturbation to the simpler geometry of a single Ag/NPL interface (eq S9). To first order, the SPP intensity in the three-layer geometry decays with the confinement length $\delta_{\text{SPP},z}$ of the Ag/NPL interface (eq S10 with $\varepsilon_d = \varepsilon_{\text{NPL}}$ and $\varepsilon_m = \varepsilon_{\text{Ag}}$). The fraction of the SPP energy located in the NPL layer compared to the total intensity in the dielectric top layers is then

$$f = \frac{\int_{0}^{d} e^{-z/\delta_{\text{SPP},z} \, dz}}{\int_{0}^{\infty} e^{-z/\delta_{\text{SPP},z} \, dz}} = 1 - e^{-d/\delta_{\text{SPP},z}}$$
(S12)

Based on this we can define the effective refractive index n_{eff} experienced by the SPP mode:

$$n_{\rm eff}(\omega) = f n_{\rm NPL}(\omega) + (1 - f) n_{\rm epoxy}(\omega)$$
(S13)

with $n_{\rm NPL}(\omega)$ according to eq S8 and $n_{\rm epoxy}(\omega)$ according to eq S7. To calculate the wave vector of SPPs strongly coupled to exciton transitions of the NPLs in a Ag/NPL/epoxy three-layer stack we then use eq S9 with $\varepsilon_{\rm d} = n_{\rm eff}^2(\omega)$ and $\varepsilon_{\rm m} = \varepsilon_{\rm Ag}(\omega)$:

$$k_{\rm SPP} = k_0 \sqrt{\frac{n_{\rm eff}^2 \epsilon_{\rm Ag}}{n_{\rm eff}^2 + \epsilon_{\rm Ag}}} \tag{S14}$$

Figure 4 compares the SPP wave vector calculated numerically using eq S11 to the approximation of eq S14, for a SPP frequency far from the lowest energy exciton transition (1.8 eV; Figure S8a,b) and one just red-shifted from the lowest energy exciton transition (2.35 eV; Figure S8c,d). We see that eq S14 is a good approximation for the real part of the SPP wave vector, which we extract from the reflectivity

measurements and reveals the strong SPP-exciton coupling. Eq S14 performs worse for the imaginary

part, but this component does not show up directly in our measurements or analysis.

S8. Supplementary References

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S9. Supplementary Tables

| | 32 nm | 79 nm | 121 nm | 138 nm | 183 nm | 275 nm |
|------------------------------|-------|-------|--------|--------|--------|--------|
| A (-) | 1.45 | 1.46 | 1.54 | 1.56 | 1.54 | 1.54 |
| <i>B</i> (eV ⁻²) | 0.047 | 0.050 | 0.038 | 0.033 | 0.038 | 0.039 |
| <i>g</i> _{НН} (meV) | 46 | 55 | 61 | 60 | 58 | 70 |
| g _{LH} (meV) | 54 | 69 | 67 | 66 | 74 | 75 |

Table S1. Cauchy parameters and coupling constants for the different NPL film thicknesses

 resulting from the coupled-mode-model fit.

| Parameter | A _{epoxy} | B _{epoxy} | $A_{\rm NPL}$ | B _{NPL} | $f_{\rm HH}$ | $\omega_{ m HH}$ | $\gamma_{ m HH}$ | $f_{\rm LH}$ | $\omega_{ m LH}$ | $\gamma_{ m LH}$ |
|------------|--------------------|--------------------|---------------|------------------|-----------------|------------------|------------------|-----------------|------------------|------------------|
| Best value | 1.358 | 0.053 | 1.580 | 0.031 | 0.069 | 2.399 | 0.020 | 0.077 | 2.557 | 0.016 |
| | | eV^{-2} | | eV^{-2} | eV ² | eV | eV | eV ² | eV | eV |

Table S2. Results of the global fit of our effective-medium model to the polariton dispersion relations measured for all NPL-layer thicknesses.

S10. Supplementary Figures



Figure S1. Sample preparation processing steps. The upper row shows the stepwise fabrication of the plasmonic Ag-hole-array structure. The lower row schematically depicts the preparation of thin NPL films backed by epoxy. The rightmost scheme shows the final structure after assembling the NPL film and the hole-array structure.



Figure S2. Height characterization of our NPL films. AFM measurements are shown for edges of NPL films drop casted from dispersions of various concentrations. The concentrations were quantified via the optical density (OD) at the heavy-hole transition assuming a 1 cm optical path length: (a) OD 10, (b) OD 20, (c) OD 30, (d) OD 40, (e) OD 60, and (f) OD 80. See sections S1 and S3 above for further details. The insets in each panel show the distribution of heights.



Figure S3. Reflection spectra extracted from Figure 1f in the main text at different in-plane momentum values: $k_{||} = 0 \ \mu \text{m}^{-1}$ (red), $k_{||} = 1 \ \mu \text{m}^{-1}$ (green), $k_{||} = 2 \ \mu \text{m}^{-1}$ (blue), and $k_{||} = 3 \ \mu \text{m}^{-1}$ (purple). The thin solid lines are sums of Lorentzian oscillators fit to the data. The full-width-at-half-maximum values resulting from the Lorentzian oscillator fits are highlighted next to the reflection minimum of each spectrum.



Figure S4. Angle-resolved reflectance maps for Ag–air hole arrays with a pitch *a* of (a) 460, (b) 480, (c) 500, (d) 520, (e) 540, and (f) 560 nm. The colored data points shown in (a–f) indicate the minima in reflectance tracing bands of the hole-array dispersion. (g) Reconstruction of the fundamental SPP dispersion from the extracted reflectance minima, obtained using $E(k_{\text{SPP}}) = E(-k_{\parallel} + 2\pi/a)$.



Figure S5. Angle-resolved reflectance maps for NPLs placed on Ag. (a) NPL film (~ 80 nm) placed on a Ag hole array with a pitch *a* of 190 nm. (b) NPL film of identical thickness as in (a) placed on flat Ag. (c) Obtained by dividing the measurement in (a) by the reference measurement in (b). See section S5 for further discussion.



Figure S6. Angle-resolved reflectance maps for Ag hole arrays with a pitch *a* of 190 nm covered with NPL films of different thickness *d*: (a) 32, (b) 79, (c) 121, (d) 136, (e) 183, and (f) 275 nm.



Figure S7. (a) The SPP wave vector as a function of energy on a Ag/NPL (orange) and a Ag/epoxy (blue) interface. (b) The transverse confinement length of the SPP on a Ag/NPL (orange) and a Ag/epoxy (blue) interface.



Figure S8. SPP wave vectors for a Ag/NPL/epoxy structure as a function of NPL-film thickness, calculated for an explicit three-layer geometry with appropriate boundary conditions at the interfaces (green, eq S11) and with our effective-medium model (red, eq S14). Gray dashed lines indicate the SPP wave vectors for a two-layer Ag/NPL or a two-layer Ag/epoxy geometry. (a) The real and (b) the imaginary part of the wave vector at an SPP energy of 1.8 eV. (c,d) Same at 2.35 eV.