Rabi splitting in photoluminescence spectra of a hybrid system of gold nanorods and J-aggregates

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ABSTRACT

We experimentally and theoretically investigate the interactions between localized plasmons in gold nanorods and excitons in J-aggregates at ambient conditions. Thanks to our sample preparation procedure we were able to track a clear anti-crossing behavior of the hybridized

modes not only in the extinction but remarkably also in the photoluminescence (PL) spectra of this hybrid systems. Notably, while previous studies often found the signal to be dominated by a single mode, here we follow the evolution of the two PL peaks as the plasmon energy is detuned from the excitonic resonance. Both the extinction and PL results are in good agreement with theoretical predictions obtained for two interacting modes with a ratio between the coupling strength and the plasmonic losses close to 0.4, indicative of the strong coupling regime with a significant Rabi splitting estimated to be ~ 200 meV. The evolution of the PL lineshape as the plasmon is detuned depends on the illumination wavelength, which we attribute to an incoherent excitation given by decay processes in either the metallic rods or the J-aggregates.

One of the main objectives of nanophotonics research is the control of light-matter interaction on the nanoscale. The coupling between plasmonic and excitonic resonances (plexcitonic coupling [[W. Ni et al \(Apell\) "Observing Plasmonic - Molecular Resonance Coupling on Single Gold Nanorods" Nanoletters 10, 77 \(2010\)](#), ["Coherent Coupling of Molecular Excitons to Electronic Polarizations of Noble Metal Nanoparticles" Nanoletters 4, 2121 \(2004\)](#) ["Plasmon-molecule interactions" Nano Today 5, 494, 2010\)](#)] is of great interest for fundamental studies and for many practical applications in integrated optics, optoelectronics, imaging and sensing.^{2, 3} The interaction between plasmons and excitons strongly affects energy and electron transfer pathways⁴ and, as a result, absorption and emission properties.⁵ Especially attractive for many applications is the so called strong coupling regime when the rate of coherent energy exchange between the excitonic and plasmonic systems exceeds the rate of the losses in the system.² If both J-aggregates and plasmon modes are modeled as coupled harmonic oscillators, the energies of the new hybrid plexcitonic modes are given by^{6, 7}

$$E_{\pm} = \frac{1}{2} [E_{pl} + E_{ex} - i \left(\frac{\kappa}{2} + \frac{\gamma_s}{2} + \gamma_d \right)] \mp \frac{1}{2} \sqrt{4g^2 + [\delta + 1i \left(\frac{\gamma_s}{2} + \gamma_d - \frac{\kappa}{2} \right)]^2} \quad (1)$$

where g is the interaction coupling strength between the two oscillators, E_{pl} and E_{ex} are the resonant energies of the plasmonic and excitonic excitations, respectively and $\delta = E_{pl} - E_{ex}$ is

the detuning. The losses are described by the plasmonic damping κ of the metallic nanoparticle and the spontaneous decay γ_s and pure dephasing γ_d rates of the emitter. For sufficiently low losses, these new eigenstates with energies E_+ and E_- reveal themselves spectrally as the upper (UR) and lower (LR) resonant peaks, respectively, that anticross as $\delta \rightarrow 0$. When the exciton resonance energy matches the plasmonic band energy ($\delta=0$), the term $Re(E_+ - E_-)$, (where Re indicates the real part) gives the energy of the Rabi splitting $\hbar\Omega_R = Re(E_+ - E_-)$. The onset of the strong coupling regime can be identified by the positive value of the Rabi splitting $\hbar\Omega_R > 0$ defined by Eq. (1), which for negligible losses reaches $\hbar\Omega_R = 2g$. A more demanding condition requires Ω_R to be at least comparable with the losses, so that the separation between the two modes is not much smaller than their width.⁹

One of the advantages of plasmonic structures is the extremely low modal volume associated to their electromagnetic resonances, one of the prerequisites for achieving strong coupling strengths g . However, due to the very fast decay rates of plasmons, it remains very challenging to achieve strong coupling $\hbar\Omega_R > 0$ for single molecules or quantum dots with moderate oscillator strengths.[["Strong coupling between a metallic nanoparticle and a single molecule" PRB 77, 115403, \(2008\), S. Savasta "Nanopolaritons: Vacuum Rabi Splitting with a Single Quantum Dot in the Center of a Dimer Nanoantenna" T. Hummers, F. J. Vidal, L. Martin-Moreno and D. Zueco "Weak and Strong coupling regimes in plasmonic QED",](#)] In this respect, coupling plasmons with excitons of organic dyes in J-aggregated state is of significant interest for the development of advanced photonic technologies based on organic-inorganic hybrid nanosystems. J-aggregates can delocalize and migrate excitonic energy over a large number of aggregated dye molecules, resulting in an extremely high oscillator strength.¹⁰

Whereas observation of Rabi splitting in extinction or transmission spectra of plexitonic structures combining metal nanoparticles and J-aggregates has been reported (Supporting Information S1 and S2), PL properties of plexitonic hybrid systems in the strong coupling regime are more elusive to experimental investigation ¹¹. Treating the system as two simple coupled modes leads to Rabi splitting in both extinction and PL spectra ^{12, 13}, but observation of the latter can be hindered by competing phenomena, such as changes in the dynamics of energy transfer and recombination processes between the levels of the complex electronic structure of the J-aggregates involving vibrational sublevels ¹⁴, defect states in J-aggregate systems and sometimes the presence of incoherent (uncoupled or undressed) states in coupled systems.¹¹ This is likely the reason why observation of emission from both UR and LR branches in PL spectra of plexitonic nanostructures has not been reported so far.

In this study we demonstrate the identification of Rabi splitting in PL spectra by investigating strong exciton-plasmon interactions in a system comprising J-aggregates of cyanine dye and gold nanorods. We first estimate Rabi splitting at zero detuning from the anti-crossing behavior of the bands in extinction spectra by tuning the resonant wavelength of the nanorods to control the spectral overlap between the exciton and plasmon bands. We obtain a Ω_R value comparable to the largest splittings observed in planar organic microcavities or in plexitonic systems based on gold particles. Next, we focus on the signature of strong coupling in the evolution of the PL modes, which we can identify due to the pronounced emission from both the UR and LR branches. The evolution of the modes is consistent with the results from extinction, which corroborates the interpretation of the modes in terms of an anti-crossing. We further use a theoretical model of emission to analyze the PL spectra and discuss their dependence on the excitation wavelength.

RESULTS AND DISCUSSION

Gold nanorods (65.5 nm x 14.9 nm - sample g in Figure 1; see also Supporting Information S3 and S4) were prepared using Ag-assisted seeded growth.¹⁵ Samples with different aspect ratios were then obtained by controlled oxidation¹⁶ (Supporting Information S3), thereby tuning the position of the longitudinal plasmon band (Supporting Information S4). This procedure yielded nanorods of similar diameter (in the range of 15 - 18 nm) but different lengths (from 34 to 65.5 nm), specifically selected to study exciton/plasmon coupling as a function of detuning with respect to position of the J-band of the J-aggregates. TEM imaging of nanorods presented in Figure 1 confirm the nanoparticles dimensions.

Figure 1: TEM images of gold nanorods with different aspect ratios and representative surface-enhanced Raman scattering spectrum of the hybrid nanostructure of gold nanorods (sample c) and J-aggregates in comparison with the Raman scattering spectrum of JC-1 dye on a gold film.

Using the poor solubility of the selected cyanine dye in water and its ability to form J-aggregates in a medium of high polarity, hybrid structures of gold nanorods and J-aggregates were produced by injection of the concentrated ethanol solution of the dye into an aqueous solution of gold nanorods in the presence of ammonia (see Methods). The main mechanism behind the formation of the hybrid system is assumed to be the electrostatic interactions between the cationic sites of hexadecyltrimethylammonium bromide (which is the surfactant stabilizing the surface of Au nanorods) and anionic groups of the J-aggregates.¹⁷ The formation of the hybrid structures has been further confirmed by surface enhanced Raman scattering (Figure 1) as the hot spots provided by Au nanorods are expected to enhance the Raman scattering response of the attached organic compounds.

Gold nanorods exhibit at least two plasmon resonances, a transverse mode (TM) due to the oscillation of the electrons perpendicular to the long axis of the rod, and a dipolar longitudinal mode (LM) caused by oscillations along the axis. The latter depends almost linearly on the aspect ratio, and it is widely tunable along the visible and near infrared regions of the spectrum (from 597 to 855 nm in our case, Figure 2a). On the other hand, J-aggregates, having extremely high oscillator strength¹⁰, show a very narrow absorption band (J-band) centered around 592 nm with a full-width-at-half-maximum (FWHM) of 8 nm. The absorption band of dye monomers is much broader and positioned at 505 nm. Both peaks are observed in Figure 2c, which is measured in the absence of nanorods. The possibility to tune the plasmonic resonance from close proximity to the J-band to large spectral separation is a key factor behind our choice of dye and plasmon structures, allowing us to investigate how the hybridized modes evolve as a function of the detuning δ .

Figure 2b shows the extinction spectra of the hybrid plasmon-exciton system formed using nanorods of various aspect ratios spectrally characterized in Figure 2a. The weak peak near 500 nm is related with the nanorods TM plasmon resonance, which remains unaffected by the presence of the J-aggregates. We focus on the other two maxima at longer wavelengths, which correspond to the two hybridized modes (UR and LR).

Figure 2: Experimental (solid lines) and simulated (dashed lines) normalized extinction spectra of gold nanorods with different aspect ratio (a), hybrid J-aggregates/gold nanorods complexes (b) and pure J-aggregates (c). In a), samples [A-G] correspond respectively to panels (a-g) in Figure 1. In (b), the different spectra are vertically shifted for clarity and the upper traces correspond to smaller detunings δ , found for lower aspect ratios of the rods in Figure 1. The theoretical spectra use $g/\kappa = -0.4i$.

The top spectrum in Figure 2b corresponds to the hybrid structure for the smaller detuning, which is as small as ~ 10 nm (estimated from the experimental spectra) and shows a clear double peak structure, with the energy separating the UR and LR peaks (the Rabi splitting for negligible losses) estimated to be 265 meV. The two peaks remain visible and redshift as the detuning increases, with much stronger shifts for the LR resonance so that total spectral separation becomes larger. The separation reaches 710 meV for the biggest detuning achieved in our experiments (bottom line in Figure 2b).

Figure 3: Results of the theoretical analysis of peak positions in the extinction spectra obtained for $g/\kappa = -0.4i$ (solid circles) in comparison with the experimental data (squares). The horizontal solid line indicates the spectral position of the J-band, and the diagonal dashed line indicates the plasmon resonances. Both lines correspond to the position of the modes obtained from the model in the absence of electromagnetic coupling. The solid red lines indicate the simple prediction of the energy of the modes using Eq. (1) with the same value of $|g|/\kappa$.

The evolution of the energy of the two branches as obtained from the extinction measurements is summarized in Figure 3, where we have approximately subtracted the influence of the peak at 500 nm to extract the values for the UR peak. The results in Figure 3 are typical of an anti-crossing behavior with Rabi splitting $\hbar\Omega_R \sim 250$ meV (see below the details on how to extract the

value for the Rabi splitting), as a result of the strong coupling of the J-band of the J-aggregates with the plasmon modes of the nanorods.

This value of splitting compares well with previous works studying strongly coupled hybrid systems formed by different silver and gold nanostructures combined with J-aggregates. To date the highest values of Rabi energies (up to 450 meV) have been reported for Ag/J-aggregates systems (Supporting Information S1). Although silver is known to suffer from rapid oxidation that strongly degrades plasmonic properties, significantly smaller values were found for Rabi splitting in Au/J-aggregates systems (up to 260 meV) (Supporting Information S2). In either case both the reported values and the Rabi splitting obtained in our experiments are of the same magnitude as the largest splittings observed in extended planar organic microcavities.^{18, 19}

The accurate determination of the Rabi splitting $\hbar\Omega_R$, defined as $\hbar\Omega_R = \text{Re}(E_+ - E_-)$ for $\delta = 0$, requires the exact values of $E_{\mp}$ (Eq. 1). This aspect is crucial to make a proper comparison with experimental data and to unambiguously identify the emergence of strong coupling. However this estimation is often challenging since the positions of the experimental maxima do not exactly correspond to the values of $E_{\mp}$. This situation is clearly a challenge for example in the case of plasmonic systems with spectral Fano-like dips,^{20, 21} where destructive interference between two weakly coupled modes can lead to the emergence of two peaks without real mode splitting.

We used a theoretical model to better identify the emergence of strong coupling in our system. Although extinction can be addressed by classical models [[Nanotechnology 25 \(2014\) 035201](#), [ACS Photonics 2014, 1, 454](#)], we used a quantum approach that allows us to model both extinction and fluorescence, with a straightforward interpretation of the different parameters involved. Specifically, we model the plexcitonic structures through the Jaynes-Cumming

Hamiltonian as a two-level system coupled to a quantized mode of a plasmonic cavity. The illumination is a classical plane-wave of weak intensity I_0 . The losses κ and resonant energy of the plasmon for each spectra is obtained from measurements of the pristine plasmonic structures. The pure dephasing γ_d and energy of the J-aggregates are chosen to match the experimental and theoretical results, and remain the same for all calculations, taking reasonable values when considering the spectra of the isolated J-aggregates. The spontaneous excitonic decay rate γ_s is assumed to be very small. The critical parameter in this model is the coupling strength g between the J-aggregate and the plasmon. We use a value of $|g|/\kappa = 0.4$, which considerably exceeds the threshold $|g|/\kappa = 0.25$ that defines the onset of the strong coupling ($\hbar\Omega_R > 0$) for negligible molecular losses. The above condition for $\hbar\Omega_R > 0$ becomes $|g|/|\kappa - \gamma_s - 2\gamma_d| > 0.25$ if molecular losses are included. For practical purposes it can be more adequate to compare g with $\kappa + \gamma_s + 2\gamma_d$.⁹ In our case, $\kappa \sim 10\gamma_d$, so that $|g|/|\kappa + \gamma_s + 2\gamma_d|$ remains larger than 0.25. Finally, we notice that we use a value of κ extracted directly from the measurements, which also includes the inhomogeneous broadening of the spectra due to the size distribution of the nanorods. Thus, $|g|/\kappa$ could be significantly larger for individual rods. The detailed description of the Jaynes-Cummings Hamiltonian used and the value of the different parameters assumed are provided in the Supporting information S5.

The predictions of the model are compared to the normalized experimental results in Figure 2b, showing very good agreement for both the UR and LR peaks for all selected nanorod sizes. The agreement is emphasized in Figure 3, where we compare the position of the theoretical peaks for $g/\kappa = -0.4i$ (circles) with the experimental values (squares). The solid red lines correspond to the theoretical position of the modes as obtained from Eq. 1, with $g/\kappa = -0.4i$. Both theoretical estimations do not superimpose because one (lines) accounts for the energy of

the actual modes whereas the other (symbols) considers the maximum of the peaks. Furthermore, in Eq. (1) we do not take into account that κ is not identical for all samples and use an average value. From Eq. (1), we can also estimate the Rabi energy at zero detuning $\delta = 0$, obtaining $\hbar\Omega_R \approx 200$ meV for $g/\kappa = -0.4i$. This value is in general agreement to our simple estimation from the position of the experimental peaks, but the more complete theoretical model has the advantage that it allows to extract the mode energy (the quantity used in the definition of Ω_R) from the peak positions (obtained from the measurements). The anticrossing for a slightly larger value of $g/\kappa = -0.5i$ is shown in Supporting Information S8. The result depends to some extent on the value for the dephasing losses γ_d , which is not known exactly. For reference, if $\gamma_d = 0$ is considered in Eq. (1), a decreased Rabi splitting of $\hbar\Omega_R \approx 180$ meV is obtained for $g/\kappa = -0.4$.

We finally study the less understood influence of strong coupling between excitons and plasmons on the photoluminescence response. The PL of plexitonic complexes nominally identical to those in Figure 2 was measured using continuous excitation at wavelength $\lambda_{ex}^{PL} = 405$ nm (Figure 4a) and $\lambda_{ex}^{PL} = 530$ nm (Figure 4b). The black line in both panels is the emission from the pure J-aggregates, which consists of a well-defined J-band centered at 600 nm and a peak from the monomer, with a maximum at 525 nm. In the following analysis we ignore the contribution of the latter (signal at wavelengths below ~ 550 nm) since it should not affect the coupling with the exciton emitting at 600 nm.

For the smallest detuning δ between the plasmonic resonance of the gold nanorods and the absorption band of the J-aggregates, the PL spectrum of the hybrid system shows two peaks (Figure 4, upper curves for both excitation wavelengths). The spectral positions of these two peaks are close to the spectral positions of the two (UR and LR) resonances in the extinction

spectrum of the hybrid structure (Figure 2), though the spectral distance between the two PL peaks is slightly smaller, on the order of 150-200 meV. The exact value is difficult to determine precisely in Figure 4b because of experimental noise.

Figure 4: Normalized PL spectra (top 7 solid lines) of the hybrid system formed by nanorods of increasing aspect ratios (top to bottom) and J-aggregates, measured using excitation wavelengths of 405 nm (a) and 530 nm (b), as compared to the PL spectra of pure J-aggregates (bottom black curves). The upper spectra correspond to the smaller detuning (i.e. aspect ratio of nanorods is increased from top to bottom). Dashed curves are the normalized results of the theoretical calculations for $g/\kappa = -0.4i$, which assume incoherent excitation of (a) the plasmon mode or (b) the J-band transition.

The observation of the emission from both the UR and LR in the spectra of the plexitonic nanosystem at room temperature is of particular interest because it enables the investigation of the recombination from both UR and LR states of the strongly coupled plexitonic system as well as the analysis of the energy transfer dynamics between UR and LR states. Notably, it has been reported that the high energy state usually does not emit at room temperature¹¹ due to an efficient population transfer to other excitonic states of the J-aggregate that are not coupled to plasmonic excitations. In our experiments, the excess of J-aggregates was separated from the hybrid nanostructures by centrifugation and redispersion of the plexitonic structures in water in a multistep manner. At each step the process was monitored by measuring the absorption spectra until the residual absorbance peak at the wavelength of the excitonic J-band completely disappeared indicating a strongly decreased amount of unbound J-aggregates which are responsible for suppressing the relaxation of the population towards uncoupled excitonic states, (particularly at the smallest detunings). This procedure, together with the strongly enhanced emission from the J-band due to the coupling, can explain why measuring the radiative recombination from UR becomes possible.

The evolution of the spectra with increasing detuning depends on the excitation wavelength. The contribution from the UR at larger energies appears in all spectra and for both illuminations, becoming clearer as detuning increases, and for excitation at 530 nm. However, for excitation at 530 nm (Figure 4b) the lower energy LR peak vanishes very rapidly with increasing detuning, and can only be clearly discerned for the two nanorod samples with smaller aspect ratios (two upper spectra). The corresponding shift between these two spectra is rather weak. For excitation at 405 nm (Fig. 4a), a contribution from the two branches is observed for all detunings, and the shift of the LR peak, when comparing the two rods of smaller aspect ratio, is larger than for

illumination at 530 nm. Nonetheless, as appreciated for large detuning, the LR shifts for excitation at 405 nm remain weaker than the shifts of the corresponding extinction peaks.

We can gain additional insight into the experimental results by tracing the signal as a function of emission wavelength λ_{em}^{PL} in a model calculation. We use the same Jaynes-Cummings Hamiltonian as for the estimation of the extinction above, but we now consider continuous incoherent pumping, as the coherence is lost in the fluorescence process. To reproduce the experimental results, it is convenient to consider pumping of either the longitudinal dipolar plasmon mode when modeling the excitation at $\lambda_{ex}^{PL} = 405$ nm (Fig. 4a), or the 2-level J-aggregate excitation transition when reproducing the measurements with $\lambda_{ex}^{PL} = 530$ nm illumination (Figure 4b). These choices are equivalent to arguing that, at the higher illumination energy, PL processes due to plasmon excitation²²⁻²⁵ are more efficient than those connected with the decay from higher energy states of the J-aggregates, and vice-versa at the lower energies.

The emission spectra are then obtained following the analytical approach introduced by Laussy et al.¹³, and checked against numerical calculations. Notably, we use very similar parameters for the calculation of fluorescence as those used for the extinction, with only small differences in (E_{pl}, κ) characterizing the plasmon, as these are extracted from the measurements of pristine rods for each set of spectra, as obtained before adding the J-aggregate. When treating the case of incoherent pumping of the plasmons, we rescale the results obtained directly from the model by a function $F(\lambda_{em}^{PL})$ obtained from the experimental spectra of the uncoupled pristine rods (See Supporting Information S6). This factorial function introduces in the model the energy dependence of the PL process in metallic samples^{24, 26} [K. Lin et al, submitted and ACS Photonics 2015, 2, 432–438], as well as other effects such as the wavelength-dependence of

dipolar emission. For the larger detunings, δ , the uncertainty introduced by $F(\lambda_{em}^{PL})$ can be comparable with the coupling-induced shifts, therefore it is convenient in this case to focus on the results for the shorter rods. Last, we add a simple saw-like background to account for other contributions. We discuss this model in more detail in the Supporting Information S5-S7.

We find a good agreement between the experiments and the model when comparing the normalized spectra for $g/\kappa = -0.4i$ with the PL spectra at both values of λ_{ex}^{PL} (Figure 4a-b). The difference in the energies of the two resonant hybridized peaks for the smallest detuning δ is ≈ 250 nm for pumping of the plasmon longitudinal mode and roughly 150 nm for pumping of the exciton transition (for the latter, the LR peak appears as a shoulder, but becomes better defined if we increase g/κ). Furthermore, as detuning increases, the two peaks for $\lambda_{ex}^{PL} = 405$ nm (Figure 4a) and the UR resonance for $\lambda_{ex}^{PL} = 530$ nm (Figure 4b) remain visible and evolve in a similar manner both for the calculations and the experiments. In particular, the strength of the LR peak for $\lambda_{ex}^{PL} = 530$ nm decays very fast, in agreement with the measurements. This is likely due to inefficient energy transfer from the more hybrid-like mode at higher energy to the plasmon-like resonance, when exciting the system via PL processes in the J-aggregate. The decay is found to be slightly faster in the theoretical modeling, which may be related to the contribution in the experiments from rods of lower aspect ratio, rods uncoupled with J-aggregates or incoherent excitation of the exciton.

DISCUSSION AND CONCLUSIONS

We have shown that integration of gold nanorods with J-aggregates of a cyanine dye leads to a strong plexitonic coupling, observed as a double-peaked feature in the extinction and PL spectra. In the resonant regime, the Rabi splitting was estimated to be ~ 200 meV, which is among the

highest values reported to date for similar systems. The corresponding value of $|g|/\kappa$ is around 0.4 when using the value of κ extracted from the measured spectra of an inhomogenous assembly or nanorods, and should be significantly larger for single nanorods. Moreover, the pronounced PL emission from both lower- and upper-energy states allowed us to demonstrate the influence of strong coupling on the PL spectra for two different excitation wavelengths. The results for both are similar for no detuning and indicative of Rabi splitting in fluorescence. However, as the detuning increases, we obtain a clearer evolution of the anti-crossing when exciting at an energy significantly larger than the transition of the J-aggregate. We explain the difference as a consequence of predominantly pumping either the plasmon mode for the higher incident energy λ_{ex}^{PL} , or the J-aggregate electronic transitions for the smaller λ_{ex}^{PL} . The PL model also suggests a value of $|g|/\kappa$ around 0.4, consistent with the value for the extinction and thus indicating the onset of strong coupling.

Notably, by assuming consistent strong coupling in equally-prepared systems, the theoretical model can explain well the observed spectral behavior. Nonetheless, the experimental situation is more complicated, and a more sophisticated model should include the correct distribution of nanorod sizes and different degrees of J-aggregate coverage, as well as providing a more accurate description of the PL process in gold and the complex electronic structure of the aggregate (with many possible paths of energy transfer). Including this complexity could explain the remaining differences, and also give a better physical understanding of the background (λ_{em}^{PL}), introduce the efficiency of the PL emission ($F(\lambda_{em}^{PL})$ factor) in a more rigorous manner and allow to better understand under which conditions the incoherent pumping of the plasmon mode or of the J-aggregate dominates the PL signal.

Our results thus support that the anti-crossing behavior typical of the strong coupling regime can be observed in our plexitonic system at room temperature, not only in extinction but also in the PL spectra. These findings could open a new avenue towards the development of novel light-emitting nanostructures with strong exciton-plasmon interactions.

METHODS

Chemicals: Cyanine dye 5,5',6,6'-Tetrachloro-1,1',3,3'-tetraethyl-imidacarbocyanine iodide (JC1), tetrachloroauric acid (HAuCl_4), sodium borohydride (NaBH_4) hexadecyltrimethylammonium bromide (CTAB), silver nitrate (AgNO_3), hydrochloric acid (HCl), ascorbic acid (AA) were purchased from Sigma-Aldrich.

Formation of J-aggregates: J-aggregates were formed using JC1 cyanine. This dye has low aqueous solubility and form J-aggregates spontaneously upon dissolution of this dye in water at pH8^{17, 27}.

Oxidation of Au nanorods: 1.38 mL, 1.25 mL, 1.10 mL, 0.85 mL, 0.50 mL and 0.30 mL of an aqueous solution of Au^{+3} -CTAB complex ($[\text{Au}]=1\text{mM}$, $[\text{CTAB}] = 100\text{mM}$) was added dropwise (0.1 mL/min) and under magnetic stirring to 6 different vials, each containing 10 mL of gold nanorods synthesized by Ag-assisted seeded growth¹⁵ and labeled a-f, respectively. Each solution was allowed to react at 30 °C for 1 h. Subsequently, the solutions were centrifuged twice (6000-9000 rpm, 40 min) to remove excess gold salt and redispersed in CTAB solution (2.5 mL, 15mM).

Formation of the hybrid structures: Hybrid structures of gold nanorods and J-aggregates were produced by addition of 10 μL of concentrated ethanol solution of JC1 dye to 1 mL of an aqueous solution of gold nanorods in the presence of ammonia at pH=8, followed by gentle stirring for 15 minutes. In order to separate hybrid structures (i.e. J-aggregates bound to

nanorods) from monomer dye molecules and J-aggregates, which did not bound to gold nanorods, the solution was centrifuged at 3800 rpm for 2 minutes, and re-dispersed in aqueous solution.

Characterization.

All experiments were performed in an ambient atmosphere at room temperature. Doubly purified deionized water from an 18 MU Millipore system was used for all dilutions. The optical absorption spectra were measured using a Cary 50 spectrometer Agilent Technologies.

Photoluminescence spectra of bare gold nanorods and hybrid structures of gold nanorods and J-aggregates with laser excitation at 405 nm were recorded using Olympus IX71 inverted confocal microscope system equipped with Ocean Optics QEPro High Performance Spectrometer. The PL spectra with wavelength of excitation 530 nm were measured using a Cary Eclipse spectrophotometer Agilent Technologies.

Raman scattering (SERS) measurements were carried out using a confocal Raman microscopy setup (Alpha300, 600 mm⁻¹ grating, 3 cm⁻¹ spectral resolution, continuous wave laser excitation at 532 nm, WITec, Ulm, Germany).

A transmission electron microscopy (TEM) image of nanorods obtained using transmission electron microscope FEG-TEM of type JEOL JEM-2100F UHR.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Rabi splitting energies reported to date in Au/J-aggregates and Ag/J-aggregates –based hybrid nanostructures; Aspect ratios and of nanorods samples and corresponding absorption spectra of gold nanorods; Description of the theoretical model used,

and discussion on the effect on the calculated signal due to the scaling function $F(\lambda_{em}^{PL})$ and the background added. Comparison of the theoretical results for two different coupling strengths.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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