Radiative Transitions and Relaxation Pathways in Plasmon-Based Cavity Quantum Electrodynamics Systems

Daniel Finkelstein-Shapiro, Pierre-Adrien Mante, Sema Sarisozen, Lukas Wittenbecher, Iulia Mindu, Sinan Balci, Tõm Pullerits, and Donatas Zigmantas

Division of Chemical Physics and Nanolund, Lund University, Box 124, 221 00 Lund, Sweden
Department of Chemistry, Izmir Institute of Technology, 35430 Izmir, Turkey
Department of Photonics, Izmir Institute of Technology, 35430 Izmir, Turkey

Molecular aggregates on plasmonic nanoparticles have emerged as attractive systems for the studies of cavity quantum electrodynamics. They are highly tunable, scalable, easy to synthesize and offer sub-wavelength confinement, all while giving access to the ultrastrong light-matter coupling regime at room temperature and promising a plethora of applications. However, the complexity of both the molecular aggregate and plasmonic nanoparticle introduces many more processes affecting the excitation and its relaxation, than are present in atom-cavity systems. Here, we follow the complex relaxation pathways of the photoexcitation of such hybrid systems and conclude that while the metal is responsible for destroying the coherence of the excitation, the molecular aggregate significantly participates in dissipating the energy. We rely on two-dimensional electronic spectroscopy in a combined theory-experiment approach, which allows us to ascribe the different timescales of relaxation to processes inside the molecules or the metal nanoparticle. We show that the dynamics beyond a few femtoseconds has to be cast in the language of hot electron distributions and excitons instead of the accepted lower and upper polariton branches, and furthermore set the framework for delving deeper into the photophysics of excitations that could be used in hot electron transfer, for example to drive photocatalytic reactions.

INTRODUCTION

Cavity quantum electrodynamics (cQED) has been a very successful testbed for the quantum mechanics of light-matter interaction [1–4], and exhibits phenomena of both fundamental and practical interest [5–16]. As the light-matter coupling strength increases, new and interesting effects arise tied to non-zero ground state occupation of the cavity, so that finding systems that can push the coupling into stronger regimes are desirable to explore new physics [17–19]. Condensed-matter cQED realizations are particularly attractive as they reach the ultrastrong coupling regime at room temperature with Rabi splittings in excess of 30% of the emitter frequency [11–13, 20–28]. This regime can be reached both by molecules placed in a microcavity [14–19], or in systems where the field has been confined by a plasmonic resonance to sub-wavelength dimensions, as is the case for plexcitons (plasmon+exciton) [18–26].

There is an increasing complexity of the dissipative environment in cQED realizations as we move from atoms in cavities, to molecules in microcavities, and finally to molecules coupled to plasmonic nanoparticles. The wealth of dissipative processes when replacing a cavity by a plasmon – for example Landau damping, electron-electron (e-e) scattering and electron-phonon (e-ph) scattering – modulate the dynamics in non-trivial ways that cannot be ignored [29]. A stronger coupling to a dissipative environment, however, needs not be necessarily detrimental and there are several examples where harnessing it increases device efficiency, and therefore should be explored [30–31].

Ultrafast pump-probe studies have reported the relaxation times of the excitation [32–37] as well as the Rabi oscillations in the case of molecules coupled to gold nanoslit arrays [35]. Unfortunately, there is no consensus on the plexciton lifetimes and dephasing processes, likely stemming from system to system differences, and non-trivial excitation wavelength dependence. For example, Hranisavljevic et al. found an exceptionally stabilized excited state with a 300 ps decay constant [34], while Balci et al. measured decay constants close to 10 ps which are pump wavelength dependent [33], on similar systems consisting of cyanine dyes adsorbed on Ag plasmonic nanoparticles. Furthermore, an understanding of the dissipation in terms of the physical mechanisms in the molecular aggregates or the plasmonic nanoparticles is lacking. The studies of microcavity QED in the infrared region (where molecular vibrations are dressed by the cavity modes) are more mature, and can provide useful guidelines as to what differences we might expect between molecular and atomic systems [38]. Notably, previous studies underscore the importance of dark states [38], although extrapolating the same physics to plasmonic-based hybrids in the visible regime should be done with care.

In this work, we explore in detail the ultrafast dynamics of plexcitons and corresponding dissipation mechanisms following light absorption. We start from a description of the plexciton linear absorption by extending the Feynman diagram formalism to non-Hermitian Hamiltonians. This forms the basis to interpret two-dimensional electronic spectroscopy (2DES) experiments and to propose a physical origin of each relaxation component ob-
served in the plexciton, either to processes inside the J-aggregates or inside the metal nanoparticle.

RESULTS

J-aggregates (TDBC, 5,5,6,6-tetrachloro-di(4-sulfobutyl) benzimidazolocarbocyanine), Ag nanoprisms and plexcitons (TDBC-Ag nanoprism) were prepared as reported previously (see Methods section, [26, 39]). The samples were prepared in solution and the reported measurements were done in transmission mode.

Linear response

The absorption spectrum can be used to infer the homogeneous linewidth (when it is much larger than the heterogeneous broadening) and the energy structure of the first excited state manifold, a prerequisite to interpret correctly the third order response signals presented below. The absorption of the plexciton clearly shows the upper and lower plexcitonic branches (Figure 1b). The minimum of the dip in the spectrum is nearly coincident with the J-aggregate absorption at 16,950 cm⁻¹ (590 nm).

In the following, we obtain through fitting of the lineshape the energy and coherence lifetime of the first excited state manifold and motivate the structure of the higher manifold based on previous measurements and theoretical models (Figure 1a and [40, 41]). An ideal J-aggregate consisting of N monomers with individual transition dipole moments μ₀ separates into a single bright state carrying all of the transition dipole moment strength μbright = √Nμ₀, and N − 1 dark states. Although this is strictly true only in the absence of disorder, its predictions are in agreement with the absorption spectrum of the J-aggregate consisting of a very strong resonance. It is well-fit by a Lorentzian with center frequency ˜ν = 17.04×10³ cm⁻¹ and full-width at half maximum (FWHM) of γJ = 120 cm⁻¹, corresponding to a dephasing time of 44 fs (Supplementary Figure S1). The double exciton states manifold consists of a band whose transition from the first exciton manifold (1 → 2) is almost isoenergetic with the first transition (0 → 1) [22], and its detuning can be calculated from the linear Frenkel exciton model [11]. While both the first and second excited states form bands, we will refer to them as single states under the viewpoint that most of the transition dipole moment strength is carried by one state. Analogously to the J-aggregate transition, we model the lineshape of the plasmon absorption in the Ag nanoparticles as a Lorentzian with center frequency ˜νp = 16.92×10³ cm⁻¹ and a width of γp = 1.78×10³ cm⁻¹ corresponding to a dephasing time of 3 fs (Supplementary Figure S2). The extracted Rabi splitting corresponds to 11% of the molecular transition frequency placing the system in the ultrastrong coupling regime.

Given this structure for the individual components, and the expected coupling between them, we arrive at the energy level structure shown in Figure 1a. We summarize the state energies and couplings in the following Hamiltonian, which is analogous to that proposed by oth-
ers [43–46], and that we have extended to a second manifold of excited states necessary to simulate the 2D maps (see Figure 1a). The Hamiltonian in the \{g, p_1, J_1, p_2, J_2\} basis (that we call here site basis) reads:

\[
H_{\text{site}} = \begin{bmatrix}
0 & F_{\mu g p_1} & F_{\mu g J_1} & 0 & 0 \\
F_{\mu p_1 g} & h\tilde{\omega}_{p_1} & V_1 & F_{\mu p_2 p_2} & 0 \\
F_{\mu J_1 g} & V_1^* & h\tilde{\omega}_{J_1} & 0 & F_{\mu J_1 J_2} \\
0 & F_{\mu p_2 p_1} & 0 & h\tilde{\omega}_{p_2} & V_2 \\
0 & 0 & F_{\mu J_2 J_1} & V_2^* & h\tilde{\omega}_{J_2}
\end{bmatrix}
\]

(1)

where \(\tilde{\omega}_j = \omega_j - i\gamma_j\) is a complex frequency that accounts for the transition frequency \(\omega_j\) and its associated dephasing rate \(\gamma_j\). \(\mu_{ji}\) are the transition dipole moments from \(i\) to \(j\), \(F\) is the field strength and \(V_i\) is the dipolar coupling between the J-aggregate and the plasmon’s \(i\)-th excited states. \(g\) is the shared ground state, and \(p_i\) and \(J_i\) are the \(i\)-th excited state of the plasmon and J-aggregate, respectively (the measured spectra are displayed in wavenumbers \(\tilde{\nu} = \omega/(2\pi c)\) where \(\omega\) is the angular frequency and \(c\) is the speed of light).

In order to use the same theoretical approach for the linear and third order response, we simulate the absorption spectrum for our model system using the Feynman diagram formalism [47]. In the polariton basis - obtained by diagonalizing \(H_{\text{site}}\) at zero-field \((F = 0)\) and without including the dephasing (that is setting \(\tilde{\omega}_j = \omega_j\)), we can express the linear absorption as a sum over polariton state contributions [48, 49]:

\[
I(\omega) = \int dt e^{-i\omega t} \sum_{a=UB,LB} \mu_{ag}^{(g)}(g) e^{-i(\omega^{(g)}_a - \omega_a - \gamma^{(g)}_a)t},
\]

(2)

where \(\mu_{ag}^{(g)}\), \(\omega^{(g)}_a\) and \(\gamma^{(g)}_a\) are the transition dipole moment from level \(g\) to the polaritonic upper or lower branch \(a \in \{LB, UB\}\), the transition frequency between \(g\) and \(a\) and the dephasing rate, respectively. The \(g\) or \((l)\) (used below) superscript refer to the approach taken to obtain the polariton branches. The transition frequencies and transition dipole moments are obtained from the diagonalization of the Hamiltonian, while the dephasing rates of each branch is introduced phenomenologically in the absorption expression (Eq. (2)). This model, labeled as the global approach fits the spectrum poorly (cyan, Figure 1c). The global approach model is equivalent to fitting the absorption spectrum to a sum of Lorentzians (here two) that in this case does not represent the lineshape measured. We instead diagonalize the non-Hermitian operator \(H_{\text{site}}\) including the imaginary part of the transition frequencies (dephasing rates \(\gamma_{J_1}, \gamma_{J_2}\)) to obtain the new (complex) polariton branch energies \(\omega^{(l)}_a\) and their respective transition dipole moments \(\mu^{(l)}_{ag}\). We modify the expression for the linear response accordingly to:

\[
I(\omega) = \int dt e^{-i\omega t} \sum_{a=UB,LB} \mu^{(l)}_{ag} \mu^{(l)}_{ga} e^{-i(\omega^{(l)}_a - \omega_a)t},
\]

(3)

where \(\mu^{(l)}_{ag}\) are Hermitian broadening added for each polariton branch, while \(\gamma^{(l)}_a \equiv \text{Im}(\omega^{(l)}_a)\) of Equation (3) arise directly from the diagonalization of the non-Hermitian Hamiltonian of Eq. (1) that includes the individual dephasing of the J-aggregates and plasmons. Thus the frequencies and dissipation rates of Equations (2) and (3) are different and depend on the step in which dephasing is added. As we see from Figure 1c in the local approach fit (magenta line) the agreement with such a simple model is excellent, with deviations attributable to

a. Separate components in solution

|                  | \(10^3\) cm\(^{-1}\) | fs   |
|------------------|---------------------|------|
| J-aggregate      |                     |      |
| \(\tilde{\nu}_{J1}\) | 17.04               | 44   |
| \(\gamma_{J1}^{-1}\) |                     |      |

|                  | \(10^3\) cm\(^{-1}\) | fs   |
|------------------|---------------------|------|
| Plasmon          |                     |      |
| \(\tilde{\nu}_{P1}\) | 16.92               | 3    |
| \(\gamma_{P1}^{-1}\) |                     |      |

b. Hybrid system in solution

|                  | Local | Global |
|------------------|-------|--------|
|                  | \(10^3\) cm\(^{-1}\) | fs   |
| site basis       |       |        |
| \(\tilde{\nu}_{J1}\) | 16.73 | 16.08  |
| \(\gamma_{J1}^{-1}\) |       | 30     |
| \(\tilde{\nu}_{P1}\) | 19.28 | 19.52  |
| \(\gamma_{P1}^{-1}\) | 0.93  | 0.98   |
| plexitonic basis |       |        |
| \(\tilde{\nu}_{L,B}\) | 16.58 | 16.42  |
| \(\gamma_{L,B}^{-1}\) |       | 11     |
| \(\tilde{\nu}_{U,B}\) | 19.43 | 19.59  |
| \(\gamma_{U,B}^{-1}\) | 1.7   | 2.1    |

TABLE I: a) Parameters of the radiative transitions of the individual components in solution (J-aggregates and plasmons measured separately). The absorption lineshape is fit with a Lorentzian (see SI for fits). b) Parameters for the radiative transition of plexitons. The spectrum is fit using equation (2) (global approach) or (3) (local approach). The upper and lower branch properties are obtained by the diagonalization of the Hermitian Hamiltonian of Eq. (1) (without dephasing) for the global approach, and of the non-Hermitian Hamiltonian (with dephasing) for the local approach. Dephasing of the branches for the global approach is added in the calculation of the absorption spectrum while for the local approach it is added in the Hamiltonian.
the simplifying assumption of representing the plasmon lineshape by a Lorentzian far away from the resonance (Figure S2). The name of the models (local vs. global) refer to the approximations implemented to reach the underlying Markovian master equation [50]. In the global approach, the bath modes couple to the eigenstates of the Hamiltonian while in the local approach, the bath modes couple to the individual sites. This is achieved here by using the eigenstates of the non-Hermitian Hamiltonian to calculate the optical response.

The parameters of the fits are reported in Table I. The plasmon dephasing time is extremely fast (1.6 fs), in agreement with previous measurements [51, 52]. This fast dephasing rate is inherited to the plexciton branches (1.7 and 16 fs for upper and lower branch respectively). The difference in dephasing rates can be attributed to the upper branch having more of a plasmonic character than the lower branch. This is clear from detuning between the plasmon (19.28×10^3 cm^-1) and the J-aggregate transition (16.73×10^3 cm^-1). The frequencies of the radiative transition in the individual components, that is of the J-aggregates in solution, and that of the plasmonic nanoparticles in solution, differ from the frequencies obtained from the fits for the J-aggregate and plasmon transitions in the hybrid. The J-aggregates when bound to plasmonic nanoparticles exhibit a red-shift of 310 cm^-1, attributable to J-aggregates structural perturbations when binding to a metallic nanoparticle. The plasmon resonance in the hybrid shows a strong blue shift, which is likely due to a surface restructuring of the nanoprisn and bears – unlike the J-aggregate red-shift – no fundamental relevance to the physics studied. In the plexciton radiative transitions, the plasmon carries most of the transition dipole moment strength (μJ,μ = 0.05μpl,μ), justifying the approximation of [43] of considering that only the plasmonic transition couples to the external radiation field. The dephasing times of the plasmon and J-aggregate in the hybrid are larger than for the individual components in solution (1.6 vs. 3 fs for plasmon, 30 vs 44 fs for J-aggregates) hinting at a contribution from interfacial processes.

With this understanding of the energy levels and homogeneous linewidths we turn to the excitation dynamics picture provided by 2DES.

**J-aggregates.** The 2D spectra of J-aggregates shows a broad excited-state absorption contribution (ESA, negative, blue) almost coincident with a ground-state bleach (GBS, positive, red) and stimulated emission signal (SE, positive, red), indicating a near isoenergetic gap between the ground and first excited bands, and between the first and second excited state bands (see Figure 2 and Supplementary Figure S3). This is in accordance to previous measurements and justifies the energy level scheme of Figure 2a. The population of the excited state decays with very little spectral shift and can be fitted with three lifetimes of 80±20 fs, 4.2±0.4 ps and a very long-lived excited state (> 100 ps). This agrees with time constants obtained by previous transient absorption experiments, that have assigned the first component to relaxation into the dark states, the second component to exciton-exciton annihilation (few ps) and the long-lived component to relaxation back to the ground state [11, 51, 55].

**Plasmons.** The 2D spectra show a single nodal line delimiting a negative and positive region (Figure 2). The dynamics are characterized by spectral shifts and sign reversals across this nodal line, and can be separated into the early time dynamics (t < 4 ps), dominated by electron-electron and electron-phonon scattering and a late time dynamics (t > 4 ps) corresponding to hot lattice ground state dynamics [29, 55–59]. We can think of the early time dynamics as corresponding to the processes that transfer the energy from the initial electron excitation into the lattice, and the late time dynamics as the response of the lattice to this excess energy, notably a possible excitation of an acoustic eigenmode and a lattice expansion due to the increase in lattice temperature. The signal can be very well fit by a phenomenological equation analogous to the two-temperature model ([10] and Supplementary Discussion III, Supplementary Figures S4-S9):

\[
I(t) = A_1(1 - e^{-t/\tau_{ee}})e^{-t/\tau_{ph}} + A_2(1 - e^{-t/\tau_{ph}})e^{-t/\tau_{phph}} + A_3(1 - e^{-t/\tau_{ph}})e^{-t/\tau_{vib}} \cos(\omega_0 t - \phi) + A_4(1 - e^{-t/\tau_{ph}})e^{-t/\tau_{vib}}
\]

where τ_{ee} = 300 ± 200 fs, τ_{ph} = 1.4 ± 0.2 ps are the inferred e-e and e-ph scattering times, \(2\pi/17.0 \text{ rad/ps}^{-1}\) is the angular frequency of the breathing mode, \(\phi = 25^\circ\) its phase, and τ_{vib} = 15 ps its dephasing time. The thermalization time of the nanoparticle with the environment on the timescale of the phonon-phonon scattering time τ_{phph} is longer than the measured population time range (> 1 ns). The asymptotic phase \(\phi\) of the breathing mode carries information on the excitation mechanism of the acoustic eigenmode. The extracted 25° phase is in reasonable agreement with a thermal expansion mechanism (predicted at
FIG. 2: 2D spectra at different population times $t_2$ as well as time traces for J-aggregates, plexcitons and plasmons (lowest row). Insets for plexcitons and plasmons show the late-time signal. The data is shown in normalized colour scale with the scaling factor shown in parenthesis.
\[ \phi = \arctan(\omega_0 \tau_{\text{e-ph}}) = 28^\circ \] and constitutes a signature that energy is dissipated inside the metal nanoparticle (see SI) [62].

**Plexcitons.** The early time 2D spectra of the plexcitons consists of two positive regions identifiable with the upper and lower branches, flanking the negative feature (Figure 2). The dynamics can be fit by the sum of four exponential decays with 40 ± 20 fs, 400 ± 100 fs, 1.6 ± 0.6 ps time constants and one very long lived state (>1 ns) that appears as a background at long times. The first time component has a large amplitude and corresponds to a pure decay without any appreciable spectral diffusion (see Supplementary Discussion IV and Figure S10-12). The second and third time constants correspond to pronounced spectral shifts. The 2D spectra show little evolution after this. The time traces (Figure 2 last row) also show fast oscillations on top of the exponential decays at 675 cm\(^{-1}\) and 1200 cm\(^{-1}\) wavenumbers. These correspond to the Raman modes observed in Surface-Enhanced Raman Spectroscopy measurements of the same plexciton systems (see Supplementary Figure S13, [39]).

**Simulations of the plexciton 2D spectra.** We simulate the third-order response in two limiting cases assuming that the electrons in the metal are in an equilibrium Fermi distribution (Figure 3 and Supplementary Discussion V and Figures S14-19 for details of the simulations). At time \( t_2 = 0 \), the excitation is dominated by the plasmon transition (i.e. dephasing has not produced a non-equilibrium distribution of electrons), whereas at very long times, all excitations have decayed to the ground-state when the third pulse arrives. The intermediate times require an involved model based on Boltzmann equations, which is beyond the scope of the current study.

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| Experiment | Local approach | Global approach |
|------------|----------------|-----------------|
| Early times | | |
| 100 fs | | |
| | | |
| Late times | | |
| 20000 fs | | |

**FIG. 3:** Measured and simulated 2D spectra at early \((t_2 = 0)\) and late times. The simulations were carried out both in the local and global approach.

As in the linear absorption spectra, the local approach model qualitatively reproduces the measurement at both
early and late times while the global approach does not. This further bolsters support for the local approach to Markovian master equations, and provides a strong support for a long-time dynamics corresponding to the thermalization of a plexciton with a hot lattice.

FIG. 4: Summary of dynamics. Top panel: representative kinetic traces of J-aggregates, plasmons and plexcitons at short and long times. Bottom panel: summary of the time constants measured in the experiments. The bars for a given time constant $\tau$ are drawn from $\tau/5$ to $5\tau$.

DISCUSSION

We now analyze each of the four components of the plexciton decay dynamics (labelled i, ii, iii, iv) to elucidate the responsible mechanism behind each one (see Figure 4). Our analysis is based on the relaxation time con-
stants, the 2D spectral signatures and the overall cohesiveness of the proposed mechanism.

The spectral signature of the first time constant $\tau$ (80 fs) is that it does not induce any spectral shift (see Supplementary Figure S10). The J-aggregate has an ultrafast component $< 100$ fs that does not cause any spectral shift while such a process is absent in plasmons. Accordingly, we suggest this decay arises predominantly from relaxation inside the J-aggregates.

During the second component $\tau_1$ (400 fs) we see a strong spectral shift. The fact that J-aggregates have no processes that induce a spectral shift while plasmons do and with a similar time constant (250 fs), suggests that this process corresponds to the e-e scattering inside the metallic nanoparticle. The third component $\tau_2$ (1.6 ps) induces a much smaller spectral shift. The time constant for this process is close to the time constant for e-ph scattering measured in the Ag nanoprisms (1.4 ps) and suggests the same underlying process. The final time constant, whose associated dynamics appears as a constant signal, lies beyond the range of our measurement. Based on simulations for a hot plexciton, we assign this final process to its equilibrium Fermi distribution. A signature of exciton-exciton annihilation - corresponding to a pure decay of the signal - is not observed, although we cannot rule out that it is a process that contributes to the third time constant.

Our measurements suggest that enough energy is dissipated outside of the metal nanoparticle so that the acoustic eigenmode cannot be excited to a detectable intensity. It is most probably dissipated in the J-aggregate, given the fast transfer rate to dark states, which can compete with e-e and e-ph scattering. While the coherence of the plexciton is limited by processes inside the metal, the energy lifetime would thus be strongly limited by ultrafast processes inside the J-aggregate. This guides synthetic efforts in the direction of storing the energy in excited states longer, and points towards a clear advantage for achieving strong coupling in the single molecule limit where the number of dark states is either eliminated or significantly reduced.

Furthermore, the observation that e-e scattering processes exist in plexcitons reveals a crucial point in plasmonic-based cQED: that one can no longer speak exclusively in terms of upper or lower branches once dephasing processes have turned the initial coherent excitation into a non-equilibrium distribution of electrons and holes. A framework beyond Rabi type Hamiltonians, including the continuum states of the metallic band is needed in order to describe anything other than the early or late times.

Many possible applications of atomic cQED have been explored throughout the years, from basic tests of quantum mechanics and quantum information, to studies of strong light-matter coupling, its usefulness has been proven many times over. In contrast, the field of molecular cQED systems - and more so when the cavity is substituted by a plasmonic mode - is relatively recent. We are still learning what these systems are capable of and in what ways they differ from the more traditional cQED versions. There are many interesting phenomena: delocalization, collective behavior, chemical reactions, remote energy transfer [5-10]. In our work, we show that we need to understand the basic excitation dynamics occurring in metals when these are coupled strongly to emitters. The stronger coupling of plasmons and J-aggregates to their baths than between each other means that the site levels are dressed by the dissipative modes. The resulting spectra and physics is more akin to an interference-type process than a Rabi splitting [64]. This type of physics has been recognized before in scattering settings [65, 66]. However, it has not been connected to the local vs. global approach to Markovian master equations. As we show in this work, taking the local approach requires an extension to non-Hermitian Hamiltonians in the double-sided Feynman diagram formalism. Thus our study provides both the motivation and groundwork to study the nonlinear response of Markovian systems in the limit of large dissipation that dominates plasmonic materials. We believe that given the short coherence times in colloidal suspensions of localized surface plasmon materials, a very interesting application of plexcitons arises in the manipulation of optical transitions to favor charge-transfer to an acceptor, or to promote catalysis, as opposed to performing coherent operations with these states.

CONCLUSION

We have presented a study of plexciton dynamics after photoexcitation using linear and third-order response. We are able to explain the lineshapes using a non-Hermitian Hamiltonian extension of Feynman diagrams, which are rooted in the local approach to Markovian master equations. We have tracked the excitation evolution identifying one dephasing and four relaxation timescales which we have attributed to either molecular-like or metallic-like processes. Remarkably, we find that a significant part of the energy is dissipated outside of the metallic lattice. Our work suggests that when considering the relaxation of plexcitons a more nuanced version of the dynamics in terms of hot electron distributions is needed.

cQED realizations continue to bring new insights into
basic quantum physics concepts and emergent behavior of hybrid systems. Because the plasmon-based cQED exists at the intersection ofstrong-light matter coupling and important condensed matter processes such asinterfacial charge transfer and photocatalysis, they are uniquely fit to bring desirable features of the former into the societally relevant applications of the latter.

**METHODS**

**Synthesis.** We synthesized plasmonic and plexcitonic nanoparticles as reported in our earlier studies \cite{26,39}. Briefly, the Ag nanoprisms with varying edge lengths were wet-chemically synthesized by using a seed-mediated protocol. Initially, isotropic seed Ag nanoparticles were synthesized, which was then followed by a slower growth of anisotropic Ag nanoprisms. By controlling the number of seed nanoparticles in the growth solution, the size of the nanoprism can be easily tuned. Concurrently, the localized surface plasmon polariton frequency of the nanoparticles vary from 400 nm to 1100 nm. Pplexcitonic nanoparticles used in this study were synthesized by self-assembly of a J-aggregate dye (TDBC, 5,5,6,6-tetrachloro-di(4-sulfobutyl) benzimidazolocarbocyanine, FEW Chemicals) on Ag nanoprisms surfaces. It should be noted that the excess dye molecules were removed by centrifugation.

**Two-dimensional electronic spectroscopy.** The 2DES spectrometer is described in detail in \cite{67}. Briefly, femtosecond broadband pulses were generated by feeding the 1,030 nm output of a Pharos laser (Light Conversion Ltd) to a commercial NOPA (Light Conversion Ltd) to generate a pulse at 590 nm. The narrowband spectrum (see Supplementary Figure S15, simulations) where generated by compressing the pulse using chirped mirrors and a prism compressor, and subsequently editing the spectrum using a blade edge to obtain a 40 nm FWHM pulse of less than 25 fs duration (used for J-aggregates and plexcitons measurements). To obtain the broadband spectrum pulse we used a home-built pulse shaper arranged in a folded 4f-geometry. The setup is based on a dual liquid crystal spatial light modulator (SLM-S640d, Jenoptik) enabling simultaneous shaping of phase and amplitude \cite{68}. Second order dispersion from material in the beam path is for the most part compensated for by a pair of chirped mirrors in combination with a prism compressor consisting of two fused silica prisms at a separation of 310 mm. Higher order phase distortions are compensated for by the pulse shaper. With this arrangement broadband pulses with a duration of 11 fs were obtained (used for the plasmonic nanoparticles measurement). All four beams are focused at the sample to the spot size of 160 µm. The pulses were attenuated to pulse energies in the range of 0.1 to 1.25 nJ/pulse. Polarizations of pulses 1 and 2 were set to magic angle with respect to pulse 3 and the local oscillator. Several measurement series were carried out across population times. The coherence time was scanned from -71.6 to 151.2 fs in 1.4 fs steps for J-aggregates, from -42 to 63 fs for plasmons and from -50.4 to 50.4 fs for plexcitons. The resolution of the measurement was 60 cm$^{-1}$ at the detection frequency and 290 cm$^{-1}$ at the excitation frequency.

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**AUTHOR CONTRIBUTIONS**

D.F.S. and D.Z. conceived the idea. D.F.S., L.W., I.M. and D.Z. designed and performed the experiments. D.F.S., P.A.M. and T.P. discussed the theory and D.F.S. carried out the simulations. S.S. and S.B. synthesized the samples. D.F.S. and P.A.M analyzed the data and D.F.S. wrote the manuscript, edited by P.A.M., T.P. and D.Z., with input from all the other authors.

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* Electronic address: daniel.finkelstein.shapiro@chemphys.lu.se
† Electronic address: donatas.zigmantas@chemphys.lu.se

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