

Energy Transfer and Interference by Collective Electromagnetic Coupling

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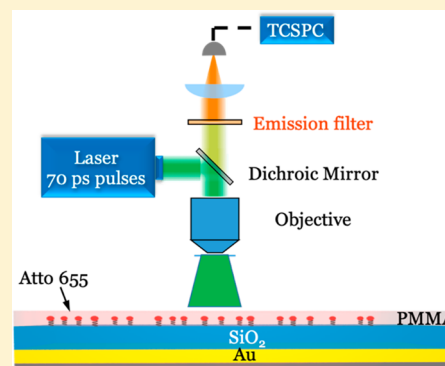
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Supporting Information

ABSTRACT: The physics of collective optical response of molecular assemblies, pioneered by Dicke in 1954, has long been at the center of theoretical and experimental scrutiny. The influence of the environment on such phenomena is also of great interest due to various important applications in, e.g., energy conversion devices. In this Letter, we demonstrate both experimentally and theoretically the spatial modulations of the collective decay rates of molecules placed in proximity to a metal interface. We show in a very simple framework how the cooperative optical response can be analyzed in terms of intermolecular correlations causing interference between the response of different molecules and the polarization induced on a nearby metallic boundary and predict similar collective interference phenomena in excitation energy transfer between molecular aggregates.

KEYWORDS: Collective fluorescence, superradiance, energy transfer



The collective optical response of atomic and molecular emitters has been discussed throughout the evolving science of light–matter interaction. In particular, the Dicke theory of superradiance emission¹ and variants such as superfluorescence² have been extensively discussed and different aspects of the phenomenon, including its quantum and classical aspects³ as well as the effect of static disorder (inhomogeneous broadening) and dephasing (homogeneous broadening), were elucidated.^{3–7} More recent discussions of cooperative molecular effects have focused on strong coupling between molecular excitons and plasmons or cavity modes, mostly manifested through the $\sqrt{N}$ scaling of the observed Rabi splitting in such systems, where N is the number of involved molecules.^{8–10} It should be noted that while both phenomena are manifestations of a collective response, Dicke superradiance is observed during the decay of a state in which all molecules in a given cluster are initially excited while the collective Rabi splitting usually involves the bright single exciton state where a single molecule excitation is delocalized over N molecules. Significantly, the radiative lifetime of such a bright exciton, which carries most of the oscillator strength of the N -molecule cluster, is $\tau_R(N) = \tau_R(1)/N$, a property which expresses itself also in energy transfer out of such a cluster.¹¹

Both this collective feature and Dicke's superradiance physics have been discussed recently with regards to their implications for the performance of energy conversion devices.^{12–21} It should be noted that the theme exploited in all these studies is the correlated behavior of a many-body system (often modeled as a cluster of N two-level atoms) supported by their mutual coupling to the radiation field, sometimes in the form of strong coupling to a cavity mode. The general physics of such systems has been extensively discussed since the middle of the previous century.^{22–31} More recent studies have placed such systems in the vicinity of metal nanostructures, where interaction between molecular emitters is mediated not only by free or cavity photon modes but also via their mutual interactions with metal plasmons.^{11,32–38}

While not usually phrased in this language, cooperative optical response can often be analyzed as interference between the response of different molecules, where correlations determine whether one observes constructive or destructive

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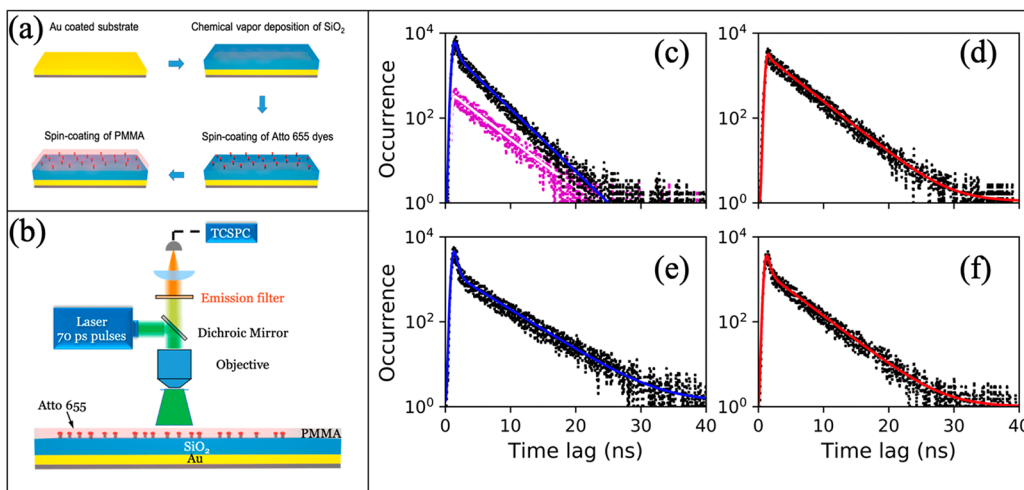


Figure 1. Panel a shows the scheme of the fabrication process. Panel b shows the experimental setup for optical measurements. Panels c–f show the semilog decay profiles of ensembles of molecules ($3 \times 10^{22} \text{ m}^{-3}$ layer density in panels c and e, $3 \times 10^{23} \text{ m}^{-3}$ in panels d and f) deposited either on a bare glass substrate (reference sample, magenta dots in panel c) or at a given distance (80 nm in panel c, 380 nm in panel d, 200 nm in panel e, and 560 nm in panel f), fixed by a silica layer, on top of the gold mirror structure (black dots). For the reference sample, the decay is monoexponential (panel c, white line) with a rate $\gamma = 0.178 \mu\text{eV}$. In the other cases, the decay is found to be best fitted by a biexponential with rates γ_L (γ_S) equal to 1.68 (0.224) μeV (panel c, blue line), 5.52 (0.191) μeV (panel d, red line), 1.64 (0.145) μeV (panel e, blue line), and 1.90 (0.184) μeV (panel f, red line).

interference. In the simplest case of a single excited molecule placed in front of a mirror, emission from the molecule and the polarization induced in the metal (or the molecule and its image) interfere, leading to oscillations in fluorescence lifetimes as a function of the distance from the surface.^{39–43} Obviously, this phenomenon is not limited to a single molecule. The response of a molecular cluster, including all the intricacies mentioned above, is expected to interfere with the response of the corresponding polarization induced on a nearby metallic boundary or a metal particle. Indeed, such effects have been very recently discussed³⁷ and observed.⁴⁴

In this Letter, we experimentally and theoretically demonstrate such collective molecular phenomena. We note that with strong dependence on intermolecular correlations, specific behaviors may reflect properties of specific structures. By studying the optical properties of such structures, we can characterize their collective nature as reflected in their steady state and relaxation behaviors, their dependence on emitter density (or number), system dimensionality and structure, as well as effects of structural and dynamical disorder. Our experimental results demonstrating such collective behavior are presented in **Experimental Results**. We discuss these phenomena within a simple theoretical model in **Theoretical Model and Computational Results** and present results of numerical simulations based on a Maxwell–Bloch model for the radiation field–molecules system. Even on this simple level, we can demonstrate dramatic effects of structure, order, and emitter density, implying new ways to control the optical properties of molecular nanodevices.

Experimental Results. The proposed samples are fabricated as described in Figure 1a (see **Experimental methods** in the Supporting Information for fabrication details). First, a flat gold substrate is covered by a silica layer with a well-controlled thickness. Such a film works as a spacer between the metallic mirror and a postdeposited molecular layer of Atto 655 fluorophores, whose number density can be varied with the concentration of molecules in solution. The fluorescent dye was chosen due to its characteristic features of strong

absorption ($1.25105 \text{ M}^{-1} \text{ cm}^{-1}$), high fluorescence quantum yield (0.3), and high thermal and photostability for a red dye emitting at 680 nm, e.g., at a wavelength where autofluorescence of the sample is drastically reduced, ensuring an extremely clean collection of the photon counts. A layer of poly(methyl methacrylate) (PMMA) is finally deposited on top of the structure in order to fix the position of the fluorescent dyes and provide similar electromagnetic boundary conditions on both sides of the layer. As a reference sample, the ensemble of fluorophores and PMMA were deposited in the same conditions on a bare glass substrate. Once prepared, the samples underwent structural and ellipsometry characterizations, ensuring that they were designed as prescribed. We then investigated the samples by time-resolved fluorescence microscopy in order to determine the emission properties of the system. As presented in Figure 1b, a pulsed laser operating at 654 nm is normally focused on the sample surface. The emitted fluorescence is then collected through the same objective and sent to the detector for the following reconstruction of the decay profiles.

The decay profiles of Atto655 molecules deposited on a bare glass substrate from a 10^{-8} M concentration of dyes in ethanol exhibit a clear single exponential decay profile with a decay rate of 0.178 μeV (Figure 1c: magenta dots fitted by a white line). This sample, with a molecular number density of $3 \times 10^{22} \text{ m}^{-3}$, is taken as reference because its measured decay rate is characteristic of nonaggregated molecules. Larger concentrations (typically larger than 10^{-6} M) lead to nonexponential decay profiles evidencing dyes' aggregation on the bare glass substrate, a behavior which we want to avoid. The decay profiles of similar molecular number densities ($3 \times 10^{22} \text{ m}^{-3}$) deposited at a controlled distance (silica spacer) of the gold mirror structure significantly deviate from a single exponential decay profile.

A biexponential function $I(t) = I_S \exp(-\gamma_S t) + I_L \exp(-\gamma_L t)$ convoluted to the instrumental response function (IRF) of the setup provides a good estimate of the small γ_S and large γ_L decay rates (Figure 1c–f). Both rates depend on the molecular

layer–gold mirror distance as well as on the molecular density of the film. We show results for molecular number densities $3 \times 10^{22} \text{ m}^{-3}$ (Figure 1c,e) and $3 \times 10^{23} \text{ m}^{-3}$ (Figure 1d,f) and for the molecular layer to the gold mirror distances in the performed range extending from 20 nm up to 680 nm with steps of 60 nm.

One notices immediately the increase of the large decay rate, γ_L , while going from lower (Figure 1c,e) to higher (Figure 1d,f) concentrations of molecules, a feature not observed for the small decay rate γ_S . This rapid behavior, as better exhibited in the fitted values reported in Figure 2a,b, indicates a

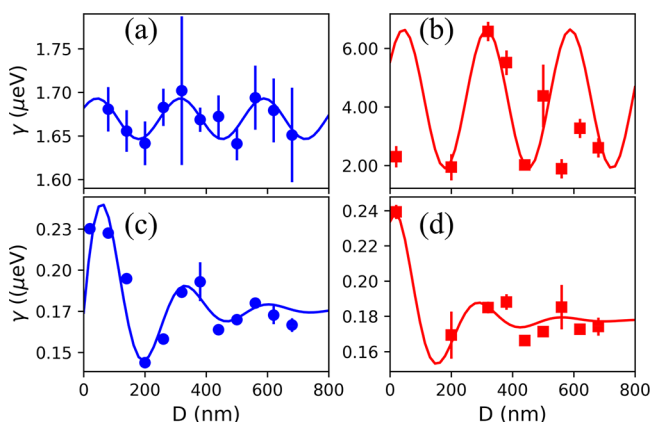


Figure 2. Panels a and b show the evolution of γ_L as a function of molecule–metal distance for $3 \times 10^{22} \text{ m}^{-3}$ and $3 \times 10^{23} \text{ m}^{-3}$ molecular number densities, respectively. Similarly, panels c and d show the evolution of γ_S . Experimental γ_L (dots and squares) in panels a and b were fitted by an appropriate sinusoidal signal, while the γ_S (dots and squares) in panels c and d were fitted by a damped sinusoid. The frequency (related to the emission frequency of the molecules and the refractive index of the surrounding medium) found in panel a was used as a fixed parameter for the three other fits. The amplitude of the sinusoid in panel b was merely adjusted by hand, which makes it more a guide to the eye than a fit.

collective relaxation behavior. Unfortunately, we could not experimentally test the density dependence in a large enough range to observe a potential linear density dependence since for larger concentrations (up to $3 \times 10^{25} \text{ m}^{-3}$), the large decay rate was beyond the time resolution of our apparatus. We could then only see a single exponential profile corresponding to the small decay rate, γ_S . Thus, while the increase of the large decay rate with density is clearly observed, we cannot speak of a linear scaling behavior given just two points.

Figure 2 exhibits the evolution of these decay rates as functions of number density and distance D from the gold mirror structure. Obviously, the small decay rates exhibit damped oscillations (Figure 2c,d), as already observed in Drexhage's experiments over 50 years ago.³⁹ These observations were shown to result from interference between an emitter and its image in the mirror.^{39,40,42,43,45} Strikingly enough, this behavior is not limited to individual molecules but is also seen in the collective relaxation. Remarkably, the γ_L oscillations are not damped over the observed distance, as seen by comparing Figure 2a,c. It should be noted that the large decay rates exhibited in Figure 2b are on the edge of our time resolution. The error bars shown in this figure are merely standard deviations of various measurements performed on the same sample and do not reflect the setup's time resolution. As such, not all decay profiles could be fitted appropriately.

Nevertheless, one can clearly see that the large decay rates are significantly higher for the $3 \times 10^{23} \text{ m}^{-3}$ layer density (Figure 2b) than for the $3 \times 10^{22} \text{ m}^{-3}$ layer density (Figure 2a). For the largest concentrations of molecules (up to $3 \times 10^{25} \text{ m}^{-3}$), the trend followed by the small decay rates is similar to those shown in Figure 2c,d.

Theoretical Model and Computational Results. For the simplest model of collective response from a molecular layer, we assume the molecules are oriented parallel to the gold mirror, thus leading to a one-dimensional electromagnetic setup. The corresponding Maxwell's equations governing the electrodynamics of molecule-to-molecule interactions are

$$\begin{aligned} \frac{\partial B_y}{\partial t} &= -\frac{\partial E_x}{\partial z}, \\ \epsilon_0 \frac{\partial E_x}{\partial t} &= -\frac{1}{\mu_0} \frac{\partial B_y}{\partial z} - J_x \end{aligned} \quad (1)$$

where z corresponds to the longitudinal coordinate perpendicular to the mirror, and J_x is the polarization current density of the molecular layer. The molecules are assumed to be two-level emitters described by the density matrix $\hat{\rho}$ and driven by a local field in accordance with

$$i \frac{d}{dt} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = \begin{pmatrix} \frac{E_x \mu_{12}}{\hbar} (\rho_{12} - \rho_{12}^*) & -\frac{E_x \mu_{12}}{\hbar} (\rho_{22} - \rho_{11}) \\ -\frac{E_x \mu_{12}}{\hbar} (\rho_{22} - \rho_{11}) - \omega_{12} \rho_{12} & -\omega_{12} \rho_{12} \end{pmatrix} \quad (2)$$

Here μ_{12} and ω_{12} are the transition dipole and the transition frequency of a single molecule, respectively. The polarization current is then calculated as

$$J_x = \frac{\partial P_x}{\partial t} = n_0 \mu_{12} \frac{\partial}{\partial t} (\rho_{12} - \rho_{12}^*) \quad (3)$$

where n_0 is the number density of molecules.

We consider the dynamics of molecules initially prepared by a sudden (short time) excitation of all molecules in a coherent superposition state such that the population of excited molecules is significantly less than 1 throughout the time propagation (this corresponds to the optical linear regime). We set it to 0.01, although we note that for the range of molecular densities and material parameters considered in this manuscript, an excited state population as high as 0.5 leads to qualitatively similar results. Thus, the initial conditions for the coupled Maxwell–Bloch equations are

$$\begin{aligned} \rho_{11} &= 1 - \rho_{22} = 0.99 \\ \rho_{12} &= \sqrt{\rho_{11} \rho_{22}} \exp(i\varphi) \end{aligned} \quad (4)$$

where the initial phase φ can be taken the same (and then chosen to be 0) for all molecules or with a random component to represent disorder, as discussed below.

The dynamics of molecules obtained from Maxwell–Bloch equations with the initial conditions (eq 4) shows that the ensemble average excited state population as a function of time follows an exponential decay law, $\exp(-\gamma t)$. The rates γ , calculated by fitting the numerical time dependent excited state population, are displayed in Figure 3.

Figure 3a shows the dependence of the decay rate on the molecular number density for different thicknesses of the

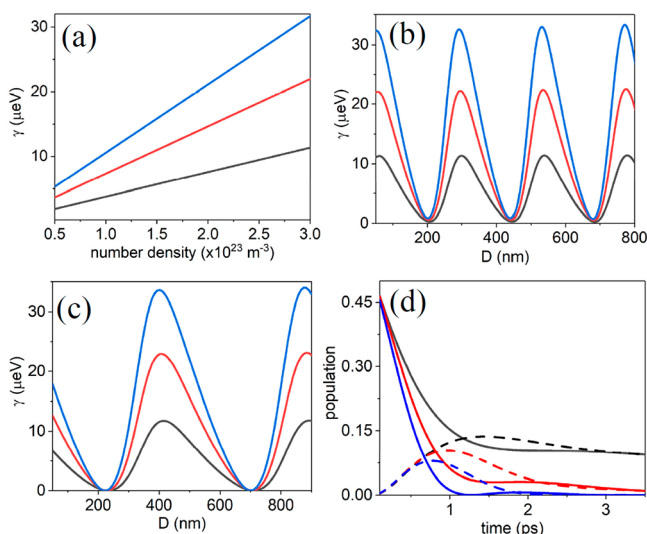


Figure 3. Panels a and b show simulations for a single molecular layer in the experimental geometry (Figure 1a,b). Panel a shows the decay rate extracted from the ensemble average excited state population as a function of the molecular density for three different thicknesses of the molecular layer: black, 5 nm; red, 10 nm; and blue, 15 nm. The thickness of the silica spacer is 300 nm. Panel b shows the spatial dependence of the decay rate on the thickness of the silica layer (distance from the gold mirror) for the same three molecular layers' thicknesses as in panel a. The molecular number density is $3 \times 10^{23} \text{ m}^{-3}$. Panels c and d explore the collective evolution in a system of two molecular layers separated by a silica spacer without mirrors. In panel c, both layers start in the same coherent superposition as defined by eq 4 and the decay of the overall excited state population is shown as a function of the interlayer distance (thickness of a silica spacer) for the same three molecular layer's thicknesses as in panel a, with the molecular number density in both layers taken as $3 \times 10^{23} \text{ m}^{-3}$. The initial state in panel d corresponds to one of the layers prepared in the state in eq 4 while the molecules in the other layer are initially in the ground state, and the dynamics of interlayer energy transfer and overall relaxation are observed. Black lines correspond to a spacer thickness of 20 nm, red lines are for 50 nm, and blue lines correspond to 80 nm. Other parameters are the molecular number density is 10^{26} m^{-3} and the layer's thickness is 10 nm. In all simulations, the phase of the coherence in eq 4 is set to 0.

molecular layer according to the experimental geometry (Figure 1a,b). It is seen that the decay rate scales linearly with the molecular number density, as expected from a delocalized single exciton state.³³ These observations nicely complement the experimental trend shown earlier and are based on two points only. For a silica thickness of 300 nm and a molecular number density of $3 \times 10^{23} \text{ m}^{-3}$, our model calculation predicts the large (collective) decay rate of $22 \mu\text{eV}$, which overestimates the experimental large rate of $6.6 \mu\text{eV}$ (Figure 2b). The overestimation is likely due to the fact that the calculation takes all molecules to be perfectly aligned parallel to the interface and to each other. In contrast, for an isotropic molecular system the averaging over all orientations of the molecular dipole leads to an effective coupling between the macroscopic polarization and the electric field which is reduced by a factor of $1/3$.⁹ This results in a decay rate of $7.3 \mu\text{eV}$, remarkably close to the observed rate.

Next consider the results presented in Figure 3b, which shows the observed decay rate as a function of the distance between the molecular layer and the gold film (as per experimental setup this corresponds to varying the thickness of

the silica layer). Since the light emitted by the molecules is reflected by the mirror, it undergoes a π -phase change (for an ideal mirror). Thus, the resonant condition corresponding to the destructive interference of the reflected and emitted waves leading to a near-zero decay rate is

$$n_{\min} \cdot \lambda_{12} = c \cdot t_{\text{roundtrip}} = c \cdot \frac{2 \cdot d}{c} \Rightarrow d = n_{\min} \cdot \lambda_{12} / 2, \\ n_{\min} = 1, 2, K \quad (5)$$

where c is the speed of light in the media between the mirror and molecules, d is the layer-to-mirror distance, and λ_{12} is the molecular transition wavelength (since molecules are embedded in PMMA the corresponding wavelength is shorter by the factor of the PMMA refractive index compared to its value in vacuum). Small deviations from (eq 5) are attributed to the finite thickness of the molecular layer (as clearly seen it affects the positions of minima in Figure 3b) and the phase change of the emitted radiation when it bounces off of a gold surface. There is also a small mismatch of the refractive indices for the silica and PMMA, in which the molecules are embedded. Nonetheless the spatial modulations of the decay rate obtained from one-dimensional Maxwell–Bloch equations agree perfectly with experimental results. Importantly, this behavior, long known for individual molecules, is predicted and observed also for the collective decay of a molecular aggregate, here a molecular layer parallel to the mirror, as indicated by the density dependence of the rate seen in Figure 3a.

It is also important to note that dephasing of intermolecular coherence is what causes the transition from collective (large decay rate) to single molecule dynamics (small decay rate) observed experimentally. In the present one-dimensional model, such dephasing, associated with dynamic or static disorder (inhomogeneous broadening), can be imposed only partially along the direction normal to the layers, since the molecular layers respond collectively by the nature of the 1-D calculation. Thus, in the simulations discussed in Figure 3, the phase in eq 4 is taken the same for all system units, i.e., all points of our one-dimensional grid. If the phase is chosen randomly between 0 and 2π for each grid point, representing system disorder, the same oscillations in the decay rate vs distance are seen, albeit with a significantly reduced amplitude than experimentally observed. Another important difference between the behaviors of the coherent and incoherent molecular systems lies in the observed distance dependence. For the geometry studied here, a system with a fully coherent molecular layer is truly one-dimensional, implying that the rate oscillates with a distance independent amplitude, as seen in the experimental fast decay (Figure 1c–f) and captured by our one-dimensional simulations. In contrast, when the emitters oscillate with random phases, the observed emission is a sum of signals generated by individual emitters so that the pertinent geometry is three-dimensional, characterized by an oscillation amplitude that decays with distance as already reported in refs 39 and 40 and seen in Figure 2c,d. The presence of an incoherent component in the molecular response may also explain why a perfect destructive interference is not observed experimentally.

Our successful modeling of the experimental observation implies the important prediction that collective interference phenomena should be observed for interacting molecular assemblies. This is demonstrated in Figure 3c,d where the two assemblies are taken as two parallel molecular layers separated

by a silica spacer. One can envision various scenarios for the time dynamics depending on initial conditions. If molecules in both layers are prepared in the same coherent superposition (Figure 3c), we observe the familiar exponential decay as in Figure 3a,b depending on the spacer's thickness, albeit with a change of phase: for a "real" molecular layer (as opposed to an "image" layer) the condition for the destructive interference between electromagnetic waves emitted by both layers is $d = (n_{\min} + 1/2)\lambda_{12}$, $n_{\min} = 0, 1, K$, showing a phase shift compared to eq 5, as seen in Figure 3c. Again, the resonant condition is clearly maintained throughout all the spacer's distances with a slight deviation due to the finite molecular layers' thickness.

In a different scenario (Figure 3d), only molecules in one of the layers are prepared in the excited coherent superposition. Here, collective relaxation and energy transfer are seen in the time evolution. The time dependence of the excited state populations reveals complex dynamics, exhibiting a clear sign of interference through the fact that the decay rate is significantly influenced by the thickness of the silica spacer. While the excited layer begins to decay by emitting the radiation, the initially relaxed molecules are picking up this radiation. The time at which the initially relaxed molecular layer reaches its maximum excitation clearly depends on the molecular density and spacer's thickness, a clear predicted evidence of the collective nature of the energy transfer. In conclusion, we demonstrated both experimentally and theoretically that the collective decay rates of molecular assemblies strongly depend on the distance between metal and molecules. They exhibit spatial modulations that are attributed to constructive/destructive interferences. Experimentally, two distinct decay rates are observed: the large decay rate oscillates with the distance from the mirror without spatial damping, whereas the small decay rate exhibits similar oscillations but shows a significant spatial damping. The latter is due to single molecule fluorescence^{39–43} while the former is of a collective nature. A simple theoretical model based on one-dimensional Maxwell–Bloch equations agrees well with experimental characteristics of the observed fast decay and provides guidance to future experiments aiming to control energy transfer at the nanoscale.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b02521.

Details of experimental setup and numerical modeling (PDF)

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Notes

The authors declare no competing financial interest.

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