

Supplementary Materials for

Suppression of photo-oxidation of organic chromophores by strong coupling to plasmonic nanoantennas

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Fig. S1. Evolution of the DF scattering spectra of strongly coupled hybrid systems with different initial Rabi splitting energies.

Fig. S2. Evolution of the DF scattering spectra of strongly coupled hybrid systems with different detuning of plasmon resonance with respect to the exciton resonance.

Fig. S3. Contribution of molecular oxygen for photobleaching.

Section S1. Evolution of the DF scattering spectra of strongly coupled hybrid systems with different initial Rabi splitting energies

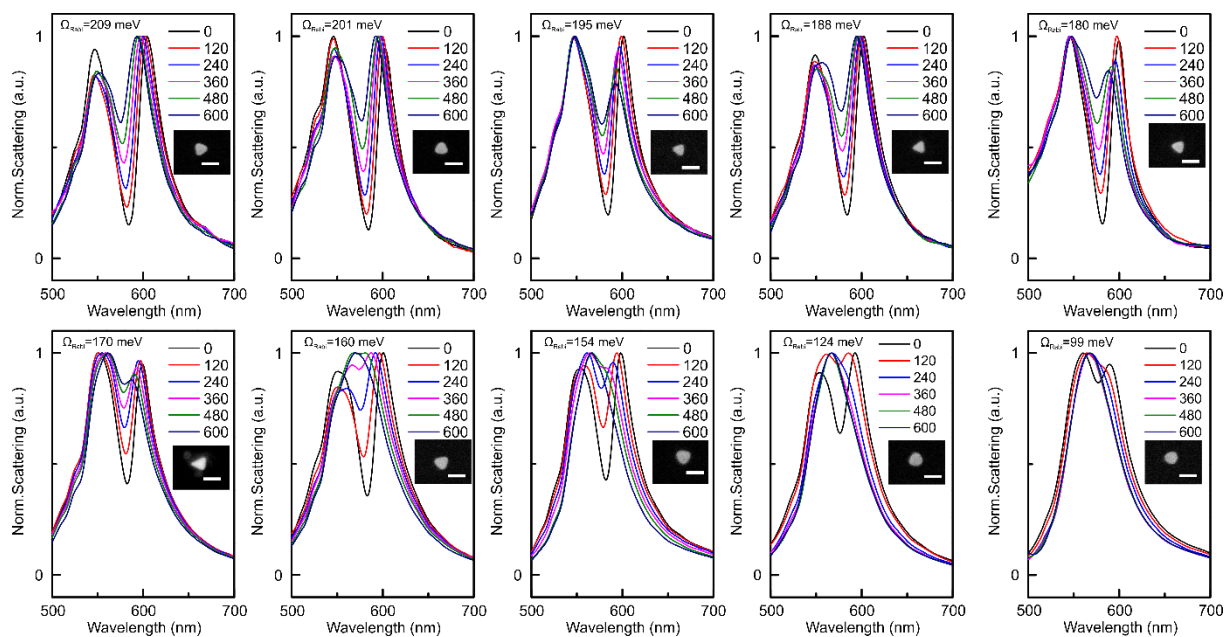


Fig. S1. Evolution of the DF scattering spectra of strongly coupled hybrid systems with different initial Rabi splitting energies. Insets show the corresponding SEM images of the plasmonic silver nanoprisms. The scale bar is 100 nm.

Section S2. Evolution of the DF scattering spectra of strongly coupled hybrid systems with different detuning of plasmon resonance with respect to the exciton resonance

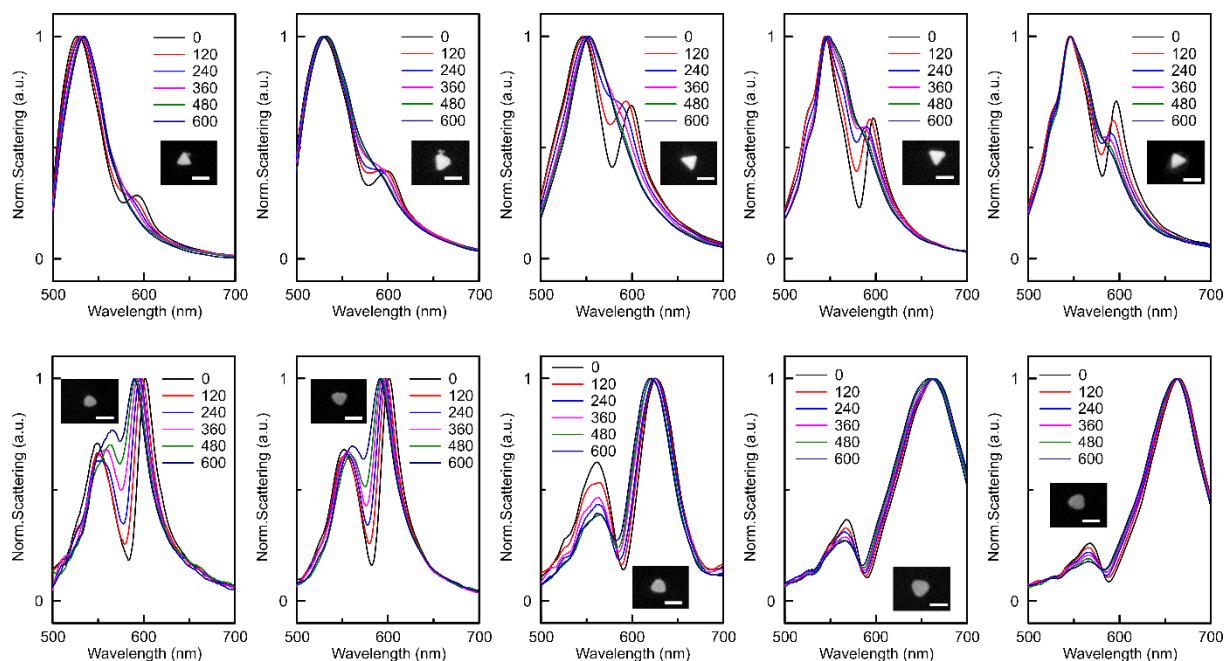


Fig. S2. Evolution of the DF scattering spectra of strongly coupled hybrid systems with different detuning of plasmon resonance with respect to the exciton resonance. Insets show the corresponding SEM images of the plasmonic silver nanoprisms. The scale bar is 100 nm.

Section S3. Contribution of molecular oxygen for photobleaching

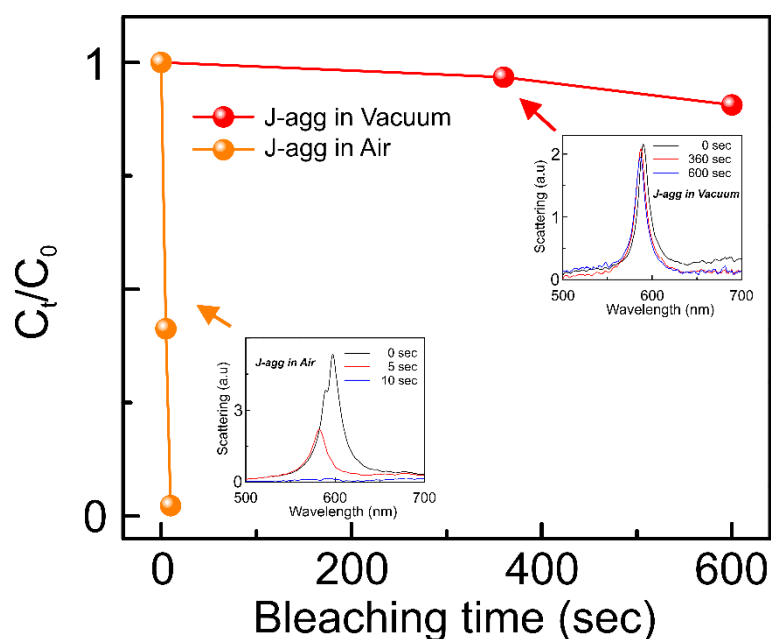


Fig. S3. Contribution of molecular oxygen for photobleaching. Photobleaching kinetics for J-aggregates in air (orange) and in vacuum (red) under 532 nm laser excitation. The insets show the corresponding DF spectra of J-aggregates in air and in vacuum.

To evaluate the contribution of molecular oxygen to the photobleaching in organic dye molecules, we performed a control experiment, as is shown in fig. S3. The photobleaching experiment is performed with a 532 nm laser excitation ($\sim 200 \text{ W/cm}^2$) using an optical cryostat vacuum chamber and a long working distance objective (Nikon, $20\times$ NA=0.45) in an upright microscope. DF scattering spectra of bare J aggregates on a silicon substrate, inside and outside of an optical cryostat vacuum chamber, are recorded before and after continuous photobleaching. While J-aggregates in the presence of oxygen is rapidly bleached within a few seconds under the laser illumination, the one inside cryostat vacuum chamber shows almost same intensity as before photo-bleaching. (see fig. S3). Obviously, it is indeed that molecular oxygen plays a major role in the photobleaching.

Section S4. Coupled system rate equations

The rate equations given below describe the temporal dynamics of the coupled system

$$\frac{dn_G}{dt} = -\gamma_{exc}n_G + \gamma_{UP}n_{UP} + \gamma_D n_D + \gamma_{LP}n_{LP} + \gamma_T n_T \quad \text{Eq. (S1)}$$

$$\frac{dn_{UP}}{dt} = \gamma_{exc}n_G - (\gamma_{UP \rightarrow D} + \gamma_{UP})n_{UP} \approx 0 \quad \text{Eq. (S2)}$$

$$\frac{dn_D}{dt} = \gamma_{UP \rightarrow D}n_{UP} - (\gamma_{D \rightarrow LP} + \gamma_D + \gamma_{ISC})n_D \approx 0 \quad \text{Eq. (S3)}$$

$$\frac{dn_{LP}}{dt} = \gamma_{D \rightarrow LP}n_D - \gamma_{LP}n_{LP} \approx 0 \quad \text{Eq. (S4)}$$

$$\frac{dn_T}{dt} = \gamma_{ISC}n_D - (\gamma_T + k[{}^3\text{O}_2])n_T \approx 0 \quad \text{Eq. (S5)}$$

$$\frac{dn_P}{dt} = k[{}^3\text{O}_2]n_T \quad \text{Eq. (S6)}$$

Here, n_i denotes the *population* of the i^{th} state ($i=G, UP, D, LP, T$ and P – the photoproduct, or bleached molecules), i.e., the fraction of molecules residing in each state, such that $\sum_i n_i = 1$, and γ_i denotes the corresponding transition rate. The condition of quasi-stationarity implies that changes in population of all intermediates occur very slowly, for which reason Eqs. (S2-S5) are all set to zero. This is justified when the excitation rate is much slower than any other relevant rate (weak excitation condition). In this regime, the populations of all states except for the ground and the photoproduct states satisfy $n_i \ll 1$, what allows us to describe dynamics of populations in a simple manner: $\frac{dn_G}{dt} = -\gamma_{bl}n_G$, and $\frac{dn_P}{dt} = \gamma_{bl}n_G$. Here $\gamma_{bl} = \gamma_{exc}\phi_{bl}$ is the photobleaching rate and ϕ_{bl} is the photobleaching quantum yield. Essentially, these two equations characterize slow transfer of population from the ground state to the photoproduct as the bleaching proceeds. The total number of molecules N participating in the coupling process thus can be well approximated by $N(t) = N(0)n_G(t)$, so that the corresponding rate equation reads: $\frac{dN}{dt} = -\gamma_{exc}\phi_{bl}N$. The transient behavior of this number N in our analysis is directly deduced from experimentally measured DF spectra. Having that in mind, we proceed to the derivation of γ_{exc} .

The excitation rate γ_{exc} in Eq. (S1) and (S2) has a physical meaning of excitation probability per unit time *per molecule*. We first obtain a general expression for the excitation rate of a single-mode optical cavity illuminated by a plane wave of intensity I_0 . Let ω_0 be the mode frequency, γ_{rad} the elastic (radiative) decay rate of the mode and γ_{nr} the rate of all inelastic (including non-radiative) decay processes. According to the temporal coupled modes theory, the power scattered and absorbed by the cavity mode reads $P_{sca} = \gamma_{rad}A_{st}\hbar\omega_0$ and $P_{abs} = \gamma_{nr}A_{st}\hbar\omega_0$, correspondingly. Here, A_{st} is

the stationary number of quanta in the excited state of the cavity. Adding up these two expressions, we obtain

$$P_{ext} = P_{sca} + P_{abs} = (\gamma_{rad} + \gamma_{nr})A_{st}\hbar\omega_0 \quad \text{Eq. (S7)}$$

On the other hand, $P_{ext} = \sigma_{ext}I_0$ with σ_{ext} being extinction cross-section of the cavity. Combining this with the rate equation for the mode population

$$\dot{A} \approx \gamma_{exc} - (\gamma_{rad} + \gamma_{nr})A \quad \text{Eq. (S8)}$$

we obtain the expression for the excitation rate: $\gamma_{exc} = \sigma_{ext}I_0/\hbar\omega_0$. From here, we recall that we wish to calculate the excitation rate per molecule. Thus, the original expression for γ_{exc} has to be normalized by the number of participating molecules, which results in the final expression for the per-molecule excitation rate $\gamma_{exc} = \frac{\sigma_{ext}I_0}{N\hbar\omega_0}$.