Picocavity-controlled Sub-nanometer Resolved Single Molecule Non-linear Fluorescence

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In this article, we address fluorescence of single molecule inside a plasmonic picocavity by proposing a semi-classical theory via combining the macroscopic quantum electrodynamics theory and the open quantum system theory. To gain insights into the experimental results [Nat. Photonics, 14, 693 (2020)], we have further equipped this theory with the classical electromagnetic simulation of the pico-cavity, formed by single atom decorated silver STM tip and a silver substrate, and the time-dependent density functional theory calculation of zinc phthalocyanine molecule. Our simulations not only reproduce the fluorescence spectrum as measured in the experiment, confirming the influence of extreme field confinement afforded by the picocavity, but also reveal Rabi oscillation dynamics and Mollow triplets spectrum for moderate laser excitation. Thus, our study highlights the possibility of coherently manipulating the molecular state and exploring non-linear optical phenomena with the plasmonic picocavity.

I. INTRODUCTION

Recently proposed concept "picocavity" refers to atomistic protrusions inside metallic nanocavities [1–12] formed by metallic nanoparticle on-film constructs [1–4], STM tip on-film structures [5–11] or metallic nanoparticle dimers [12]. The atomic protrusions enhance the local field in an atomistic scale due to a non-resonant lighting-rod effect [12] over hundreds fold of enhanced local field afforded by the resonant gap plasmon of the metallic nanocavities. Since the extreme confined field can be smaller than the spatial extension of molecules, its interaction with the molecules can not be addressed with the typical form of light-matter interaction, which assumes large extension of the electromagnetic field over the molecule, i.e. the dipole approximation. This particular situation requires us to go beyond and address the influence of the atomistic local field on the light-matter interaction [13, 14], and on the resulting optical phenomena, such as surface-enhanced Raman scattering [1–3, 5] and surface-enhanced fluorescence [6, 7, 11].

In Ref. [7], B. Yang et al, reported experimentally fluorescence imaging with subnanometer resolution from single zinc phthalocyanine (ZnPc) molecule inside a STM-based metallic picocavity (Fig. 1a). To verify the involvement of the picocavity, the authors have also studied the influence of the STM tip-molecule distance on the surface-enhanced fluorescence signal, the fluorescence linewidth and line shifts. However, in the corresponding theoretical study, the different quantities are studied with separated formulas, and the internal connection between them is lost.

In the present article, we go beyond the theory developed in [7], and propose a semi-classical theory by combining the macroscopic quantum electrodynamics theory [15, 16] and the open quantum system theory [17]. Our theory units different quantities in a coherent manner, and more importantly allows us to calculate the fluo-
ence spectrum, as measured directly in the experiment, which thus provide more insights. Furthermore, we equip our theory with the classical electromagnetic simulations and the time-dependent density functional theory (TDDFT) calculation to investigate the response of the ZnPc molecule to the laser excitation with varying wavelength and intensity. Our simulations not only reproduce the fluorescence spectra measured in the experiment, see Fig. 1 for an example, but also predict the possibility of observing the coherent Rabi-oscillation in the excited state population dynamics and the Mollow side-peaks spectrum under moderate laser excitation.

Our article is organized as follows. In the following section, we present our semi-classical theory, including the quantum master equation for the system dynamics and the formula to compute the fluorescence spectra. In Sec. III and IV we study the plasmonic response of the ZnPc molecule via the TDDFT calculation. In Sec. V we investigate the molecule-local field coupling, the transition energy and transition current density of the ZnPc molecule via the TDDFT calculation. In Sec. VI we study the plasmonic response of the ZnPc molecule to the laser excitation with varying wavelength and intensity. Our simulations not only reproduce the fluorescence spectra measured in the experiment, as measured directly in the experiment, which thus provide more insights. Furthermore, we equip our theory with the classical electromagnetic simulations and the time-dependent density functional theory (TDDFT) calculation to investigate the response of the ZnPc molecule to the laser excitation with varying wavelength and intensity. Our simulations not only reproduce the fluorescence spectra measured in the experiment, see Fig. 1 for an example, but also predict the possibility of observing the coherent Rabi-oscillation in the excited state population dynamics and the Mollow side-peaks spectrum under moderate laser excitation.

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III. PLASMONIC RESPONSE OF STM-BASED PICOCAVITY

To study the plasmonic response of the STM-based picocavity, as shown in Fig. 1, we carry out the electromagnetic simulations by solving the Maxwell’s equation with boundary element method (BEM) [18, 19] as implemented in metallic nanoparticle BEM toolkit [20, 21], and utilize the permittivity of silver given by Johnson-Christy [22].

To mimic the experiment, we illuminate the plasmonic picocavity with a p-polarized plane-wave field at an incident angle of 30° with respect to the substrate normal (Fig. 1a). Fig. 2 shows the computed far-field scattering cross section (black solid line, left axis), and the near-field enhancement of the z-component at the center of picocavity (blue solid line, right axis), and of the x-component at a point 0.5 nm away horizontally from the center (blue dashed line, right axis). The scattering spectrum shows four peaks at 700 nm, 480 nm, 390 nm and 340 nm, while the near-field enhancement spectra show mainly two peaks at 707 nm, 425 nm. The peaks at 700 nm and 480 nm can be attributed to the (10) and (20) mode according to the nomenclature proposed in [23], and the peaks are due to the higher order plasmonic modes. The maximum of the peaks is about 850, 190 for the field z-component, and is however about three times smaller for the field x-component.

As a comparison, we have also calculated the spectra for a corresponding nano-cavity (without the atomic protrusion), see Fig. 7 in Appendix C and found that the scattering spectrum is the same but the near-field enhancement is much smaller, and also does not show the sharp peak at around 410 nm. This comparison indicates that the atomic protrusion affects mainly the local field but not the far-field, and the sharp peak at around 410 nm might be caused by the Fabry-Perot-like mode formed in the atomic protrusion [24].

To further understand the plasmonic response, we have also computed the near-field map in the middle plane of the picocavity for the 633 nm plane-wave illumination, see Fig. 2b. The x-component of the local field is minimal at the center, and maximal at two points about 0.6 nm away horizontally from the center (red dashed lines) and the imaginary part (green dotted lines) of the scattered dyadic Green’s function for the STM tip about 0.5 nm away from the molecular center.

Figure 2. Plasmonic response of the picocavity. (a) shows the far-field scattering cross-section (black solid line, left axis), and the enhancement of local field z- and x-component (blue solid and dashed line, right axis) as a function of wavelength of plane-wave illumination. Here, the z- and x-component are evaluated at the molecular center and a point about 0.5 nm away from the molecular center, respectively. (b) shows the map of the x-component field enhancement in the middle of the picocavity for the 633 nm plane-wave illumination. (c) shows the similar results as the near-field component in (a) except that the STM tip-molecule distance $d_{tip}$ varies from 0.4 nm to 0.7 nm. (d) shows the field enhancement of the z-component (black lines, left axis) and x-component (blue lines, right axis) as a function of the tip-molecule horizontal distance for increasing $d_{tip}$. (e) and (f) show the real part (red dashed lines) and the imaginary part (green dotted lines) of the scattered dyadic Green’s functions by the transition dipole moment $d_{eg}$, and the dyadic Green’s functions by $G\left(\mathbf{r}_{m}, \mathbf{r}_{m}; \omega_{eg}\right)$, $G\left(\mathbf{r}_{d}, \mathbf{r}_{m}; \omega_{eg}\right)$.
away from the center along the x-axis. The y-component shows similar pattern except that the maximum occurs along the y-axis (Fig. 3a in Appendix C). The both components concentrate in an area of 5 nm size. The field z-component shows the maximum at the center, and is much larger compared to other field components, as well as concentrate in an area of 1 nm size over a broad background (Fig. 3b in Appendix C).

Since we shall study the change of fluorescence as the STM tip moves away from the molecular center later on, we examine here the influence of the tip-molecule distance \( d_{\text{tip}} \) on the local field enhancement. Fig. 2 shows that the field enhancement reduces by about 2 times as \( d_{\text{tip}} \) increases from 0.4 nm to 0.7 nm, and the wavelength of the plasmonic resonance blue-shifts slightly. Furthermore, Fig. 3 shows that accompanying with the reduced enhancement, the spatial extension of the field component becomes also slightly broadened. Here, we focus on the field x-component, since it will affect dominantly the fluorescence, as shown later on.

After examining the near-field enhancement, we study now the response of the dyadic Green’s function of the picocavity. Fig. 2f shows the real part (red dashed line) and the imaginary part (green dotted line) of the xx- and zz-component of the dyadic Green’s tensor. The yy-component of the dyadic Green’s tensor is very small (Fig. 3c in Appendix C) and thus is not shown here. The imaginary part shows two peaks at the same wavelength of maximal field enhancement but does no show peak around 700 nm. Here, we see also two Fano-features around 420 nm and 380 nm in the real part (red dashed line) of the dyadic Green’s function. These results indicate that the dyadic Green’s function is mainly determined by the gap structure formed by the atomic protrusion and the substrate [25].

IV. TIME-DEPENDENT DENSITY FUNCTIONAL CALCULATIONS OF ZnPc MOLECULE

In this section, we present the TDDFT calculations of the ZnPc molecule (Fig. 3). To obtain these results, we firstly optimize the structure of the ZnPc molecule (Fig. 3a), and then calculate the atomic ground and excited states by using Gaussian 09 program [26] with B3LYP functional and 6-31G(d) basis set. We identify that the transitions HOMO → LUMO (LUMO+1) contribute mostly to the \( S_0 \) → \( S_1 \) (\( S_2 \)) excitonic transitions (Fig. 3a) with the same excitation energy 2.26 eV, which is smaller than the value 1.90 eV measured in the experiment since the TDDFT often overestimates the transition energy. In the following, we will utilize the measured wavelength in our simulation to ensure the comparison with the experimental results. To calculate the transition current \( j_{eg}(r) \) according to Eq. (2), we obtain the wave-functions \( \Psi_{g}(r) \), \( \Psi_{e}(r) \) of the HOMO, LUMO (LUMO+1) level, which are normally given by \( \Psi_{g(e)}(r) = \sum C_{i} \chi_{i}(r) \) with the Gaussian-type \( i \)-th basis function and the expansion coefficients \( C_{i} \), and calculate the spatial derivative analytically as \( \nabla \Psi_{g(e)}(r) = \sum \nabla C_{i} \chi_{i}(r) \). Furthermore, using the relation \( d_{eg} = \frac{\hbar}{2 \omega_{eg}} \int d^{3}r j_{eg}(r) \), we calculate also the transition dipole moment \( d_{eg} \) and then verify our calculation by comparing the calculated values with those given in the TDDFT output file.

The calculated wave-functions and the transition current \( j_{eg}(r) \) are already presented in our previous article [14]. To gain more insights into \( j_{eg}(r) \), we show the transition current as vectors around the nitrogen-carbon bonds of the molecule (Fig. 3c and d). We find that for the \( S_0 \) → \( S_1 \) transition the transition current flows upwards along the y-axis, while for the \( S_0 \) → \( S_2 \) transition the transition current flows rightwards along the x-axis. Thus, the transition dipole moment, obtained by integrating the transition current over the space, points along the y-axis and x-axis for the \( S_0 \) → \( S_1 \) and \( S_0 \) → \( S_2 \) transition, respectively.

V. MOLECULE-LOCAL FIELD COUPLING, PLASMONIC LAMB SHIFT AND PURCELL-ENHANCED DECAY RATE

We can now combine the quantities calculated in previous sections to determine the molecule-picocavity couplings (Fig. 1), which include the molecule-local field coupling \( h \nu \) for given laser intensity \( J_{\text{las}} = 10^{2} \mu \text{W/\mu m}^{2} \) (black solid line), the plasmonic Lamb shift \( h \Omega /2 \) (green...
dashed line) and the Purcell-enhanced decay rate $\hbar \Gamma$ (red dotted line), and the propagation factor $K$ (blue dash-dotted line). Here, we focus on the $S_0 \rightarrow S_2$ transition since it dominates the fluorescence under the detection condition as considered here (see Fig. 10 in Appendix C). We find that $h\nu$ follows the shape of the near-field enhancement, and reaches the maximal value around 10 meV at the wavelength of 420 nm. $\hbar \Omega/2$ follows the shape of the real part of the dyadic Green’s function, and changes in the range of $[-50,30 \text{ meV}]$. $\hbar \Gamma$ follows the shape of the imaginary part of that function, and varies in the range of $[0,160 \text{ meV}]$. For the wavelength 652 nm of the ZnPc excitonic transition, we obtain $h\nu = 1.2 \text{ meV}$, $\hbar \Omega/2 = -12.5 \text{ meV}$, $\hbar \Gamma = 0.2 \text{ meV}$.

Furthermore, we investigate with Fig. 4b how the molecule-local field coupling $h\nu$, the plasmonic Lamb shift $\hbar \Omega/2$, the Purcell-enhanced decay rate $\hbar \Gamma$ and the propagation factor $K$ change with the STM tip-molecule distance $X$ in the horizontal direction. We see that the absolute value of these quantities increase first and then decreases with the increasing distance $X$. More precisely, the former three quantities reach their maxima around $1.2 \text{ meV}$, $-14.5 \text{ meV}$, and $0.25 \text{ meV}$ for the distance $X$ around 0.6, 0.5, 0.6 nm, while the propagation factor reaches the maximum at the distance $X$ around 0.25 nm. As a reference, we have also calculated these parameters by modelling the molecule as a point in the dipole approximation (see Fig. 4a,b in Appendix C), and found similar results except that the values are relatively larger, and the Lamb shift and the propagation factor reach the maximum at zero distance.

VI. PICOCAVITY-CONTROLLED FLUORESCENCE SPECTRA

We are now in the position to study the picocavity-controlled non-linear fluorescence of single ZnPc molecule. In Subsec. VIA we will investigate the change of the fluorescence spectrum as the STM tip moves horizontally and vertically, and demonstrate that our calculations can reproduce the experimental results. In Subsec. VIB we go beyond the experiment, and explore the influence of the laser wavelength and laser intensity on the molecular dynamics and the fluorescence spectrum.

A. Fluorescence Spectra for Different Tip-Molecule Distances

In the experiment [7], B. Yang et al. had investigated the dependence of the fluorescence spectrum on the tip-molecule distance to verify that the sub-nanometre resolution of fluorescence mapping is afforded by the extremely confined field inside the plasmonic picocavity. Thus, to verify the validity of our theory of the picocavity-controlled fluorescence, in this section, we calculate also the fluorescence spectrum for the different tip-molecule distance for the $S_0 \rightarrow S_2$ excitonic transition (Fig. 5). We have also computed the fluorescence spectrum for $S_0 \rightarrow S_1$ transition (Fig. 9c in Appendix C) and found that it is orders of magnitude smaller due to the smaller propagation factor for the detection condition as considered here.

Fig. 5 shows that as the tip-molecule horizontal distance $X$ increases from 0 to 3 nm, the fluorescence spectra blue-shift slightly, and their maximum increases firstly and then decays to zero, as well as the distance for the vanishing spectrum increases. These results agree qualitatively with Fig. 2 in Ref. [7]. As a comparison, we show also the result within the dipole approximation (the rightmost panel of Fig. 5), and find a larger red-shift of the spectrum for smaller horizontal distances, which is caused by the overestimated plasmonic Lamb shift within the dipole approximation, as explained in the previous.
section.

To further quantify the influence of the tip-molecule distance, we study the fluorescence intensity \( I_{flu} \) integrated over the wavelength range [648, 662] nm as a function of the tip-molecule vertical distance \( d_{tip} \) for different tip-molecule horizontal distances \( X \) (Fig. 3). We can see that all the lines increase first and then decrease with the increasing \( X \). In that figure, we see also that the distance \( X \) to reach the maximum increases with the increasing \( d_{tip} \). All these results agree qualitatively with Fig. 2b,c in Ref. [7].

B. Fluorescence Spectrum for Different Laser Wavelength and Intensity

So far, most of studies on the picocavity have focused on the sub-nanometre resolution of the optical imaging afforded by the extreme field confinement [2, 3, 5–7, 11, 24]. However, less attention has been paid to the extremely large field enhancement, which accompanies also with the picocavity. Thus, in this subsection, we explore how the large enhancement can affect the molecular dynamics and the fluorescence spectrum, see Fig. 6.

Fig. 6a,b show the dynamics of the excited state population \( P_e = (\langle \sigma^+ \rangle + 1)/2 \) and the fluorescence spectrum for the 652 nm laser illumination with increasing intensity \( I_{las} \). For \( I_{las} = 10^4 \mu W/\mu m^2 \), \( P_e \) increases monotonously and then saturates, and the fluorescence spectrum shows single peak. For larger \( I_{las} \), \( P_e \) shows oscillatory behavior before reaching the saturated values, and the fluorescence spectrum shows three peaks. With further increased \( I_{las} \), the period of the oscillations reduces, and the saturated population increases. In the meanwhile, the spectral intensity increases, and the peaks with large and small wavelength blue-shift and red-shift, respectively. These results indicate that for large \( I_{las} \), the molecule can be coherently excited to the superposition of the electronic ground and excited state, forming the so-called dressed states and leading to the Mollow triplet in the spectrum [28, 29]. In Fig. 6c, we summarize the evolution of the saturated \( P_e \) (black solid line, left axis) and the integrated fluorescence intensity \( I_{flu} \) (blue dotted line, right axis) with increasing laser intensity \( I_{las} \). We see that both \( P_e \) and \( I_{flu} \) increase linearly for small \( I_{las} \), and then sub-linearly for moderate \( I_{las} \), and finally saturate for larger \( I_{las} \).

Furthermore, we investigate with Fig. 6d the influence of the laser wavelength \( \lambda_{las} \) on the fluorescence spectrum for given laser intensity \( I_{las} = 10^4 \mu W/\mu m^2 \). As \( \lambda_{las} \) approaches the molecular resonance at 652 nm, the spectrum intensity increases, and the Mollow side peaks with smaller wavelength blue-shift and finally merge with the dominated Mollow peak with larger wavelength. In the end, we emphasize that the laser intensity up to \( I_{las} = 10^4 \mu W/\mu m^2 \) can be achieved with CW laser, and the much stronger intensity can be realized with the pulsed laser [30].

VII. CONCLUSIONS

In conclusion, to address the plasmonic picocavity-controlled fluorescence of single molecule, as demonstrated in the recent experiment [7], we have proposed a semi-classical theory by combining the macroscopic quantum electrodynamics theory and the open quantum system theory. Our simulations not only reproduce the experimental observation, but also predict that the molecule can be coherently excited, and the Mollow triplets can be observed in the fluorescence spectrum for...
Figure 6. Molecular dynamics and fluorescence. (a) and (b) show the dynamics of the excited state population and the fluorescence spectra of single ZnPc molecule, respectively, for the resonant CW laser excitation with wavelength $\lambda_{\text{las}} = 652$ nm and increasing intensity $I_{\text{las}}$ from $1 \mu W/\mu m^2$ to $10^5 \mu W/\mu m^2$. (c) shows the steady-state population of the excited state (black solid line, left axis), and the integrated fluorescence intensity (blue dashed line, right axis) as a function of $I_{\text{las}}$ for $\lambda_{\text{las}} = 652$ nm. (d) shows the fluorescence spectrum for the laser excitation with varying $\lambda_{\text{las}}$ from 590 nm to 652 nm (from low to top curve) and $I_{\text{las}} = 10^4 \mu W/\mu m^2$.

sufficient strong laser illumination, which however can be achieved with CW or pulsed laser. Thus, our study highlights the possibility of manipulating coherently the molecular states and exploring the non-linear optical phenomena with the plasmonic picocavity.

ACKNOWLEDGEMENT

We acknowledge project Nr. 12004344 from the National Natural Science Foundation of China, joint project Nr. 21961132023 from the NSFC-DPG. The calculations with Matlab and Gaussian 16 were performed with the supercomputer at the Henan Supercomputer Center.

AUTHOR CONTRIBUTIONS

Yuan Zhang has devised the theory. Yuan Zhang and Siyuan Lyu have developed the numerical code. Yao Zhang has carried out the TDDFT calculation, and Siyuan Lyu has carried out all the other simulations. All the authors contribute to the writing of the manuscript.

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According to the macroscopic quantum electrodynamics theory \cite{15,16}, the electromagnetic field can be described as a continuum via the Hamiltonian...
The formal solution of Eq. (A4) is
\[ \hat{E}(r, \omega_f) = i \sqrt{\frac{\hbar}{\pi \epsilon_0}} \int d^3r \left( \frac{ie}{\omega_{eg}} \hat{j}_{eg}(r) \right) \cdot \hat{E}(r, \omega_f) \]
\[ \times \sqrt{\epsilon_r(r', \omega_f) G(r, r'; \omega_f) \cdot \hat{f}(r', \omega_f)}, \quad (A1) \]
with the imaginary part of the dielectric function \( \epsilon_r(r', \omega) \) and the classical dyadic Green’s function \( G(r, r'; \omega) \). To study the interaction of single molecule with the picocavity, we model the molecule as two-level system via the Hamiltonian \( \hat{H}_m = (\hbar \omega_{eg}/2) \hat{\sigma}^z \) with the transition frequency \( \omega_{eg} \) and the Pauli operator \( \hat{\sigma}^z \). In the rotating wave approximation, the molecule interacts with the quantized electric field given by
\[ \hat{f}(r', \omega_f, t) = -i \omega_{eg}^2 \sqrt{\frac{\epsilon_r(r', \omega_f)}{\pi \hbar \epsilon_0}} \int d^3r' \hat{j}_{eg}(r') \cdot G^*(r, r'; \omega_f) \int_0^t dt' e^{-i\omega_{eg}(t-t')} \cdot \hat{\sigma}^z(t') \cdot \hat{\sigma}^z(t), \quad (A5) \]
The equation for the conjugate field operator \( \hat{f}_c(r, \omega_f, t) \) and its formal solution can be achieved by taking the conjugation over Eq. (A4) and (A5).

Inserting Eq. (A5) into Eq. (A3), we will obtain a differential and integral equation. By solving this equation, we are able to study not only Markov dynamics in the weak coupling regime, but also the non-Markov dynamics in the strong coupling regime [13]. Since here we focus on the former regime, we carry out the Born-Markov approximation to the formal solution (A5). To do so, we replace \( \hat{\sigma}^z(r) \) by \( e^{i\omega_{eg}(t-r)} \cdot \hat{\sigma}^z(t) \) in this expression, and then define a new variable \( \tau = t - t' \) to change the integration over the time, and finally change the upper limit of this integration into infinity to achieve the following expression
\[ \hat{f}(r', \omega_f, t) \approx -i \omega_{eg}^2 \sqrt{\frac{\epsilon_r(r', \omega_f)}{\pi \hbar \epsilon_0}} \int d^3r' \hat{j}_{eg}(r') \cdot G^*(r, r'; \omega_f) \int_0^t dt' e^{-i\omega_{eg}(t-t')} \cdot \hat{\sigma}^z(t') \cdot \hat{\sigma}^z(t), \quad (A6) \]
In the last step, we have utilized the relationship \( \int_0^\infty d\tau e^{i(\omega_{eg} - \omega_f)\tau} = \pi \delta(\omega_{eg} - \omega_f) + i\mathcal{P} \frac{1}{\omega_{eg} - \omega_f} \). Inserting Eq. (A6) (and its conjugation) into Eq. (A3), using the property of the dyadic Green’s function
\[ \left( \frac{\omega_f}{\epsilon_0} \right)^2 \sum_j \int d^3r \epsilon_r(r', \omega_f) G_{kj}(r, r'; \omega_f) \times G_{kj}(r, r', \omega_f) = \text{Im} G_{kj}(r_1, r_2; \omega_f), \quad (A7) \]
and applying the Kramer-Kronig relation
\[ \mathcal{P} \int d\omega_f \omega_f \text{Im} G_{kj}(r, r'; \omega_f) = \pi \omega_{eg}^2 \text{Re} G_{kj}(r, r'; \omega_f), \quad (A8) \]
we obtain the following effective Heisenberg equation
\[ \frac{\partial}{\partial t} \hat{\sigma}^z(t) = -i \left[ \hat{\sigma}^z(t), \hat{\sigma}^z(t) \right] \hat{\sigma}^z(t) J^{(1)}(t) \]
\[ -i J^{(2)}(t) \hat{\sigma}^z(t), \hat{\sigma}^z(t), \quad (A9) \]
where \( J^{(1)}(t) = \frac{e^2}{\hbar \epsilon_0 c^2} \int d^3r \int d^3r' \int d\omega_{eg} \text{Im} G_{kj}(r, r'; \omega_{eg}) \cdot \hat{j}_{eg}(r') \]
\[ \hat{j}_{eg}(r') \cdot G_{kj}(r, r'; \omega_{eg}) \cdot \hat{j}_{eg}(r'), \quad (A10) \]
\[ J^{(2)} = \frac{e^2}{\hbar \epsilon_0 c^2} \int d^3r \int d^3r' \int d\omega_{eg} \text{Re} G_{kj}(r, r'; \omega_{eg}) \cdot \hat{j}_{eg}(r') \]
\[ \hat{j}_{eg}(r') \cdot G_{kj}(r, r'; \omega_{eg}) \cdot \hat{j}_{eg}(r'), \quad (A11) \]
Furthermore, we consider the equation for the expectation value $\text{tr} \{ \hat{\rho} (t) \hat{\rho} \} = \text{tr} \{ \hat{\rho} (t) \}$, which can be computed either with the time-dependent operator $\hat{\rho} (t)$ and the time-independent density operator $\hat{\rho}$ in the Heisenberg picture (left side), or with the time-independent operator $\hat{\rho}$ and the time-dependent density operator $\hat{\rho} (t)$ in the Schrödinger picture (right side). Using this relation and the cyclic property of the trace, we obtain the master equation for the reduced density operator

$$
\frac{\partial}{\partial t} \hat{\rho} = -i J^{(1)} [\hat{\sigma}^-, \hat{\rho}] + i J^{(2)} [\hat{\rho} \hat{\sigma}^-, \hat{\sigma}^-].
$$

Introducing new parameters $\Omega = J^{(1)} + J^{(2)}, \Gamma = -i [J^{(1)} - J^{(2)}]$, we can rewrite the spectral densities as $J^{(1)} = \frac{1}{2} \{ \Omega + i \Gamma \}, J^{(2)} = \frac{1}{2} \{ \Omega - i \Gamma \}$. Inserting these expressions into Eq. (A12), we achieve the following effective master equation

$$
\frac{\partial}{\partial t} \hat{\rho} = -i \frac{1}{2} \omega_{eg} [\hat{\sigma}^z, \hat{\rho}] + i \frac{1}{2} \Omega [\hat{\sigma}^1 \hat{\sigma}^-, \hat{\rho}]
+ \frac{1}{\Gamma} \left( 2 \hat{\sigma}^- \hat{\rho} \hat{\sigma}^+ - \hat{\rho} \hat{\sigma}^+ \hat{\sigma}^- - \hat{\sigma}^- \hat{\rho} \hat{\sigma}^+ \hat{\sigma}^- \right).
$$

Here, we have incorporated the molecular Hamiltonian $H_m = (\hbar \omega_{eg} / 2) \hat{\sigma}^z$. It is clear that $\Omega / 2$ shifts the molecular transition, i.e. the plasmonic Lamb shift, and $\Gamma$ describes the excited state decay, i.e. the Purcell-enhanced decay rate. On the basis of this equation, we can further introduce the molecular coupling with the plasmon-enhanced local field, and the excited decay due to other processes and the molecular dephasing to arrive at the master equation (1) in the main text.

**Appendix B: Far-field Spectrum**

In this Appendix, we present the derivation of the far-field radiation from the single molecule in the picocavity. According to Refs. [28][31], the far-field spectrum can be computed with

$$
\frac{dW}{d\Omega} (\omega) = \frac{\epsilon_0 r^2}{4 \pi^2} \Re \int_0^\infty e^{i \omega \tau} d\tau \text{tr} \left\{ \hat{\mathcal{E}}^\dagger (r_d, 0) \cdot \hat{\mathcal{E}} (r_d, \tau) \hat{\rho} \right\}.
$$

(B1)

In this expression, $r$ is the distance between the molecule and the detector, $\hat{\mathcal{E}} (r_d, \tau) = \int d\omega \hat{E} (r_d, \omega, \tau)$ is the electric field operator at the detector position $r_d$, and is obtained by the integration of the electric field over the frequency $\omega$. Inserting Eq. (A6) into Eq. (A1), we obtain the following expression

$$
\hat{\mathcal{E}} (r_d, \omega, \tau) \approx \frac{he}{\pi \omega_{eg} \epsilon_0} \frac{\omega^2}{c^2} \Im \int d^2 r' \int d^2 r' G (r_d, r'; \omega_f) \cdot j_{eg}^* (r') \hat{\sigma}^- (\tau)
\cdot \left( \pi \delta (\omega_f - \omega_{eg}) + i \mathcal{P} \frac{1}{\omega_{eg} - \omega_f} \right).
$$

(B2)

Here, we have utilized the relation (A7). Using the above expression and Eq. (A5), we obtain the following expression for the electric field operator at the position $r_d$ of the detector

$$
\hat{\mathcal{E}} (r_d, \tau) = -\frac{i e \omega_{eg}}{\epsilon_0 c^2} \int d^2 r' G (r_d, r'; \omega_{eg}) \cdot j_{eg}^* (r') \hat{\sigma}^- (\tau).
$$

(B3)

Applying the conjugation to the above equation, we obtain the expression for the conjugated field operators $\hat{\mathcal{E}}^\dagger (r, \tau)$. Inserting these results to Eq. (B1), we can rewrite the spectrum as

$$
\frac{dW}{d\Omega} (\omega) \approx K \Re \int_0^\infty d\tau e^{i \omega \tau} \text{tr} \left\{ \hat{\sigma}^d (0) \hat{\sigma}^- (\tau) \hat{\rho}_{ss} \right\},
$$

with the propagation factors

$$
K = \frac{r^2 \omega_{eg}^2 \epsilon_0}{4 \pi^2 c^3} \int d^2 r'' \int d^2 r' \left[ \overline{G} (r_d, r''; \omega_{eg}) \cdot j_{eg} (r'') \right] \cdot \left[ \overline{G}^* (r_d, r'; \omega_{eg}) \cdot j_{eg}^* (r') \right].
$$

(B5)

To compute the spectrum with Eq. (B4), we have to evaluate the two-time correlations $\text{tr} \left\{ \hat{\sigma}^d (0) \hat{\sigma}^- (\tau) \hat{\rho}_{ss} \right\}$, where $\tau$ labels the difference of time relative to the steady-state labeled as $0$, and $\hat{\rho}_{ss}$ is the density operator at steady-state. To compute these correlations, we consider a pure quantum system. In this case, we can introduce the time-propagation operator $\hat{U} (\tau)$ to reformulate the correlations as

$$
\text{tr} \left\{ \hat{\sigma}^d (0) \hat{\sigma}^- (\tau) \hat{\rho}_{ss} \right\} = \text{tr} \left\{ \hat{\sigma}^d \hat{U}^\dagger (\tau) \hat{\sigma}^- \hat{U} (\tau) \hat{\rho}_{ss} \right\}
= \text{tr} \left\{ \hat{\sigma}^- \hat{U} (\tau) \hat{\rho}_{ss} \hat{U}^\dagger (\tau) \right\} = \text{tr} \left\{ \hat{\sigma}^- \hat{\gamma} (\tau) \right\},
$$

(B6)

where we have defined the operator $\hat{\gamma} (\tau) = \hat{U} (\tau) \hat{\rho}_{ss} \hat{U}^\dagger (\tau)$. In essence, we have transformed the expression in the Heisenberg picture to that in the Schrödinger picture. To deal with the quantum system in the presence of loss, we should replace $\hat{U} (\tau) \ldots \hat{U}^\dagger (\tau)$ with the time-propagation superoperator $\hat{U} (\tau)$, which indicates the formal solution of the master equation (1) in the main text with loss. Finally, we can compute the spectrum as

$$
\frac{dW}{d\Omega} (\omega) \approx K \Re \int_0^\infty d\tau e^{i \omega \tau} \text{tr} \left\{ \hat{\sigma}^- \hat{\gamma} (\tau) \right\},
$$

(B7)

where $\hat{\gamma} (\tau)$ satisfies the same master equation (1) as $\hat{\rho}$ in the main text with however the initial condition $\hat{\gamma} (0) = \hat{\rho}_{ss} \hat{\sigma}^d$.

**Appendix C: Supplemental Numerical Results**

In this Appendix, we provide extra results to facilitate the discussions in the main text.

1. **Plasmonic Response of STM-based Nanocavity**

In the main text, we have studied the plasmonic response of the STM-based picocavity. As a comparison,
here, we investigate the response of a STM-based nano-cavity, which resembles the picocavity except for the exclusion of the atomic protrusion. Fig. 7 shows the computed far-field scattering cross section (black solid line, left axis), and the enhancement of the field x- and z-component at the center of nanocavity (blue solid line), and of the x-component at a point 8.0 nm away horizontally from the center (blue dashed line). We find that the scattering spectrum is similar as that of the picocavity, indicating no influence of the atomic protrusion on the far-field field. In addition, the near field enhancement shows broad peaks with moderate values around 410 nm in strong contrast to the sharp and strong peak at 430 nm in the pico-cavity case (see Fig. 2a).

2. Extra Near-field Mapping and Green’s Function Component

In the main text, we have characterized the main components of the near field and the dyadic Green’s function for the plasmonic pico-cavity. Here, we provide the corresponding results for other components. Fig. 8a and b show the mapping of the local field y-component (a) and z-component (b) in the middle of the picocavity for a plane-wave illumination of 633 nm wavelength. The y-component field mapping is similar to the x-component field mapping except that the maximum occurs along the y-axis. The field z-component concentrates at the origin in an area of 1 nm size over a broad background of 10 nm size. Fig. 8c shows the real part (red dashed line) and the imaginary part (green dotted line) of the yx-component of the dyadic Green’s tensor. The imaginary part shows a dip at around 420 nm and a peak at around 350 nm.

Figure 8. Local field mapping and dyadic Green’s function. (a,b) show the mapping of the local field y-component (a) and z-component (b) in the middle of the picocavity for a plane-wave illumination of 633 nm wavelength. (c) shows the real part (red dashed line) and imaginary part (green dotted line) of the scattered dyadic Green’s function for the STM tip about 0.5 nm away horizontally from the molecule center. There, we see also two Fano-features around 420 nm and 360 nm in the real part (red dashed line) of the dyadic Green’s function.
3. Molecule-Picocavity Coupling and Picocavity-controlled Fluorescence within Dipole Approximation

In the main text, we have studied extensively the coupling and the fluorescence with the model accounting for the atomistic detail of the molecule. As a comparison, here, we study the results within the dipole approximation, which in principle is not valid for the system considered here.

In Fig. 9a, we calculate the molecule-local field coupling $\hbar v$ for given laser intensity $I_{\text{laser}} = 10^3 \mu W/\mu m^2$ (black solid line), the plasmonic Lamb shift $\hbar \Omega/2$ (blue dashed line) and the Purcell-enhanced decay rate $\hbar \Gamma$ (red dotted line) as a function of wavelength for the STM tip about 0.5 nm away from the molecule center, where the vertical black dashed line shows the wavelength of the molecular transition. (b) shows the change of $\hbar v$, $\hbar \Omega/2$, $\hbar \Gamma$, $K$ as the STM tip moves away from the molecular center along the x-axis for the wavelength of molecular transition.

4. Picocavity-controlled Fluorescence of the $S_0 \rightarrow S_1$ Transition

In Fig. 10, we investigate how the molecule-local field coupling, the plasmonic Lamb shift and the Purcell-enhanced decay rate change with the STM tip molecule horizontal distance X. We see that the absolute value of these quantities increases first and then decreases with the increase of the distance X. More precisely, the molecule-local field coupling, the plasmonic Lamb shift and Purcell-enhanced decay rate reach their maximum 1.5 meV, -26 meV, 0.4 meV for the distance X around 0.5, 0.5, 0.5 nm, respectively. The propagation factor reaches the maximum at the distance X = 0 nm.

Figure 10. Picocavity-controlled fluorescence of single ZnPc molecule for $S_0 \rightarrow S_1$ transition. Here, we utilize dephasing rate $\hbar \chi = 2.3$ meV, the intrinsic decay rate $\hbar \gamma = 8.2$ meV.

Figure 9. Response within dipole approximation. (a) shows the molecule-local field coupling $\hbar v$ (black solid line) for the input power $10^3 \mu W/\mu m^2$, the plasmonic Lamb shift $\hbar \Omega/2$ (blue dashed line), and the Purcell-enhanced decay rate $\hbar \Gamma$ (red dotted line), and the propagation factor $K$ (dash-dotted line) as a function of wavelength for the STM tip about 0.5 nm away from the molecule center, where the vertical black dashed line shows the wavelength of the molecular transition. (b) shows the change of $\hbar v$, $\hbar \Omega/2$, $\hbar \Gamma$, $K$ as the STM tip moves away from the molecular center along the x-axis for the wavelength of molecular transition.
transformation.