Single molecules probe local density of modes (LDOS) around photonic nanostructures

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Summary

According to Fermi's golden rule, the fluorescence decay rate is directly proportional to the projected local density of photonic modes (LDOS) at the molecule location. The relevant LDOS depends on the molecule orientation. In this paper, the direct measurement of the fluorescence lifetime near gold dot photonic structures is investigated and compared to calculated LDOS. Detailed analysis of the decay channels is presented on the basis of numerical simulations.

Introduction

Since the work of Purcell, it is well known that spontaneous emission is governed by the local density of photonic modes (LDOS) \( \rho \) (Purcell, 1946). Considering weak coupling between the excited molecule and the electromagnetic environment, Fermi’s golden rule expresses the fluorescence decay rate \( \Gamma \) (inverse of fluorescence lifetime \( \tau \)) in terms of the number of allowed electromagnetic modes available for the emission of a photon:

\[
\Gamma(r_m) = \frac{\pi \omega_0}{\hbar} |\mu|^2 \rho_u(r_m, \omega_0),
\]

In this expression, \( \rho_u(r_m, \omega_0) \) is the projected LDOS (PLDOS) along the direction \( u \) of the transition dipole moment \( \mu = \mu u \) at the molecule position \( r_m \) and fluorescence frequency \( \omega_0 \) (Novotny and Hecht, 2006). Because of boundary conditions, \( \rho_u \) depends strongly on the molecule location and orientation in the system. This property can be used to tune the fluorescence rate by tailoring the optical surroundings of the molecule. For instance, by placing an emitter in a microcavity, one can cancel all transitions except the one in resonance with the cavity, with applications in single photon source elaboration (Lounis & Orrit, 2005). On the other hand, Rigneault et al. recently proved that increasing the fluorescence decay avoids saturation effects in fluorescence correlation spectroscopy studies (Rigneault et al., 2005).

We report here the measurement of the single molecule fluorescence lifetime near photonic structures (in the 'experiment' section). In the 'Discussion' section, the lifetime is compared to the PLDOS numerically evaluated inside the system. Moreover, a detailed analysis of the PLDOS reveals the decay channels for the molecule relaxation.

Experiment

We place the molecule in so-called optical corrals because it has been previously demonstrated that it is possible to modulate differently the X, Y and Z-LDOS inside the corral (Chicanne et al., 2002). Optical corrals of various shapes are obtained by standard electron beam lithography technique. They are made of gold pads of 100-nm diameter and 45-nm height on a thin glass substrate forming a circle, an ellipse or stadium, as shown in Fig. 1(a). Dye molecules (DiD, molecular probes, Invitrogen, Carlsbad, CA, USA) are diluted in polymethylmethacrylate (PMMA, Acros, USA) at concentration \( 10^{-8} \) mol. L\(^{-1}\) and spin coated on the substrate. Fluorescence intensity is collected by confocal scanning fluorescence microscopy (Zeiss Axiovert 200, inverted microscope, Carl Zeiss Ltd, UK) with an oil immersion objective lens (Olympus NA 1.3, 100× Olympus UK Ltd, Watford, UK) (Sánchez-Mosteiro et al., 2006). Circularly polarized light (\( \lambda_{\text{exc}} = 635 \) nm, ps laser diode head LDH-635, PicoQuant) was used as excitation through the same objective and separated from the excitation light by the
combination of a dichroic mirror (Omega 650DRLP) and a long pass filter (Omega 665ALP). The fluorescence light was then sent to two avalanche photodiodes (APD, SPCM-AQ-14, EG&G Electro Optics). A polarizing beam splitter in front of the APDs separates the light into two orthogonal polarizations. Because of the gold luminescence (see Fig. 1b), the optical corrals are clearly seen, so that it is possible to locate with confocal resolution the position of molecules inside the system. Typical fluorescence images are represented in Fig. 2. The optical corrals are easily identified and each spot is the fluorescence signal of individual molecules spread on the substrate. Direct analysis of the far-field emission reveals the molecule orientation, which is indicated by a false colour code. Green pixels refer to horizontal polarized light, red pixels refer to vertical polarization. Finally, focusing on each spot, we record the fluorescence lifetime for each molecule. In this preliminary study, we present a statistical analysis of the lifetime modification by the optical corral. The distribution of recorded lifetimes is reported in Fig. 2(d).

Discussion

Formalism

The LDOS involved in the Fermi’s golden rule [Eq. (1)] is a classical quantity that is related to the classical electric Green’s dyad \( G \) associated with the molecule surroundings. This dyad describes the electric field scattered at any point \( r \) of the system by a dipole \( u \) located at \( r_m \):

\[
E(r) = \frac{k_0^2}{\epsilon_0} G(r, r_m, \omega_0) \cdot u, \quad k_0 = \omega_0/c
\]

is the free-space wavenumber

and the PLDOS can be expressed as (unit is in s. m\(^{-3}\))

\[
\rho_p(r, \omega) = \frac{2\omega}{\pi c^2} \text{Im} [u \cdot G(r, r, \omega) \cdot u]. \tag{3}
\]

Because the dipolar transition moment of the molecule is unknown, it is easier to consider the normalized decay rate

\[
\gamma = \frac{\Gamma(r_m)}{\Gamma_0} = \frac{6\pi}{k_0} \text{Im} [u \cdot G(r_m, r_m, \omega_0) \cdot u]. \tag{4}
\]

in which \( \Gamma_0 = 1/\tau_0 = (3.5 \text{ ns})^{-1} \) is the free-space molecule decay rate considered as a parameter.

The expression of Green’s dyad is analytical only for a few highly symmetric systems but can be numerically evaluated for any arbitrary system (Girard & Dereux, 1996). In the following, we describe the construction of Green’s dyad associated with
the optical system of the experiment described above, the gold dots stadium embedded in the polymer slab. We first described Green’s dyad associated with the bare slab that has to be considered to analyze the fluorescence lifetime distribution far from the structures. Using Dyson’s equation, the stadium perturbation is then numerically evaluated and compared to the lifetimes measured inside the optical corral.

![Fluorescence images of single molecules spread on optical corals.](image1)

**Fig. 2.** Fluorescence images of single molecules spread on optical corals. Red/green colour indicates the molecule’s dipole orientation in the substrate plane. (a) 30 × 30 μm² image of circular corals, (b) 30 × 30 μm² image of corral stadiums, (c) 10 × 10 μm² image of a single corral stadium and (d) fluorescence lifetime distribution for molecules far from (filled bars) and inside (open bars) the stadium corals.

![Graphs showing normalized decay rate and fluorescence lifetime.](image2)

**Fig. 3.** (a) Normalized decay rate calculated for a molecule parallel (solid line) or perpendicular (dashed line) to the surface and located in the middle of the PMMA slab when varying the thickness. (b) Corresponding fluorescence lifetime. For a thick film, the normalized decay rate tends towards its value in a homogeneous PMMA background (γ = n₂ = 1.49). The index of refraction is given in the inset of Fig. b.)
**Lifetime dispersion inside the PMMA slab**

We define first the reference system as the PMMA film lying on the glass substrate and exposed to air (see the inset of Fig. 3b). The fluorescence decay rate is easier expressed considering the angular spectrum representation of the dipole field (Novotny & Hecht, 2006):

\[
\gamma_{\text{slab}}(r_m) = \frac{6\pi}{k_0} Im\left[\mathbf{u} \cdot \mathbf{G}_{\text{slab}}(r_m, \mathbf{r_m}, \omega_0) \cdot \mathbf{u}\right] = \int_0^\infty dk_p P(k_p),
\]

where the normalized power \(P(k_p)\) emitted by a dipole embedded inside the dielectric slab is straightforwardly expressed as a function of the Fresnel coefficients (Novotny & Hecht, 2006). The decay rate and corresponding lifetime of a single molecule embedded in the PMMA slab are represented in Fig. 3 for several slab thickness. Small interferences oscillations appear because of reflections at the interfaces. Because the tangential electric field is continuous at the interfaces, the parallel lifetime is only weakly perturbed by the polymer. On the contrary, the perpendicular lifetime is strongly modified below thickness of about half wavelength (Lukosz, 1980; Rahmani et al., 1997). Finally, as the number of allowed modes (decay channels) decreases, the lifetime increases up to 7.5 ns.

The plane wave spectrum of the emitted power, represented in Fig. 4, provides some information about the available decay channels. For a dipole perpendicular to the surface, almost all the light is radiated into the substrate, whereas the main contribution for a horizontal transition dipole moment comes from light tunnelled from the PMMA into the glass substrate (1.492 < \(k_p/k_0\) < 1.51) (Fan et al., 1997; Danz et al., 2002). Finally, the measured lifetime distribution is in good agreement with this model as described before (Vallée et al., 2001). However, in the previous experiment, polystyrene (\(n_2 = 1.58\)) was used instead of PMMA. The calculated lifetime dependence on the position inside the PMMA film is given in Fig. 5. Although a lifetime dispersion ranging from 2.2 ns to 7.5 ns is expected from dipolar model, the experimental data present a lifetime distribution from 1.6 ns to 3 ns for molecules far from the stadium. Confocal single molecule detection mainly shows in-plane or close to in-plane molecules, because of the in-plane excitation field component. As a result, the long lifetimes up to 7.5 ns are not found in the experiment (Vallée et al., 2001). The presence of a range of lifetimes reveals the inhomogeneity of the polymer film (Vallée et al., 2001, 2003, 2005).

**Fig. 4.** Angular spectrum dependence of the normalized emitted power \(P(k_p)\). The molecule is placed at the centre of a 35 nm PMMA slab. (a) Parallel decay rate and (b) perpendicular decay rate. Vertical lines indicate the limits for radiative mode in air (\(k_p/k_0 < 1\)) or in substrate (\(k_p/k_0 < 1.51\)).

**Fig. 5.** Fluorescence lifetime calculated inside the film for an in-plane (solid line) and out-of-plane (dotted line) oriented dipole.

**Lifetime dispersion inside the optical corral**

**LDOS modulation inside the optical corral.** Green’s dyad associated with the optical corral embedded into the PMMA slab is deduced from the bare slab dyad thanks to Dyson’s equation (\(\Delta \epsilon = \epsilon - \epsilon_2\) with \(\epsilon\) the object (gold) dielectric function (Palik, 1985) and \(\epsilon_2 = n_2^2\) the PMMA dielectric function (Palik, 1985)).
function) (Martin & Piller, 1998):

$$G(r, r', \omega) = G_{\text{slab}}(r, r', \omega) + k_0^2 \int_{\text{dots}} dr'' G_{\text{slab}}(r, r'', \omega) \Delta \epsilon(r'', \omega) G(r'', r', \omega).$$

(6)

This self-consistent equation can be numerically solved by discretizing the gold dots (Girard & Dereux, 1996). Then, the PLDOS and fluorescence lifetime are obtained from Eqs (3) and (4), respectively.

The calculated Z-LDOS inside the stadium is shown in Fig. 6. To avoid time calculation limitations, we consider a single interface air/PMMA because the substrate and the PMMA film have very similar optical index. Moreover, we use the nonretarded (static) form for Green’s dyad (Gay-Balmaz & Martin, 2000). Obviously, this forbids us to take into account the slab modes discussed above. This point will be discussed hereafter. The LDOS’s maps show characteristic modulations inside the stadium as previously studied using a scanning near-field optical microscope (SNOM) (Chicanne et al., 2002). The retardation effect (dynamic theory) is included in the numerical simulations of Fig. 6(b). We present both X- and Z-LDOS compared to the bare slab. Because of new boundaries conditions, similar variations are expected for both in-plane and out-of-plane molecules. Nevertheless, even in the most favourable situation (out-of-plane molecule, dynamic theory), the LDOS decrease (lifetime increase) does not explain the observed change in the fluorescence lifetime (3% instead of 35%). Indeed, LDOS variation inside the corral is small. Nevertheless, these first calculations show that the main effects appear near the gold dots. We explore this point in more details in the next paragraph.

**Decay channels**

A better insight of the relaxation process can be achieved throughout Green’s dyad formalism. Indeed, applying the classical point of view for the fluorescence emission, the dissipative contribution to the fluorescence decay rate writes (Kuhn, 1970; Jackson, 1998; Colas des Francs et al., 2005):

$$\gamma_{\text{nonrad}}(r_m) = \frac{6\pi}{k_0} \int_{\text{dots}} \text{Im} \left[ \epsilon(r, \omega_0) \right] |G(r, r_m, \omega_0) \cdot \mathbf{u}|^2 dr.$$ 

(7)

Obviously, the radiative contribution is the difference $\gamma_{\text{rad}} = \gamma - \gamma_{\text{nonrad}}$. Figure 7 shows both the radiative and nonradiative decay channels’ contribution to the total decay rate calculated near one gold pad inside the PMMA film. The real PMMA slab is considered here.

The number of allowed modes increases dramatically near the gold pad (Fig. 7a). Figure 7(b) clearly shows that the dissipative coupling to the metallic nanostructures is responsible for the opening of new decay channels, hence a strong quenching of the fluorescence. Finally, as the main effects occur near the metallic structures, we report in Fig. 8 the lifetime calculated inside the cavity formed by two gold dots inside the PMMA slab. The distance between the two pads is fixed at 500 nm, which corresponds to the experimental mean distance measured in the lithographed optical corrals. In the centre of the cavity, the lifetime is near the lifetime calculated in the bare slab (about 6 ns). However, strong lifetime enhancement of about 15% appears near the gold dots just before the fluorescence quenching. This enhancement is only 10% when considering molecules slightly out of plane (dipole moment making an angle of 30° with the interface plane). This is in good qualitative agreement with the experimental data.
agreement with the measured shift of the maximum lifetime measured in Fig. 2(d). Therefore, according to Fermi's golden rule, the broadening of the fluorescence lifetime distribution can be attributed to the stadium perturbation of the LDOS. Indeed, although lifetime up to 7.5 ns can be expected in the PMMA slab alone for molecules oriented out of plane (see Fig. 5), the experiment is mainly sensitive for in-plane molecules with lower lifetime. Thus, the fact that a significant number of molecules show both shorter and longer lifetimes is attributed to the stadium effect.

Conclusion

Using confocal scanning microscopy, we have measured fluorescence lifetime of a single molecule near photonic nanostructures. The observed broadening of the lifetime distribution compared to molecules far from any structures is correlated to the LDOS modulation inside the optical corral. Numerical simulations based on dyadic Green's function technique identify the channels involved in the relaxation process, where it is possible to discriminate radiative and nonradiative decay rate. Moreover, the slab effect on the radiative decay rate is analyzed. Further investigation is planned. Particularly, direct comparison between PLDOS and individual lifetime, taking into account the molecule orientation, is needed for more quantitative understanding.

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