Long-range plasmon assisted energy transfer between two fluorescent emitters

Supplemental Material

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In this note we show that by combining experimental data and modelling, we can estimate theoretically the energy transfer efficiency.

1 Enhancement of the decay rate of an emitter in the near field of a silver mirror (theory)

In order to estimate theoretically the energy transfer efficiency, we first need to calculate the enhancement of the decay rate of an emitter close to a silver mirror. The decay rate of an emitter at a position $\mathbf{r}$, with emission frequency ω and transition dipole $\mathbf{p}$, reads [1]

$$\Gamma = \frac{2\mu_0\omega^2}{\hbar}|\mathbf{p}|^2\,\mathrm{Im}[\mathbf{u}\cdot\mathbf{G}(\mathbf{r},\mathbf{r},\omega)\mathbf{u}], \qquad (1)$$

where $\mathbf{u}$ is the unit vector along the direction of the dipole and $\mathbf{G}(\mathbf{r},\mathbf{r},\omega)$ is the electric Green function describing the electrodynamic response of the environment. The Green function can be expressed analytically in the case of a flat interface separating two semi-infinite media [2].

The spontaneous decay rate Γ_0 of an emitter in free space is

$$\Gamma_0 = \frac{\omega^3}{3\pi\hbar\epsilon_0 c^3}|\mathbf{p}|^2, \qquad (2)$$

where c is the speed of light in vacuum. In a homogeneous medium with refractive index n, the spontaneous decay rate becomes $\Gamma_n = n\Gamma_0$. Using this decay rate Γ_n as a reference, the normalized decay rate Γ/Γ_n reads

$$\frac{\Gamma}{\Gamma_n} = \frac{6\pi c}{\omega n}\,\mathrm{Im}[\mathbf{u}\cdot\mathbf{G}(\mathbf{r},\mathbf{r},\omega)\mathbf{u}]. \qquad (3)$$

Experimentally, we deal with a large number of emitters with arbitrary orientations. It is relevant to consider the normalized decay rate averaged over the orientation $\mathbf{u}$ ot the transition dipole:

$$\left\langle\frac{\Gamma}{\Gamma_n}\right\rangle_{\mathbf{u}} = \frac{2\pi c}{\omega n}\,\mathrm{Im}[\mathrm{Tr}\ \mathbf{G}(\mathbf{r},\mathbf{r},\omega)] \qquad (4)$$

where Tr denotes the trace of the tensor Green function. Equation (4) allows us to analyze the dependence of the decay rate enhancement on the distance z to the silver mirror (Fig. 1), for two different wavelengths corresponding to the maximum of the emission spectrum for the donor (blue curve) and the acceptor (red curve). Since in the experiment the emitters are embedded in a PVA layer, n is set to 1.5 in the calculation. The dielectric constant of silver is calculated using a Drude-Lorentz model [3].

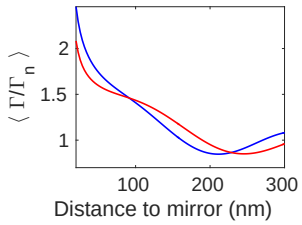

Figure 1: Calculated enhancement of the decay rate of an emitter interacting with a flat surface of silver, computed for λ = 610 nm (blue) and λ = 695 nm (red), and averaged over three orthogonal dipole orientations.

2 Enhancement of the donor and acceptor decay rates due to the silver surface (experiments)

The coupling of donors and acceptors to the silver surface is estimated by measuring Γ_{Ag}/Γ_n, where Γ_n is the decay rate of the emitter embedded in an infinite PVA layer and Γ_{Ag} is the decay rate of the same emitter in PVA deposited on the silver surface. For the donor, $\Gamma_{D,Ag}$ and $\Gamma_{D,n}$ are measured on a sample made of a PVA layer containing donor beads, laying on a silver film and a glass coverslip respectively. We obtain $\Gamma_{D,Ag}/\Gamma_{D,n}$ = 1.72 (Fig. 2a). For the acceptors, we obtain $\Gamma_{A,Ag}/\Gamma_{A,n}$ = 1.58 (Fig. 2b).

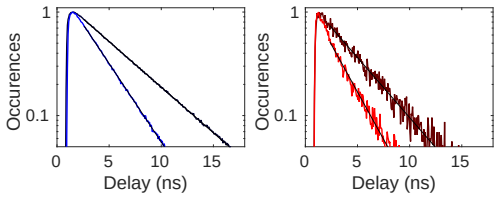

Figure 2: a) Decay rate of the donor in the presence (blue) and in the absence (dark blue) of the silver surface. b) Decay rate of the acceptor in the presence (red) and in the absence (dark red) of the silver surface.

Using these data and the calculated values shown in Fig. 1, we estimated the distance between the emitters and the silver surface to be 50 nm for both the donor and the acceptor. This estimate is consistent with the geometrical features of the sample that were measured separately (the thickness of the SiO_2 spacer and of the PVA layer are on the order of 10 nm and 50 nm, respectively).

3 Estimation of the energy transfer efficiency

The spontaneous decay rate of the donor is modified in the presence of the acceptor. The energy transfer rate Γ_{et} is defined by $\Gamma_D^A = \Gamma_D + \Gamma_{et}$, where Γ_D^A and Γ_D are the decay rate of the donor in the presence and in the absence of the acceptors, respectively. It can be shown that the energy transfer rate depends on the square modulus of the Green function, and can be written in the form [4]

$$\frac{\Gamma_{et}}{\Gamma_0} = 18\pi\sigma(\omega)|\mathbf{u}_A \cdot \mathbf{G}(\mathbf{r}_A, \mathbf{r}_D, \omega)\mathbf{u}_D|^2, \qquad (5)$$

where Γ_0 is the spontaneous decay rate of the donor in vacuum, $\sigma(\omega)$ is the absorption cross-section of the acceptor, and the subscripts D and A refer to the position and orientation of the donor and acceptor, respectively. As specified by the provider company, acceptors (Atto 665, Atto-tec GmbH) have a molar extinction coefficient of $1.6 \times 10^5\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ at their maximum absorption wavelength (λ_{max} = 663 nm), and therefore an absorption cross-section $\sigma(\omega_{max}) = 0.061$ nm^2.

Taking Γ_n instead of Γ_0 as a reference and averaging over the dipole orientations, the normalized energy transfer can be rewritten as

$$\left\langle \frac{\Gamma_{et}}{\Gamma_n} \right\rangle_{\mathbf{u}} = \frac{2\pi\sigma(\omega)}{n} \sum_{i,j=1}^{3} |\mathbf{G}(\mathbf{r}_A, \mathbf{r}_D, \omega)|^2. \qquad (6)$$

The energy transfer efficiency can be defined as

$$\eta_{et} = \frac{\Gamma_{et}}{\Gamma_D + \Gamma_{et}}. \qquad (7)$$

One can also define the energy transfer enhancement f_{et}

$$f_{et} = \frac{\Gamma_{et}}{\Gamma_{et,n}} \qquad (8)$$

that compares the energy transfer rate in the presence of the silver mirror and in a homogeneous environment of refractive index n. Both η_{et} and f_{et} can be computed using Eqs. (4) and (6).

We show in Fig. (3) the energy transfer efficiency η_{et} and the enhancement factor f_{et} computed for two emitters located 50 nm above the silver mirror, as a function of the distance between the donor and the acceptor.

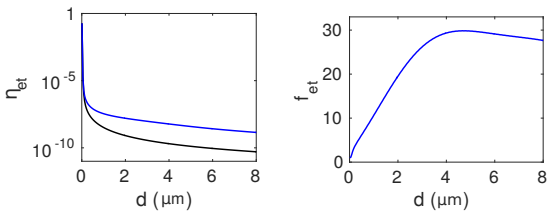

Figure 3: a) Energy transfer efficiency for two emitters separated by a distance d in the vicinity of the mirror (blue) and in homogeneous medium (black). b) Enhancement factor versus the distance d.

As shown in Fig. 3a, the energy transfer efficiency decays rapidly when increasing the donor-acceptor interdistance, both in the presence of the silver mirror (blue curve) and in a homogeneous medium (black curve, computed with $n = 1.5$). This supports the statement that the observed enhancement of the donor decay rate in the presence of the acceptors is determined by dipole-dipole interactions between the donor and the surrounding acceptors.

The enhancement factor of the energy transfer rate is shown in Fig. 3b. For distances between 2 and 8 μm, the enhancement is substantial, with a maximum value $f_{et} \sim 30$. This means that the presence of the plasmonic channel increases by a factor of 30 the energy transfer rate compared to the rate in a homogeneous medium for the same donor-acceptor interdistance.

4 Statistics of intensity and decay rate of donors on silver

In this section we report on the intensity and decay rate of 10 different donors on a silver surface.

Qualitatively, the quantum yield of a donor lying on a silver film is related to its decay rate Γ and to its fluorescence intensity I. We measured both I and Γ for 10 different donor beads in the absence of acceptors. Fluorescence histograms are shown in Fig. 4.

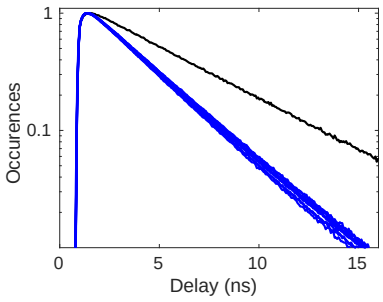

Figure 4: Fluorescence histogram of 10 donors on silver (blue). The decay rate of a donor on glass (black) is shown for comparison.

The mean decay rate of the donor on the silver surface is 0.352 ns^{-1} and the standard deviation associated with these 10 different measurements is 0.008 ns^{-1}.

The mean count rate of the donor on the silver surface is 32000 cps/s and the standard deviation associated with these 10 different measurements is 2600 cps/s.

References

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