Fundamental figure of merit for engineering dipole-dipole interactions

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Abstract: Over the last decade there has been a debate regarding the role of the photonic environment in enhancing, inhibiting and imparting coherence to dipole-dipole interactions. We develop a unified figure of merit to conclusively explain multiple recent experiments. © 2019 The Author(s)

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Föster resonance energy transfer (FRET) is a striking manifestation of resonant dipole-dipole interactions (RDDI). There has been a long standing debate regarding the influence of the photonic environment on FRET. Though FRET is understood and accepted for homogeneous systems, the fundamental nature of FRET in complex photonic environments remains poorly understood and has been widely debated table 1. In this paper, we show that the QED perturbative approach to analyzing dipole-dipole interactions in a nanophotonic environment can be captured by an effective near-field dipole model. Furthermore, the widely used concept of Purcell factor variation is an incorrect figure of merit (FOM) for analyzing FRET. To this end we define a FOM, the FRET rate enhancement factor (F_{ET}) which characterizes FRET in a complex photonic environment. The introduced FOM captures the contradictory regimes of FRET completely in the widely used planar and spherical nanostructured geometries.

Table 1. Experimental Results of FRET

	Enhancement	Suppression	No effect
Microcavity	[1]	[2]	[3]
Nanoparticles	[4]	[5]	[6]

Spontaneous emission rate and FRET rate : Using Fermi's Golden rule and the first order transition amplitude, one arrives at the general expression of the spontaneous emission(SE) rate

$$\gamma_{D,rad} = \frac{2\omega_D^2|p_D|^2}{\hbar\varepsilon_0 c^2}[\mathbf{n}_D \cdot \mathrm{Im}\{\bar{\bar{G}}(\mathbf{r}_D,\mathbf{r}_D;\omega_D)\} \cdot \mathbf{n}_D], \qquad \rho_E(\mathbf{r}_D;\omega) = \frac{6\omega}{\pi c^2}\mathbf{n}_D \cdot \mathrm{Im}\{\bar{\bar{G}}(\mathbf{r}_D,\mathbf{r}_D;\omega)\} \cdot \mathbf{n}_D, \tag{1}$$

for an atom in an inhomogeneous environment. ω_D is the radial frequency, and $\bar{\bar{G}}(\mathbf{r},\mathbf{r};\omega)$ is the classical dyadic Green's function related to the electric field of the dipole. The molecule is described by dipole moment $\mathbf{p}_D = p_D\mathbf{n}_D$ in the dipole approximation. The spontaneous emission is proportional to the local density of states (LDOS) Eq. 1 and is a property of the photonic environment. FRET on the other hand can be understood as spontaneous emission of a donor molecule to the specific location of the acceptor molecule triggered by near-field dipole-dipole interaction. Within the semi-classical picture, a donor dipole induces a dipole moment in a nearby polarizable acceptor. If the donor and acceptor have an overlapping emission and absorption spectra (see Fig. 1(b)), then resonant energy transfer occurs.

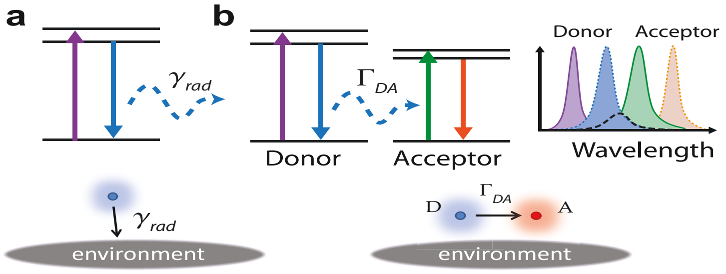

Fig. 1. **(a) Energy-level diagram depicting spontaneous emission.** γ_{rad} denotes the rate of radiative energy transfer to any location in the environment, acceptor is not considered as part of the environment. **(b) Energy-level diagram depicting FRET**. FRET occurs when two neighboring atoms or molecules, have overlapping emission and absorption spectra and couple due to a Coulombic dipole-dipole interaction. The FRET rate Γ_{DA} denotes the energy transfer to the acceptor location.

$$\Gamma_{DA} = \frac{2\pi}{\hbar^2}\int d\omega\, |V_{EE}(\omega)|^2 \sigma_D(\omega)\sigma_A(\omega), \qquad V_{EE}(\mathbf{r}_A,\mathbf{r}_D;\omega) = -\frac{\omega^2}{\varepsilon_o c^2}\mathbf{p}_A \cdot \bar{\bar{G}}(\mathbf{r}_A,\mathbf{r}_D;\omega)\cdot \mathbf{p}_D, \tag{2}$$

Note that LDOS and FRET rate are both dependent on the dyadic Green's function which contains all information regarding the photonic environment. The FRET rate is clearly not dependent on the LDOS, as debated in [3] and several other papers. Nevertheless, it is dependent on the environment through the two-point Green's function $\bar{G}(\mathbf{r}_A,\mathbf{r}_D;\omega)$. While the LDOS is a measure of the energy transfer rate to any location in the environment, the RDDI is a measure of the energy transfer rate to the acceptor location only (see Fig.1). Analogous to the Purcell factor, we now introduce the FRET rate FOM as,

$$F_p = \frac{\gamma_{D,rad}}{\gamma^o_{D,rad}} = \frac{\rho_E(\mathbf{r}_D;\omega)}{\rho^o_E(\mathbf{r}_D;\omega)}, \qquad F_{ET} = \frac{\Gamma_{DA}}{\Gamma^o_{DA}}, \tag{3}$$

where, $\rho_E(\mathbf{r}_D;\omega)$ and $\rho^o_E(\mathbf{r}_D;\omega)$ are the LDOS in nanophotonic environment and vacuum respectively. The FRET rate figure of merit is theoretically calculated for the experimental situations described in [3, 6]. In Fig. 2 a, we theoretically calculate the FRET figure of merit for situation described in [3] to be $F_{ET} \approx 1$ over a wide range of separation distances **d** from the mirror. This is in good agreement with the experiment (plotted at the donor's peak emission wavelength of 525 nm). Theoretical Purcell factor F_p also shows excellent agreement with experimental results (lower inset). However, using our theoretical model, we predict a drastic change in the FRET FOM near the Ag surface plasmon resonance in the limit $\mathbf{d} \rightarrow 0$ (top inset). This shows that FRET rate can be modified for the same experiment if the regime is modified. In Fig. 2 b,c we theoretically calculate the FRET figure of merit for situation described in [6], The donor-acceptor pair is embedded inside a nanocrystal (4 nm diameter) with assumed refractive index $n = 1.7$ ($LaPO_4$). By varying the refractive index of the surrounding medium, we find that $F_{ET} \approx 1$ in agreement with our analysis. Note that we also predict the linear dependence of the Purcell factor as measured in the experiment (inset). However, we predict that a silver-coated nanocrystal would produce a drastic change in the FRET FOM as well as the Purcell factor. This result would require the donor-acceptor overlap spectrum to lie around the 400 nm wavelength range. Note that the above results clearly show that FRET can be engineered by the environment even though it is extremely difficult in comparison to modifying spontaneous emission. The dyadic Green function formalism and results from QED theory were used to calculate all results and parameters were obtained from the experiments.

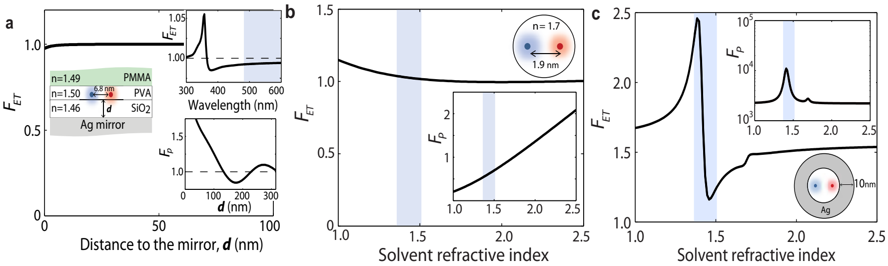

Fig. 2. **Comparison to experiments. (a)** Theoretical comparison to experiment in ref. [3]. **(b)** Theoretical comparison to experiment in [6]. **(c)** Silver-coated nanocrystal

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