Förster resonance energy transfer in absorbing environment

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ABSTRACT

We present an analytical model for Förster resonance energy transfer between donors and acceptors in the presence of a metal surface. We find that energy transfer to the metal results in a reduction of the Förster radius, leading to a suppression of concentration quenching for high molecule concentrations.

Keywords: Resonance energy transfer, Fluorescence, Foerster radius, Concentration quenching

1. INTRODUCTION

Förster resonance energy transfer (FRET) between a donor and an acceptor situated near planar metal surfaces or metal nanostructures has been extensively studied both experimentally and theoretically [1]. Excitation of surface plasmon polaritons (SPP) or localized surface plasmons (LSP) by the donor provides an additional energy transfer (ET) channel to the acceptor resulting in significant enhancement of FRET magnitude and extension of the FRET range well beyond the Förster radius R_F, which is about 5 nm for most dye molecules. However, the plasmon-mediated channel is inefficient for molecules separated by a distance R_F or smaller since it requires a comparably small molecules' proximity to the metal surface, while in this case, both fluorescence and FRET for individual molecules are quenched due to energy dissipation in the metal. On the other hand, if molecules concentration is sufficiently high, the fluorescence is quenched due to efficient Förster transfer from excited fluorophores to neighboring molecules within the distance R_F. Such concentration quenching results in fast fluorescence decay with increasing concentration as observed, e.g., in polymer films doped by dye molecules deposited on a glass substrate [2]. One would expect that if metal surface is used as the substrate, the fluorescence should be further suppressed due to additional quenching by the metal. Instead, it was recently reported that in a wide range of film thickness, the fluorescence rate slows down, indicating the reduction of concentration quenching due to the metal absorption [3,4]. Furthermore, for high molecule concentrations, the measured effective fluorescence decay rate shows non-monotonic behavior with varying film thickness and exhibits a pronounced minimum at intermediate thicknesses. These observations point to a highly non-trivial interplay between the metal quenching, which is due to ET from molecules to the metal, and concentration quenching, which is due to FRET between the molecules.

In this paper, we outline an analytical model for FRET between donor and acceptor molecules in the presence of an inhomogeneous absorbing environment such as metallic structures characterized by a complex dielectric function. Specifically, we show that energy transfer to the environment, which accompanies FRET, results in a reduction of the Förster radius R_F characterizing FRET efficiency between the molecules. For large concentration of molecules situated near a metal surface, this leads to a suppression of fluorescence concentration quenching for small average molecule separations from the metal and to a reduction of the effective fluorescence decay rate relative to that in homogeneous environment. Our numerical calculations of the effective fluorescence decay rate for molecules embedded in a dielectric slab on top of a metal surface reveal a characteristic minimum at intermediate slab thicknesses for high molecule concentrations, consistent with the experiment [3,4].

2. MODEL

The probability rate of acceptor excitation by the donor's electric field [2]

$$W_a(R_{ad},t)=\frac{3c\kappa_{ad}^2}{2\pi\hbar\omega R_{ad}^6}\sigma_a(\omega)|\boldsymbol{p}_d(\mathrm{t})|^2$$

where $\sigma_a(\omega)$ is acceptor's absorption cross-section at the transition frequency ω, R_{ad} is the donor-acceptor separation, $\boldsymbol{p}_d$ is the excited donor's dipole moment causing the transition, and κ_{ad}^2 characterizes molecules' mutual polarization. In the presence of metal surface, the donor's dipole moment is time dependent, $\boldsymbol{p}_d(t)=\boldsymbol{p}_d e^{-\Gamma_d t/2}$, where $\Gamma_d=\gamma_d+\gamma_s$ is

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the donor's full decay rate comprised of the fluorescence rate γ_d and the energy transfer rate to the metal $\gamma_s \gg \gamma_d$. In this case, to properly define the Förster radius, the FRET probability rate should be averaged over the fluorescence time:

$$\mathrm{W}'_a = \tau_d^{-1} \int \mathrm{W}_a(t)\mathrm{d}t = \left(\frac{\gamma_d}{\Gamma_d}\right) \mathrm{W}_a$$

The modified Förster radius R'_F is determined from the condition $\tau_d \mathrm{W}'_a(R_{ad}) = 1$, where τ_d is the free donor's fluorescence decay time, and we obtain

$$\frac{R'^6_F}{R^6_F} = \frac{\gamma_d}{\Gamma_d}$$

indicating that in an absorbing environment the effective Förster radius is reduced.

The emission kinetics is obtained in a standard way by averaging out over random position of the acceptors [3] and we obtain the time-dependent fluorescence intensity as

$$I_d(t) \sim e^{-\Gamma_d t - N'_A \sqrt{\pi \gamma_d t}}$$

where $N'_A = n_A V'_F$ is the acceptor number within modified Förster volume $V'_F = 4\pi R'^3_F/3$ and n_A is the acceptor concentration. Thus, in the absorbing environment, the number of acceptors that can be efficiently excited by the donor is effectively reduced by the factor $\sqrt{\gamma_d/\Gamma_d}$, leading to an interplay between the metal quenching and concentration quenching at intermediate distances to the metal surface.

3. NUMERICAL RESULTS

Here we compare the results of our numerical calculations with the experimental data [3,4]. In Fig. 1a, we show the calculated effective fluorescence decay rate from dielectric film doped by HITS:PMMA dye molecules on top of Ag surface versus the film thickness at various die concentrations. These calculations are compared with the experimental data taken on a similar system shown in Fig. 1b [4]. A clear minimum of the effective decay rate is observed for high molecule concentrations indicating that, for intermediate average molecule distances to the metal surface, the metal quenching is weakened while the concentration quenching is still suppressed. The mechanism of this suppression is a reduction of the effective Förster radius in an absorbing environment due to competition between two energy transfer channels.

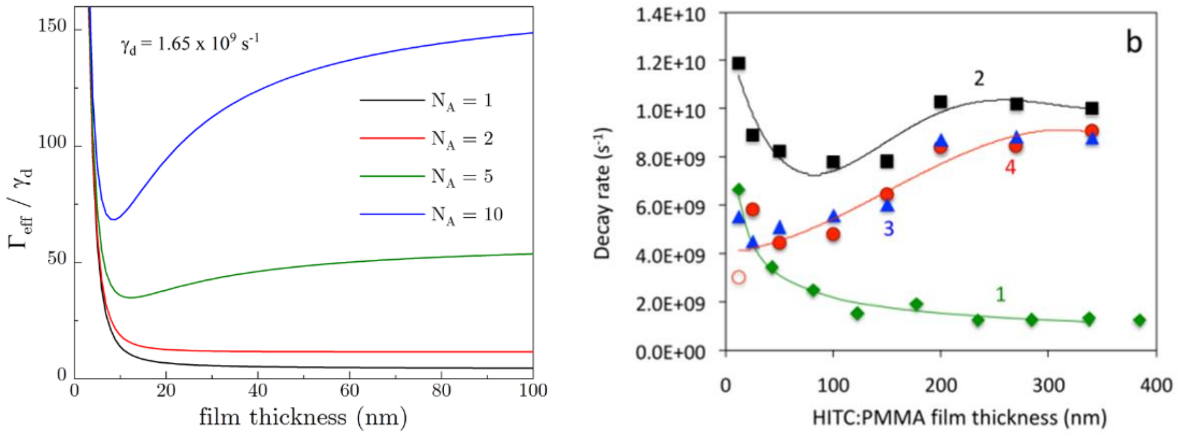

Figure 1. (a) Calculated effective decay rate from dielectric film doped by HITS:PMMA die molecules on top of Ag surface vs. film thickness for various molecule concentrations. (b) Experimental data for the effective decay rate taken on a similar system [4].

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