Control of Concentration Quenching with Metallic Substrates and Cavities

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Abstract: We found that inhibition of concentration quenching of HITC dye in Fabry-Perot cavities is almost similar to that on top of silver. Low convexity of the emission kinetics suggests strong coupling mediated by surface plasmons. © 2020 The Author(s).

Close proximity to metallic surfaces, lamellar metal-dielectric metamaterials and other nanostructures can strongly affect many physical phenomena, including spontaneous emission and Förster energy transfer. In multiple recent studies, Förster transfer was claimed to be enhanced [1], inhibited [2] or not affected [3] by non-local metal-dielectric environments. This unsettled controversy motivated the present study.

In the recent works, we have shown that (i) Förster energy transfer (or the related concentration quenching of luminescence) is inhibited in the vicinity of metallic surfaces and lamellar hyperbolic metamaterials [2,4] and (ii) the rate and intensity of spontaneous emission can be strongly enhanced in thin metal-insulator-metal (MIM) waveguides (or Fabry-Perot cavities) [5]. In this study, focused on the effect of Fabry-Perot cavities on the energy transfer (which was found to be very different from that in Ref. [1]), we report on several important observations that shed light on the underlying physics of a broader range of related phenomena.

Our experimental samples were films of dye-doped polymer HITC:PMMA deposited on glass and Ag substrates or sandwiched between two Ag films to form a Fabry-Perot cavity. The HITC:PMMA film thicknesses ranged from d=12 nm to d=340 nm, and the dye concentrations (in solid state) were equal to c=2 g/l and c=30 g/l. In the kinetics measurements, the samples were excited at λ=795 nm with ~150 fs pulses of a Ti:sapphire laser and the emission was detected with a VIS/IR streak camera. In our data analysis, we first treated all kinetics as single-exponential and determined effective decay rates γ. In the second step, we studied the deviation of emission kinetics from exponential functions and analyzed it in terms of "convexity" factors ζ, proportional to the second derivative of the kinetics plotted in semi-logarithmic coordinates. The major results and their analysis are summarized below.

1. *Dye-Doped Films Deposited on Glass* In agreement with Ref. [4], the emission kinetics shorten at high dye concentration (c=30 g/l), indicating concentration quenching – energy transfer to quenching centers. Such quenching was very modest at low dye concentration (c=2 g/l).

Since some donor molecules have quenching centers (acceptors) nearby and others do not, the energy transfer emission kinetics of ensembles of donors deviate from single exponential functions. Correspondingly, the convexity factors ζ measured at high dye concentration were greater than those at the low dye concentration.

A modest decrease of γ was observed with the reduction in the film thickness d. In thin films, donors are surrounded by smaller numbers of acceptors, which leads to a reduction in the energy transfer and concentration quenching.

The convexity factors ζ slightly increase as film distances d reduce. As film thickness decreases, the energy transfer transitions from the 3D regime to the 2D regime. Correspondingly, $\propto \exp(-\sqrt{t/\tau})$ emission kinetics [6] (with smaller ζ) change to $\propto \exp(-\sqrt[3]{t/\tau})$ kinetics [7] (with larger ζ). Note that this and the previous explanations are plausible when the film thickness is comparable to the Förster radius ≤10 nm and become less likely at d≥10 nm.

2. *Highly Doped HITC:PMMA Films (c=30 g/l) Deposited on Silver* At large film thicknesses d, the emission decay rates γ and convexity factors ζ are almost the same as those measured on top of glass. This is expected, since at large distance from the interface, the effect of metal is small [4].

The difference between the decay rates on top of glass and on top of silver increases with the reduction in the film thickness d. Such slowing down of the emission kinetics on top of Ag and the corresponding reduction of concentration quenching (Fig. 1, trace 1) is consistent with Ref. [4]. A strong reduction in convexity ζ is observed on top of silver at d ranging between ~100 nm and ~200 nm. Accordingly, the emission kinetics, plotted in semi-logarithmic coordinates, look nearly linear. This suggests that donors transfer their energy to acceptors in a synchronized manner. Strong coupling of excited molecules with propagating surface plasmons and with each other (*via* coupling to plasmons), can be a possible explanation of this effect (in analogy with coherent spontaneous emission of dye molecules strongly coupled with plasmonic substrates [8,9]). An increase of both emission decay rates γ and convexity factors ζ were observed at small film thicknesses, $d \leq 50$ nm. Both effects can be due to the expected luminescence quenching in close vicinity to metal [10] (energy transfer to metal or lossy waves).

3. *Highly Doped HITC:PMMA Films (c=30 g/l) in Fabry-Perot Cavities* The decay rates γ of highly concentrated dye (c=30 g/l) in cavities (Fig. 1, trace 2) are the sums of the spontaneous emission rates γ_{sp}, which are, presumably, independent of c, and the energy transfer (concentration quenching) rates γ_{et}, $\gamma = \gamma_{sp} + \gamma_{et}$. The latter were obtained by subtracting the spontaneous emission rates γ_{sp} measured in similar cavities in Ref [5] (Fig. 1, trace 3) from the experimental decay rates γ measured in this study (Fig 1, trace 2). Intriguingly, the result of this subtraction (Fig. 1, blue circles) closely follows the decay rates measured on top of silver (Fig. 1, trace 1). Therefore, the effect of a cavity on the concentration quenching does not extend beyond the mere effect of the silver substrate (the bottom Ag layer), and the semi-transparent silver mirror on the top makes almost no difference. This result is strikingly different from that of Ref. [1], claiming enhancement of the energy transfer in cavities. On the other hand, strongly different contributions to the concentration quenching of the top and bottom Ag films are in line with Ref. [11], claiming that frequency shifts of absorbers or emitters in the vicinity of a metallic surface strongly depend on its thickness. The convexity factors ζ in cavities were slightly smaller than those on top of glass.

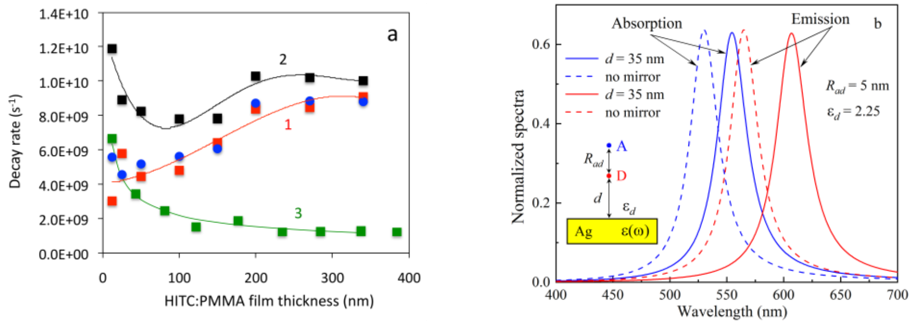

Fig. 1. (a) Trace 1 and red squares: dependence of the emission decay rate on the thickness of the HITC:PMMA film on top of Ag at dye concentration 30 g/l. Trace 2 and black squares: same as above in Fabry-Perot cavities. Trace 3 and green squares: same as above at low dye concentration 3 g/l [5]. Blue circles: Trace 3 subtracted from Trace 2. (b) Calculated normalized absorption and emission spectra in the absence of mirror (dashed lines) and for a vertical donor-acceptor arrangement near the mirror (solid lines)

4. *Non-Exponential Spontaneous Emission in Vicinity of Air/Dielectric Interface* The convexity of the emission kinetics did not originate solely from the energy transfer. Thus, the calculated spontaneous emission kinetics (in absence of any energy transfer) deviated from exponential functions due to gradients of the photonic density of states (PDOS) in the vicinity of the air/dielectric interface [12]. However, the calculated ζ factors were much smaller than those measured in any experimental samples studied in this work. Therefore, the effect of PDOS on the shapes of spontaneous emission kinetics existed but was small.

5. *Theoretical Model* We have developed the theoretical model predicting that near a metallic mirror, frequency shifts, caused by interaction of molecular dipoles with their mirror images, lead to a suppression of the Förster energy transfer between donors and acceptors located at different distances from the mirror. This model can explain, at least partly, the experimentally observed inhibition of the concentration quenching in the vicinity of a metallic surface.

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