Effect of Fabry-Perot Cavities on Concentration Quenching

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SMART
SCIENCE, MATHEMATICS, AND RESEARCH FOR TRANSFORMATION
PART OF THE NATIONAL DEFENSE EDUCATION PROGRAM

NORFOLK STATE UNIVERSITY

Abstract

We show that concentration quenching of emission of dye molecules – an energy transfer to quenching centers – is inhibited on top of silver films and in subwavelength Fabry-Perot cavities (or metal-insulator-metal, MIM, waveguides).

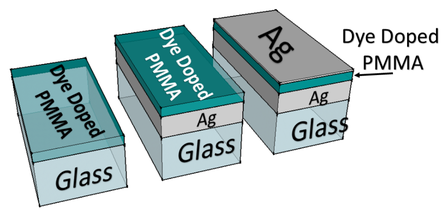
Introduction and Motivation

Energy transfer between donors and acceptors is important for a range of physical phenomena and applications ranging from photovoltaics to biosensing devices. It has been shown that energy transfer (as well as spontaneous emission) can be affected by metallic nanostructures, nanoparticles, surfaces and cavities. The full spectrum of experimental results reported in the literature includes enhancement of the energy transfer by non-local metal-dielectric environments, its inhibition and its indifference. Particularly, in the study of the Förster energy transfer between donor and acceptor molecules, it was shown that the same environments, such as metallic surfaces or hyperbolic metamaterials, which boost spontaneous emission, inhibit energy transfer.

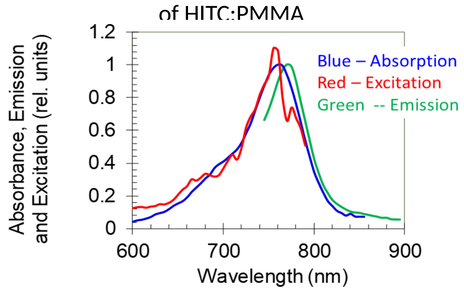
The broad range of results and opinions reported in the literature poses three questions which motivated our studies: (i) can energy transfer be affected by Fabry-Perot cavities (or metal-insulator-metal, MIM, waveguides), (ii) is the effect of a cavity any different than the mere effect of two metallic surfaces, and (iii) is the energy transfer affected by cavity resonances?

Here we report on inhibition of concentration quenching for dye molecules on top of Ag films and in MIM cavities. We attribute it to a suppression of Förster energy transfer near metallic mirror caused by frequency shifts due to optical dipole interaction with its image. We present a theoretical model supporting such interpretation of the experimental data.

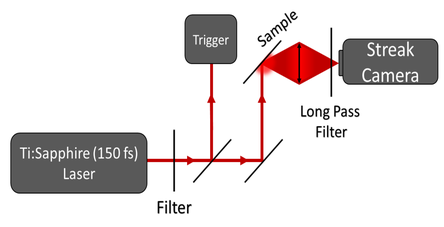
Experimental Samples



Absorption, Emission, and Excitation Spectra of HITC:PMMA

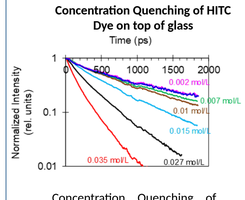


Experimental Setup

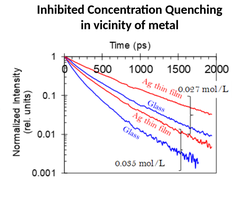


High Dye Concentration

Concentration Quenching and its inhibition in vicinity of silver films and lamellar metal/dielectric metamaterials

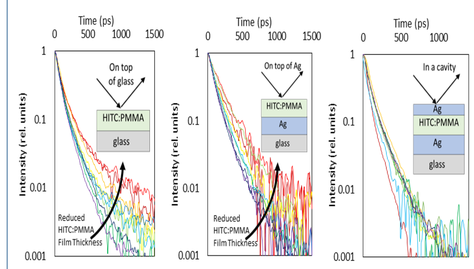


Concentration Quenching of HITC emission at high dye concentrations on top of glass.

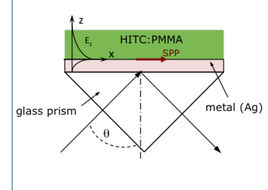


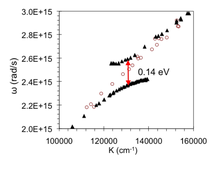
Inhibition of concentration quenching by Ag films

Effect of cavities and control substrates on concentration quenching



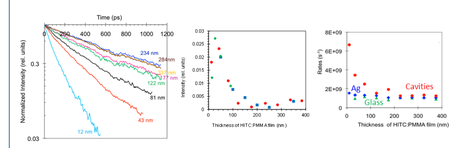
- At large film thicknesses, emission kinetics of dye on glass, silver, and cavity are almost the same.
- On glass and Ag substrates, effective emission decay times, determined by fitting experimental curves with exponential function, are getting longer as the film thickness is reduced.
- Most emission kinetics deviate from exponential functions: some donors have close acceptors and some do not. Averaging over large ensembles of donors results in deviation from single exponents.
- With reduction in the HITC:PMMA film thickness, emission kinetics on top of silver becomes nearly single exponential. This can be due to a strong coupling of dye molecules and SPPs at silver-dye interface.
- Rabi splitting consistent with strong coupling is observed in the Kretschmann geometry experiment.





Low Dye Concentration (small concentration quenching)

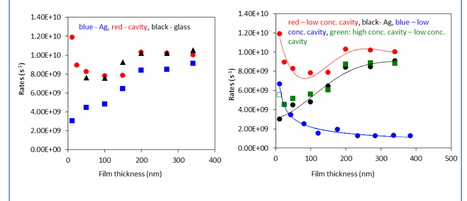
Enhancement of emission in MIM waveguides (Fabry-Perot cavities)



Emission kinetics in cavities of different sizes. Decay rate as the function of the cavity size. Emission intensities normalized by the number of molecules.

- Strong shortening of emission kinetics at reduced cavity sizes,
- Strong enhancement of emission intensity (normalized by the number of dye molecules in the cavity) with the reduction of the cavity size.
- Practically no enhancements in control samples (on top of glass and silver films).

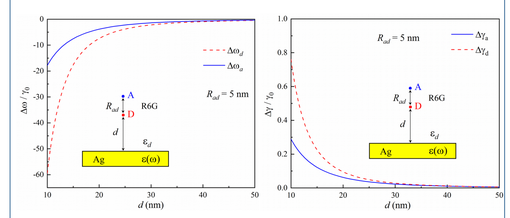
Summary of Emission Kinetics Rates in cavities and on top of control substrates



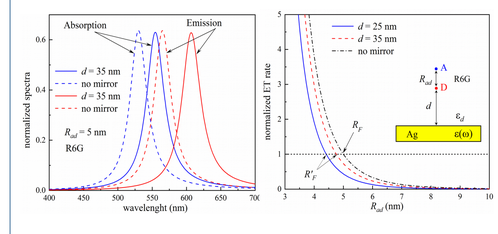
- Contributions of intracentral relaxation and concentration quenching to the cavity's emission are separated.
- The effect of cavity on concentration quenching is found to be nearly the same as effect of a simple Ag surface.

Modeling Förster energy transfer near metallic mirror

- Near a metal film, the interaction of dye's optical dipole with its image leads to a redshift of the spectral band central frequency and to a linewidth increase due to metal absorption.
- For dyes' excitation and emission bands located well below the surface plasmon resonance, the frequency shift is considerably larger that the linewidth increase.



- In this regime, absorption and emission spectra experience substantial redshifts without significant change of the spectral shape. For two dye molecules located at different distances from the film, such spectral changes result in a smaller donor-acceptor spectral overlap and, hence, in a reduction of the Förster distance and energy transfer rate.



- The reduction of Förster energy transfer rate is most pronounced for vertically-arranged donor-acceptor pairs, but persists also for large dyes ensembles randomly distributed near the metal film, causing suppression of the concentration quenching.

Acknowledgements

The authors acknowledge NSF grants 1646789, 1610427, 1830886, 1856515, and the DoD SMART Scholarship Program .