

Effect of Thickness of a Dye-doped Polymeric Film on the Concentration Quenching of Luminescence

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Abstract: We have studied the dependence of concentration quenching of luminescence on the thickness d of dye-doped polymeric films (HITC:PMMA) and found a strong inhibition of the donor-acceptor energy transfer (concentration quenching) at small values of d .

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Quantum emitters, including dye molecules, are widely used in a variety of nanophotonics fundamental studies and applications. At high dye concentrations, which are of interest at the stimulated emission and strong coupling, the concentration quenching of luminescence and its inhibition in vicinity to metallic surfaces and lamellar metal/dielectric metamaterials have been studied in [1,2]. While the particular focus of these studies was on effects of non-local metallic environments, the effect of film thickness on the luminescence kinetics in purely dielectric systems was never researched. In this work, we study the dependence of the luminescence concentration quenching and its inhibition on the thickness of dye-doped polymeric films deposited on glass substrates. The effect is discussed in terms of the reduced number of acceptors available to donors in thin films.

The experimental samples in our studies were PMMA polymeric films doped with HITC dye molecules. The dye concentration ranged between $\nu = 2$ g/l and $\nu = 40$ g/l (in solid state) and the film thickness was varied between 11 nm and 3.6 μm .

In the emission kinetics measurements, the samples were excited with ~ 150 fs pulses of a mode locked Ti:sapphire laser (Mira 900 from Coherent). The laser spot was ~ 2.5 mm in diameter, the average power was ~ 60 mW, and the repetition rate was 76 MHz. The emission kinetics were recorded using a visible and near-IR streak camera (Model C5680 from Hamamatsu). The time resolution, determined by the jitter of the laser and the wide-open entrance slit of the streak camera, was ~ 100 ps. The emission decay rates were determined by fitting the experimental kinetics with exponential functions.

The spectroscopic properties of HITC:PMMA films have been reported in the recent study [1]. The absorption and excitation bands of HITC:PMMA films have the maxima at 762 nm, and the emission band has its peak position at 772 nm. Knowing the experimental spectra of emission $F(\omega)$ and absorption cross section $\mu(\omega)$, we determined the Förster radius for HITC molecules (the distance between two molecules at which the transfer rate is equal to the emission decay rate [3]) to be equal to

$$R_F^6 = \frac{9\chi^2 c^4 \eta}{8\pi} \int \frac{F(\omega)\mu(\omega)}{\eta^4 \omega^4} d\omega = 5.3 \text{ nm.} \quad (1)$$

Here χ^2 is the factor describing relative orientation of dipoles ($\chi^2=2/3$ for random orientations), $\int F(\omega)d\omega = 1$, ω is the angular frequency, $n=1.5$ [4] is the index of refraction, $\eta = 0.07$ [5] is the spontaneous emission quantum yield, and c is the speed of light.

The emission kinetics of low concentrated HITC dye ($\nu=2$ g/l and $\nu=3.6$ g/l) deposited on glass substrates were nearly single exponential and their decay rates were practically independent of the film thickness (Fig. 1, squares and diamonds). The emission decay was predominantly determined by the combination of radiative and non-radiative intra-central relaxation processes, and the effect of the concentration quenching was small [1].

At the same time, at large dye concentrations, the emission kinetics had significantly higher decay rates (larger at $\nu=40$ g/l than at $\nu=30$ g/l) and deviated from exponential functions. This behavior is consistent with the concentration quenching of HITC molecules reported in Ref. [1].

At the dye concentration equal to $\nu=40$ g/l, the emission kinetics were measured at various thicknesses of HITC:PMMA films, ranging from 11 nm to 3.6 μm . In the data set represented by solid black circles in Fig. 1, the film thickness was controlled by the viscosity of the solution. The emission decay rates were maximal at the film

thicknesses $d \sim 1 \mu\text{m}$ and they decreased significantly at smaller values of d . The characteristic length scale of the decay rate reduction, $d_0 = 33 \text{ nm}$, was determined by fitting the data points with the function $A+B(1-\exp(-d_0/d))$, solid line in Fig. 1. A qualitatively similar pattern has been observed in the series of HITC:PMMA films with dye concentrations equal to $\nu = 30 \text{ g/l}$, green triangles in Fig. 1.

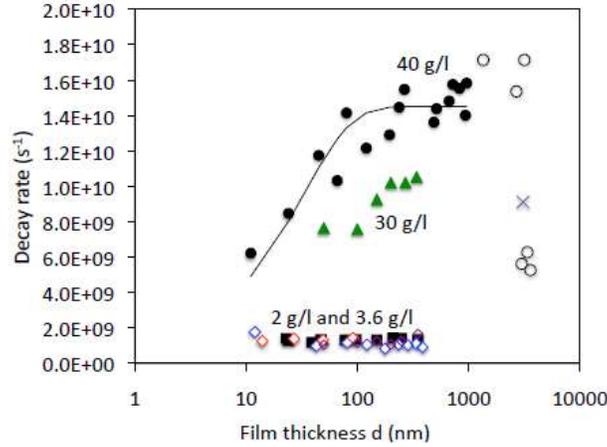


Figure 1. Dependence of emission decay rates in HITC:PMMA films as the function of the film thickness d : $\nu = 40 \text{ g/l}$: filled black circles (varied viscosity), open black circles (varied spinning rate), cross (drop casting), and solid line – fitting with the formula $A+B(1-\exp(-d_0/d))$; $\nu = 30 \text{ g/l}$: green triangles; $\nu = 3.6 \text{ g/l}$: open red, blue, and purple diamonds; $\nu = 2 \text{ g/l}$: filled black squares.

We infer that shortening of the emission kinetics in thin films is due to a small number of acceptors, to which donors can transfer their excitation energy, leading to inhibition of the Förster energy transfer and the concentration quenching. Intuitively, this effect can be significant only at the film thickness $d \leq R_F$. However, as we show below, the characteristic length of the excitation migration can be larger than this. We assume that the energy migration over donors (delivering excitation energy to acceptors) is diffusion, with the diffusion coefficient given by

$$D = \frac{1}{2} \frac{R^2}{\Delta t} = \frac{1}{2\tau_0} \frac{R_F^6}{R^4}, \quad (2)$$

where Δt is the time of the excitation “hop” between two molecules, W is the energy transfer rate, τ_0 is the emission decay time, and R is the average distance between molecules. Correspondingly, the characteristic diffusion length (the standard deviation of the diffusion spread of excitation) is equal to

$$\sigma = \sqrt{2Dt} = \frac{R_F^3}{R^2} \sqrt{\frac{t}{\tau_0}}. \quad (3)$$

Thus, at $t = \tau_0$, $\nu = 40 \text{ g/l}$ and $R = 2.7 \text{ nm}$, $\sigma(\tau_0) = R_F^3/R^2 = 20 \text{ nm}$. This means that over the luminescence lifetime, the excitation migrates over 20 nm. Correspondingly, the energy transfer within 20 nm from the film’s interface is sensitive to the presence of the interface and the effective deficit of acceptors. As each film has two interfaces, the net volume sensitive to the vicinity of the interface is 40 nm thick, close to $d_0 = 33 \text{ nm}$ determined experimentally.

Another intriguing phenomenon was found in thick and highly doped HITC:PMMA films ($d \geq 3 \text{ mm}$, $\nu = 40 \text{ g/l}$), in which the decay rate dropped abruptly to approximately one third of its maximal value. These samples were highly scattering and had anomalously strong absorption. This behavior can be due to what is known in literature as the crystallinity of PMMA [6], which can depend on the fabrication and processing conditions, such as the varied spinning rate used in this series of samples. More experimental details and theoretical analysis will be presented at the conference.

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