

Effect of Nonlocal Metal-Dielectric Environments on Concentration Quenching of HITC Dye

S. Prayakara, C. E. Bonner, M. A. Noginov*

Center for Materials Research, Norfolk State University, Norfolk, VA 23504

*mnoginov@nsu.edu

Abstract: We have experimentally demonstrated the inhibition of luminescence self-quenching in heavily doped HITC:PMMA polymeric films in vicinity of lamellar metal-dielectric metamaterials with hyperbolic dispersion and metallic surfaces.

© 2017 Optical Society of America

OCIS codes: (160.3918) Metamaterials, (260.2160) Energy transfer

Metamaterials, in particular metamaterials with hyperbolic dispersion, have been shown to control scores of physical phenomena including stimulated and spontaneous emission [1, 2], van der Waals interactions [3], energy transfer [4] and rates of chemical reactions [5]. Many applications of metamaterials and plasmonic systems suffer from absorption loss in metal. This loss can often be offset by optical gain in an adjacent dielectric medium, provided by, for example, excited dye molecules or quantum dots. However, high concentration of dye molecules accelerates luminescence quenching (the phenomenon known as concentration quenching), limiting the magnitude of the population inversion and the optical gain.

The two most likely reasons of the concentration quenching include (1) increase of concentration of quenching centers c with increase of the concentration of the dye molecules n and (2) migration-assisted energy transfer to quenching centers, which accelerates with increase of n . As it has been shown in Ref [4], the rate of the Förster energy transfer in an ensemble of donor and acceptor molecules is inhibited in vicinity of metallic and lamellar metal/dielectric hyperbolic metamaterial substrates. At this time, we study the effect of nonlocal metal-dielectric environments on concentration quenching of luminescence of the 2-[7-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-1,3,5-heptatrienyl]-1,3,3-trimethyl-3H-indolium iodide (HITC) laser dye.

In our experiments, (poly (methyl methacrylate)) (PMMA) films (70 ± 10 nm) doped with different concentration of HITC dye molecules were spin coated on top of (1) thick (290 nm) Ag films, (2) same Ag films with 35 nm MgF₂ layers deposited on top, (3) lamellar Ag (25 nm)/MgF₂ (35 nm) metamaterials with Ag topmost layer and (4) the same metamaterials with MgF₂ topmost layer. The Ag/MgF₂ metamaterial with this filling factor of Au has hyperbolic dispersion at $\lambda = 370$ nm [6]. HITC:PMMA films on the glass substrate were used as the reference samples. The samples were excited with ~ 200 fs pulses of the mode-locked Ti:sapphire laser (at $\lambda = 795$ nm) and the luminescence emission kinetics were detected (at $\lambda > 850$ nm) with the VIS/IR streak camera (80 ps time resolution).

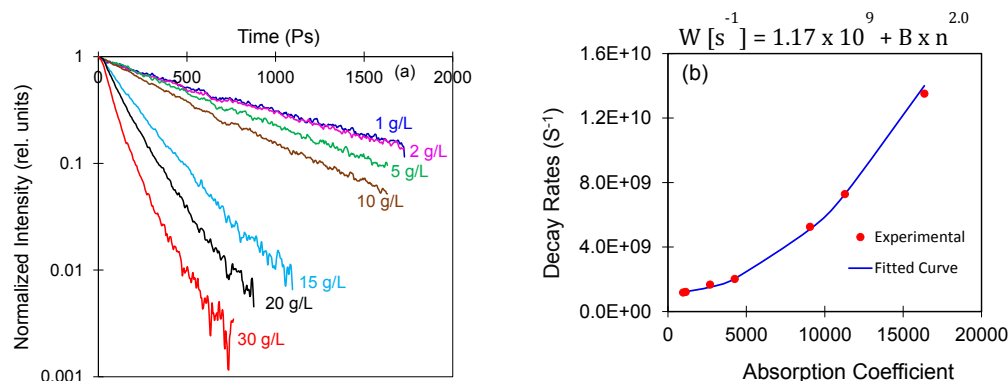


Fig.1. (a) Emission kinetics of HITC: PMMA films at various dye concentrations (in solid state).
(b) Concentration dependence of the decay rates of HITC:PMMA films on glass substrate.

The emission kinetics in HITC:PMMA films deposited on glass (see Fig. 1a) demonstrate strong increase of the luminescence decay rate with increase of the dye concentration (self-quenching). The measured decay rates, plotted as the function of the dye concentration n (Fig. 1b), were fitted with the formula $W = A + Bn^X$, where A is the rate of the (predominantly radiative) emission decay at small dye concentration, X is the coefficient determining the concentration power dependence and B is the scaling factor. The best fit has been obtained at $A = 1.17 \times 10^9 \text{ s}^{-1}$

and $X = 2.0$, suggesting that the rate of quenching is proportional to the dye concentration squared. The later dependence can be expected when (i) quenching centers are pairs of aggregated molecules, $c \propto n^2$, or when (ii) the concentration of the quenching centers is proportional to that of the dye molecules ($c \propto n$), and the rate of migration-assisted energy transfer is also proportional to n .

The HITC:PMMA films deposited on Ag film have demonstrated the concentration quenching as well (see Fig. 2a), with the concentration dependence of the self-quenching rate $\propto n^{2.0}$. However, the emission decay rate at high dye concentration was smaller than that in the films deposited on glass, manifesting inhibition of the self-quenching in vicinity of metal. Qualitatively similar emission behavior has been observed on top of Ag films coated with a thin MgF_2 layer.

In one particular experiment, we studied the dependence of the quenching rate on the thickness d of the MgF_2 spacer separating HITC:PMMA film and Ag. The emission kinetic rate was found to change monotonically with d (reduction of inhibition with increase of the spacer size), with the characteristic length scale of 47 nm. The latter quantity was nearly one order of magnitude larger than the characteristic radius of the Förster energy transfer, 5 - 7 nm, and much smaller than penetration depth of the surface plasmon polariton field to a dielectric, $\sim 250\text{nm}$.

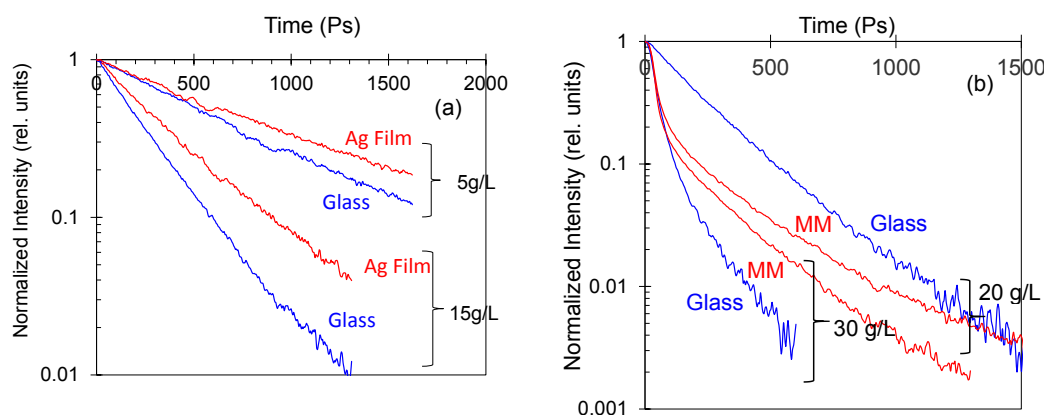


Fig. 2.(a) Emission kinetics of HITC dye on silver and glass substrates at the dye concentrations equal to 5g/L and 15g/L. (b) Emission kinetics of HITC dye on Ag/ MgF_2 metamaterial (with silver on top) at the dye concentrations equal to 20g/L and 30g/L.

The emission kinetics of HITC:PMMA thin film on top of the metamaterial featured characteristic initial drop (Fig. 2b), which we attribute to the Purcell effect, and the broadband singularity of the photonic density of states in hyperbolic metamaterials [6]. Apart of this particularity, the HITC emission kinetics on top of the metamaterial was qualitatively close to that on top of Ag film: the self-quenching of luminescence was inhibited. This behavior was qualitatively the same in the metamaterials samples with Ag on top and MgF_2 on top.

We, thus, have experimentally demonstrated inhibition of luminescence self-quenching in heavily doped HITC:PMMA films in vicinity of metallic surfaces and lamellar metal-dielectric metamaterials with hyperbolic dispersion. This result is in line with our recent study of the donor-acceptor energy transfer involving different molecules [7]. In both cases, characteristic system dimensions (film thicknesses) were much larger than the Förster radius. Therefore, the observed effect cannot be explained in terms of the model involving individual donor and acceptor centers. The adequate description of the systems studied is likely to be sought in terms of the model taking into account coupling of donor and acceptor ensembles to surface plasmons and, through coupling with plasmons, to each other.

The work was supported by the NSF PREM grant DMR-1205457, ARO grant W911NF-14-1-0639 and AFOSR grant FA9550-14-1-0221.

- [1] J. K. Kitur et al., ACS Photonics, **2**, 1019-1024 (2015).
- [2] T. U. Tumkur et al., Appl. Phys. Lett., **99**, 151115 (2011).
- [3] M. A. Noginiv et al., Sci. Reports, **6**, (2016).
- [4] T. U. Tumkur et al., Faraday Discuss., **178**, 395-412 (2015).
- [5] V. N. Peters et al., Sci. Reports, **5**, (2015).
- [6] T. U. Tumkur et al., Appl. Phys. Lett., **117**, 103104 (2015).
- [7] Z. Jacob et al., Appl. Phys. Lett., **100**, 181105 (2012)