Bright magnetic dipole emission in Langmuir-Blodgett monolayers and its control with plasmonics

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ABSTRACT

Monolayers with closely packed molecules of amphiphilic EuTTA deposited on plasmonic metal demonstrate bright luminescence in contrast with diluted systems and theoretical predictions of full quenching. In order to better understand the role of intermolecular interactions and surface plasmons, we study the spontaneous emission in EuTTA ultra-thin films in dielectric and plasmonic environment. The emission kinetics in systems with closely packed emitters strongly differs from that in diluted emitters. The kinetics and spectra are very sensitive to the environment. Using multilayered structures, we were able to enhance the magnetic to electric dipole transition branching ratio by more than order of magnitude.

Keywords: magnetic dipole transitions, plasmonics, rare earth ions, amphiphilic complex, Langmuir-Blodgett technique

1. INTRODUCTION

Optical magnetism, i.e. a strong modification of optical magnetic fields in or in a close vicinity of the structures, is one of the most important new effects associated with specially designed nanostructured systems. This phenomenon practically does not exist in natural materials [1], but can be created artificially with the nanoscale geometry [2] and is responsible for many unusual optical properties predicted and demonstrated in metamaterials and metasurfaces [3,4]. Magnetic dipole emitters provide possibilities to probe modifications of the optical magnetic fields via the magnetic-Purcell factor [5,6]. They also present interest for various applications in nanophotonics as sources of magnetic light [7]. Quantum dots, transition ions, and rare earth ions have magnetic dipole transitions in visible and infra-red [8,9]; however, they are commonly weak. Yet, these materials can show an enhanced magnetic dipole emission when are placed near metamaterials that have been engineered to have a magnetic resonance at optical frequencies. Eu^{3+} is one of the most convenient systems for optical magnetism studies, since it has a relatively strong magnetic dipole transition at visible (590 nm), which is close to the main emission peak at 610 nm corresponding to electric dipole transition [10]. Various methods have been studied to achieve control and enhancement of the magnetic dipole emission, including gold nanoholes, dielectric nanocylinders, SPPs gratings, and cavities [7,11-14]. However, in those experiments, the enhancement of the magnetic dipole emission was not significant. This is because both electric and magnetic dipole transitions occur from the same level, and both electric and magnetic emitter rates are affected by the environment [14].

Surface plasmons are expected to have very strong effect on both electric and magnetic emitters when they are close to the plasmonic structure [12]. Yet at distances closer than 20 nm or less to the metal, the emitters are significantly quenched [15]. Practically no far field emission is expected for dipoles closer than 10 nm to metal [15]. It can be compared with the concept “black hole horizon” in astrophysics meaning that no light can escape to the far field from emitters at this distance from metal or below.

However, it was found that this is not always the case. Recent experiments done with the amphiphilic complex $Eu(TTA)_3(DPT)$, Figure 1 (a), show that a monolayer (~ 4 nm thick) deposited directly on silver or gold demonstrate bright emission comparable with the emission from a monolayer deposited on a glass substrate [16]. This material is highly luminescent, has well resolved distinct peaks with primarily electric and magnetic transitions (Figure 1 (b)), can be excited with UV, and is capable to produce thin films with controllable thicknesses. Since the $Eu(TTA)_3(DPT)$ complex is amphiphilic, it can produce ultra-thin film with Langmuir-Blodgett techniques, where molecules are first spread on the water, then compressed to a well arranged densely packed monolayer, and transferred to a substrate.

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In the current work, in order to better understand the origin of the strongly reduced quenching reported in [16], we study the kinetics of the emission of Eu(TTA)$_3$(DPT), diluted and dense systems. We also explore the possibility to affect the magnetic dipole emission in this material with tri-layer plasmonic cavity structures.

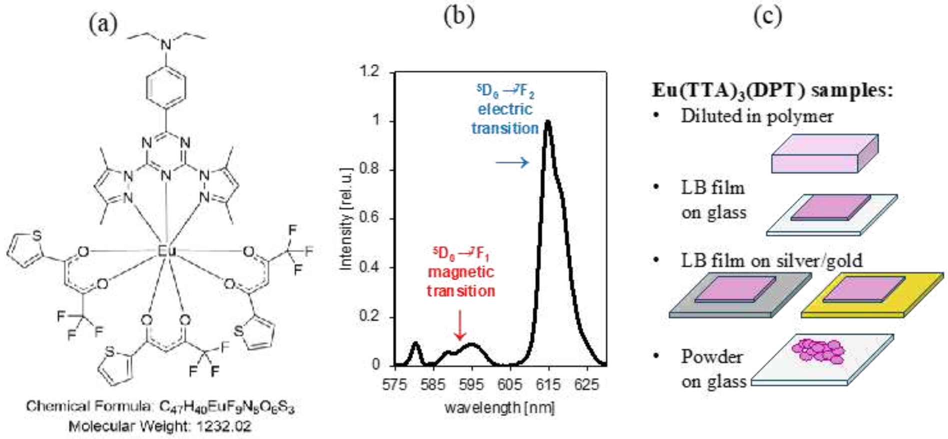

Figure 1. (a) Chemical formula of Eu(TTA)$_3$(DPT); (b) spontaneous emission of Eu(TTA)$_3$(DPT) powder; (c) samples under study.

2. EXPERIMENTAL

The synthesis of the amphiphilic complexes with the trivalent lanthanide ion, $Eu^{3+,}$ was followed adhering to the method used in [16,17]. The samples used in the kinetic studies included: (1) Eu(TTA)$_3$(DPT) diluted in polystyrene (50:50 by weight), (2) films with monolayers of Eu(TTA)$_3$(DPT) deposited on flat glass, gold, and silver substrates using the Langmuir-Blodgett technique, and (3) Eu(TTA)$_3$(DPT) powder. The powder was formed by leaving a drop cast of the solution on a glass slide to dry and then collected by scraping. The samples are illustrated in Figure 1 (c).

Langmuir-Blodgett technique: A solution of the previously prepared Eu(TTA)$_3$(DPT) complex and chloroform were mixed in the proportion 1:3. Small drops of the diluted solution was spread on the water surface. After the evaporation of chloroform, a thin film was formed on the water surface. This process produced films with practically uniform thickness (which was confirmed with the profilometer after transferring the film to a flat surface). To collect a monolayer of film on the substrate, it is immersed in the water and lifted upwards, where the film is transferred to the substrate covering the metal layer. The thickness of the Eu^{3+} complex films was 25 nm for five layers, and about double for ten layers.

Emission kinetics setup: The samples are illuminated with the 3rd harmonics of the Q-switched Nd:YAG laser (λ = 355 nm, pulse duration $\approx$ 5 ns). The emission is recorded with a PMT through an interferometric filter for 610 nm (electric dipole transition) or 590 nm (magnetic dipole transition).

Electromagnetic dipole emission: These spectra are acquired with a spectrofluorometer using a front-face collection arrangement with a 22.5° angle between the input light (excitation) and the collected light (emission). The excitation wavelength is 360 nm, which corresponds to the peak of the excitation band. The spectral data is collected in the range of 570 nm to 630 nm, which encompasses both the magnetic dipole transition and the strongest electric dipole transition.

3. RESULTS AND DISCUSSION

Figure 2 (a) shows the intensity of the emission kinetics vs the response time in semi-log scale. Both magnetic and electric dipole emissions have the same kinetics as expected since the transitions occur from the same energy level. The curve corresponding to the diluted sample is slowest and can be described with a single exponential with a time of 0.43 ms. The kinetics of emission from LB films on glass (in blue) and on silver (in red) are much faster and cannot be described with a single exponent. Overall, the emission kinetics is faster on metal substrates and in closely packed systems. This demonstrates that the emitters "feel" each other confirming the hypothesis of the collective emission [16], which is responsible for reduced quenching.

Since our material does not show significant quenching near metal, we can try to explore the possibility to affect magnetic dipole emission with plasmonic structures. The tri-layer structures (cavities) consist of a thick silver base layer (100 nm), five (or ten) LB layers of Eu(TTA)$_3$(DPT), and a thin layer of silver (20 nm) on top. In Figure 2 (b), we can see there are strong changes in magnetic-to-electric branching ratio and a relative enhancement of the magnetic dipole transition up to the order of magnitude.

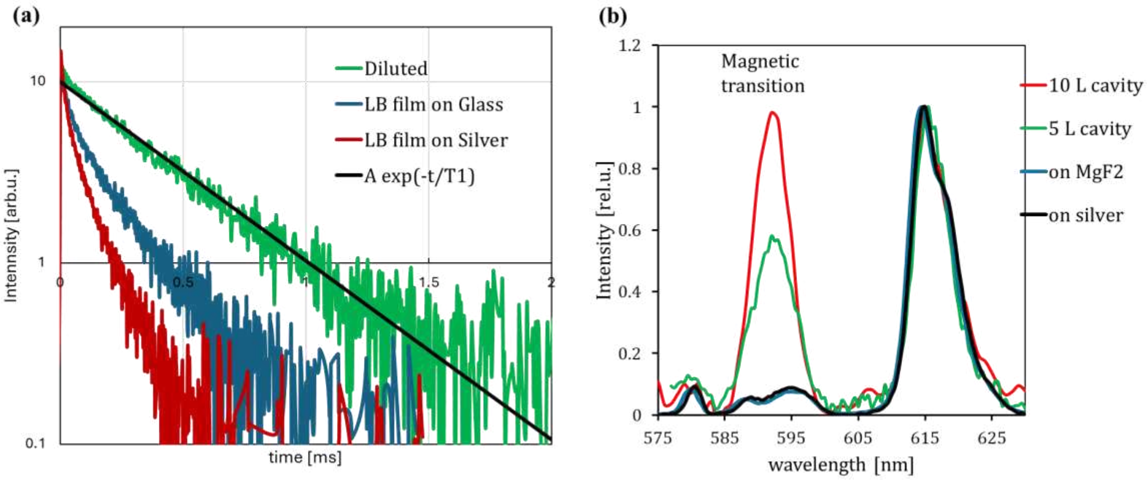

Figure 2: (a) kinetics of Eu(TTA)3(DPT) diluted in polymer and LB films; (b) spontaneous emission of Eu(TTA)3(DPT) LB films on dielectric and in multi-layered cavities.

4. CONCLUSION

We experimentally compare optical behavior of dense and dilute arrangements of electric and magnetic emitters in close vicinity of plasmonic films and cavities. Monolayers of Langmuir Blodgett films of closely packed Eu(TTA)$_3$(DPT) molecules demonstrate reduced quenching in metal in comparison with diluted systems. Emission kinetics in diluted Eu(TTA)3(DPT) is exponential with the time constant of 0.43 ms. Closely packed Eu(TTA)$_3$(DPT) demonstrate faster non-exponential kinetics. Emitters "feel" each other and the presence of metal. Strong modification of emission spectra with the 10-fold relative enhancement of magnetic dipole transition is demonstrated in tri-layered silver-emitting layer-silver structures.

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