Highly luminescent ultra-thin films with rare earth for plasmonic applications

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Abstract: Amphiphilic complexes with luminescent rare earth metal ions suitable for Langmuir-Blodgett (LB) deposition have been synthetized. LB monolayers with closely packed Eu complexes deposited directly on silver demonstrate significant far-field emission in contrast to the theoretical predictions of full quenching. Angular radiation and polarization patterns of the electric and magnetic dipole emission of Eu³⁺ point to a high excitation efficiency of surface plasmon polaritons. Different luminescent behavior of closely packed emitters in comparison to diluted systems is tentatively attributed to the collective state of emitters in LB layers formed via near-field coupling with surface plasmons.

Introduction

Luminescent rare earth metal ions in dielectric matrices find multiple optical applications ranging from light sources and displays to biosensors [1-5]. They present opportunities for fundamental studies as well, where, for example, they can serve as spectroscopic probes for various photonic structures, metamaterials, and systems with optical magnetism [6-11]. The latter application is related to the presence of magnetic dipole transitions in the spontaneous emission spectra of rare earth ions [12-14]. Both electric and magnetic dipole emission can be significantly modified in nanostructured environment [9-11, 15-22] providing opportunity to probe and map local distributions of electric and magnetic optical field components in characterization of nanostructured systems or to create sources with an enhanced magnetic dipole emission for new applications.

 Eu^{3+} ions are among the most convenient systems for optical magnetism studies; they demonstrate a prominent welldefined magnetic dipole emission at ~590 nm (${}^{5}D_{0} - {}^{7}F_{1}$ transition) which is spectrally close to the electric dipole transition at ~ 610 nm (${}^{5}D_{0} - {}^{7}F_{2}$), the strongest in the spectrum [12]. When a material with Eu^{3+} is placed in the vicinity of nanostructured structures designed to have a magnetic resonance at optical frequencies [8,11,21,22], the magnetic dipole emission intensity can be significantly enhanced. Organic systems with Eu^{3+} or other rare earth ions are especially attractive for such studies and applications due to an ease for thin film fabrication and an opportunity of excitation via an organic ligand which absorbs in UV [15,16]. The closer are the emitters to the plasmonic structure, the stronger is the effect of surface plasmons on both electric and magnetic dipole emissions [23], providing better opportunities to tune optical properties with the geometry of the structures. However, at very close distances to metal (20 nm or closer), emitters are strongly quenched due to the excitation of lossy surface waves [24-26]. According to the estimations [26], Eu³⁺ emitters which are closer than 10-12 nm (of optical path) from plasmonic metal are expected to be almost completely quenched (<2 % of the maximum value).

In this work, we develop amphiphilic complexes with rare earth ions, which allow one to use Langmuir Blodgett (LB) technique for fabrication of monolayers or multilayers with dense packing of emitters. We show that in contrast to the theoretical predictions, such ultra-thin films show bright luminescence when directly deposited on metal. A possible hypothesis for reduced quenching is discussed.

Materials and Methods

The amphiphilic complexes R^{3+} (TTA)₃ L, where R is the rare earth metal, are synthetized using the method depicted in Fig. 1. We demonstrate it using two different ions, Europium and Neodymium, and expect that similar complexes with other ions can be fabricated using the same approach.

Step A. Synthesis of 4-(4,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl)-N,N-diethylaniline (L), following Ref.[16]. Potassium (0.08g, 2.07 mmol) is added to a stirred solution of 3,5- dimethyl pyrazole (0.288 g, 3.0 mmol) in dry tetrahydrofuran (THF) under N₂ at 70^o C. After the metal dissolves, the obtained colorless solution is cooled to 10° C. N,N-diethyl-4-(dichloro-1,3,5-triazinyl)aniline (1.0 mmol, 0.297 g) is added. The reaction mixture is stirred at room temperature for 0.5 hour, and then refluxed for 5 hours. Most of the solvent is then evaporated under reduced pressure. The residue is columned on the silica gel using a mixture of petroleum and benzene as the eluent. Yield is 0.36 g (86%) and the Melting point (M.p.) is 235-236 °C.

Step B. Synthesis of Eu (TTA)₃L and Nd (TTA)₃L. A solution of Eu(TTA)₃·3H₂O (87 mg, 0.1 mmol) in THF (10 mL) is added to a solution of the material L produced in the Step A (41.6 mg, 0.1 mmol) in THF (10 mL), resulting instantaneously in a yellow solution with very bright red luminescence under daylight. After evaporation of the solvent, the residue is redissolved in a small amount of diethyl ether. Addition of *n*-hexane to the ether solution precipitates the ternary complex of Eu(TTA)₃L as an orange powder. Yield: ~68%. M.p. 138-139 °C. Neodymium complex Nd(TTA)₃L is prepared following the similar procedure by the reaction of L and tris(2-thenoyltrifluoroacetonate)Neodymium(III) at room temperature.



Fig. 1: Synthesis of Eu amphiphilic complex. Arrows show addition of Potassium 3,5-dimethylpyrazolate (a) and Eu(TTA)₃·3H₂O (b).

The produced complexes are amphiphilic and suitable for Langmuir-Blodgett (LB) deposition. Chloroform solution of the complex is spread on the top of water in the LB trough and left for a few minutes to allow the solvent to evaporate. Then the barriers are slowly moved toward each other, compressing the surface layer. Fig. 2 (a) shows the isotherm for Nd complex; similar isotherms are observed in the complex with Eu ions. A sharp increase of the surface pressure upon the decreasing area manifests the formation of a monolayer with well-oriented and densely packed molecules [27]. Note that working with the Eu complex one can easily observe the film formation and check its quality by illuminating the surface with UV light; even a monolayer film on the surface of water is brightly luminescent (red). The deposition of the compressed film on a substrate can be performed using Langmuir-Schaefer (LS) method, by immersing the substrate from air to water or from water to air. This method yields films with better homogeneity and covering than using a standard vertical dipper, particularly, in multilayer deposition.



Fig. 2. (a) Pressure-area isotherm of Nd (TTA)₃L complex. (b-d) Schematics of the samples with Eu complex used in optical studies.

For our optical studies, we prepare several samples with monolayers or multilayers of Eu complex, Fig. 2 (b-d). The substrates include glass, silver flat surfaces and grating structures, produced from the commercial DVD discs. Fabrication of DVD-based substrates and plasmonic properties of DVD-based structures are discussed in [28]. The derived polycarbonate substrates have approximately square-wave profile modulation with the modulation period of 740 and modulation height of 100-120 nm. Silver with the thickness of 150 nm is deposited onto the substrates with the thermal deposition method. Thickness of obtained films on flat substrates is checked with the profilometer. Since films on both DVD and flat substrates are deposited simultaneously, we assume that the thickness of deposited metal is the same. Layers of the Eu complex are deposited by immersing of the substrate horizontally from air to water. One sample is specially prepared for the comparison of luminescent properties of monolayers deposited on silver and glass. First, silver is deposited on the half of a glass slide. Then, a monolayer of Eu complex is transferred from the water surface to glass and silver simultaneously at the same deposition process, ensuring the same quality of the film on glass and silver, Fig. 2 (c).

Results

First, the fabricated samples are visually inspected using illumination with UV lamp (l = 250-365 nm). Films on silver show red emission with the brightness comparable (or even higher, depending on the incidence angle) to that in films on glass. For a quantitative assessment, we use the half glass - half silver sample, Fig. 2 (c), with a monolayer film, and record the spontaneous emission spectra with the spectrofluorometer separately from the silver half and glass half of the sample. The excitation wavelength is 360 nm, which corresponds to the excitation of the complex via ligand [16]. The collection angle, θ , is 25 deg. Special care is taken to ensure that the illuminated area of the sample is placed exactly at the same position and orientation for both tests.

The spectra recorded in the range of 570-630 nm are shown in Fig. 3 (a). The peaks correspond to the purely electric dipole transition ${}^{5}D_{0} - {}^{7}F_{0}$ at 580 nm, primarily magnetic dipole transition ${}^{5}D_{0} - {}^{7}F_{1}$ around 590 nm, and primarily electric dipole transition ${}^{5}D_{0} - {}^{7}F_{1}$ around 590 nm, and primarily electric dipole transition ${}^{5}D_{0} - {}^{7}F_{2}$ at ~ 613 nm (the strongest in the spectrum). As one can see, the emission intensities from glass and silver are comparable to each other with a different branching ratio of magnetic dipole (MD) and electric dipole (ED) transitions. Comparing the MD peak at 590 nm and ED peak at 613 nm, the ratio of the peak magnitudes, $I_{MD} / I_{ED} = 0.18$ and 0.09 in silver and glass samples, correspondingly. We should note that the excitation intensity can be different in silver and glass samples due to different refractive indices of the substrates. Another factor which should be considered that emitters on silver radiate only into the half of space, that is not the case for emitters on glass. However, from this measurement and our visual observations, it becomes clear that there is no significant quenching of emitters deposited directly on silver, contrary to the expectations.



Fig. 3. (a) Emission spectra of Eu^{3+} in a monolayer on silver and glass (as indicated); (b) sample orientation in the spectrophotometer; (c) typical spectra obtained in s and p-polarization; (d-f) the p-to-s peak ratio vs angle for ED (blue symbols) and MD (red symbols) emissions in a monolayer on (points) in (d) monolayer on flat silver, (e) three layers on flat silver and (f) three layers on the silver gratings. Green dashed line shows the results from a monolayer in glass.

Films deposited on silver demonstrate significantly different angular and polarization patterns than films on glass substrates. Under the UV lamp, films on silver show a significant p-polarized emission at large angle. For the quantitative assessment, we use the spectrofluorometer and record the emission spectra at p- and s-polarizations in our samples. The ratio of the p-polarized to s-polarized peak intensities at MD and ED transitions is plotted as the function of the observation angle in Figs. 3 (d-e). As one can see, the emission is predominantly p-polarized at large angles. This is especially true in monolayers, where the ratio of p- to s-polarized intensities reaches 14, Fig. 3 (d). The p-to-s ratio is lower for MD transition but still shows a significant increase upon increasing angle. Practically no difference between the two polarizations is observed in the monolayer film on a glass substrate. In the three-layer film on flat silver, both MD and ED transitions show growth of p-to-s ratio with the increase in the angle, however, to a smaller extent than in the monolayer, Fig, 3 (e). Strongly p-polarized emission observed at large angles can be indicative of surface plasmons which are excited by the emitters and then decouple due to a surface roughness. The film on a grating structure (Fig. 2 (d)) provides the opportunity to probe the presence of surface plasmon polaritons (SPPs), since SPPs are decoupled contributing to the p-polarized emission at a certain angle determined by the period of the gratings. Indeed, the grating sample shows a well-defined peak in the angular dependence of p-to-s ratio, which is observed in both ED and MD emission around 24 deg, see Fig. 3 (f).

The spectrophotometer setup (Fig 3 (b)), where the orientation of the sample is varied, is not optimal for measuring the radiation pattern of the emission since the area of the excitation spot, and correspondingly, the intensity of the excitation vary with the rotation of the sample. In the next experiment, Fig 4 (a), a three-layer film deposited on the grating structure is placed on the stage with grooves oriented vertically and illuminated with the HeCd laser at l=325 nm. The orientation of the sample does not change in the experiment. The intensity of the emission is collected with the photomultiplier at horizontal (p) and vertical (s) polarization separately as the function of the angle θ , Fig 4 (a).



Fig. 4. Radiation pattern measurements. (a) Setup, (b) Intensity at p- and s-polarization (symbols) as indicated. The dashed lines are guide for eyes.

The results are shown in Fig.4 (b). The radiation pattern recorded at p-polarization shows significant peak around 22 deg, while s-polarization monotonously decreases with the increase in the angle approximately following $cos^2\theta$ dependence. Note, that in this experiment, we measure the total emission. However, as follows from Figs. 3(e, f), in three-layer structures both MD and ED emissions show similar p-to-s ratio.

Discussion

Bright luminescence observed from monolayer films deposited directly on silver is a surprising finding. The thickness of such a film can be estimated as 3 - 4 nm. However, emitters located closer than 10 nm from the metal are expected to be strongly quenched due to near-field excitation of high-*k* plasmonic modes. Emission near flat surface can be estimated in frames of the dyadic Green's function approach [29], considering photonic fields as functions of in-plane component of the optical wave-vector, k_x ($0 < k_x < \infty$). The power emitted by an individual electric or magnetic dipole into the photonic modes in the range between k_x and k_x+dk can be found as

$$dP_e = \frac{ck_0}{2} Re \left\{ \frac{k_x}{k_z} \left[\frac{p_{\parallel}^2}{2} \left[k_z^2 (1 - R_p e^{2ik_z h}) + k_0^2 (1 + R_s e^{2ik_z h}) \right] + p_{\perp}^2 k_x^2 (1 + R_p e^{2ik_z h}) \right] \right\} dk_x,$$
(1)

$$dP_m = \frac{ck_0}{2} Re \left\{ \frac{k_x}{k_z} \left[\frac{m_{\parallel}^2}{2} \left[k_z^2 (1 - R_s e^{2ik_z h}) + k_0^2 (1 + R_p e^{2ik_z h}) \right] + m_{\perp}^2 k_x^2 (1 + R_s e^{2ik_z h}) \right] \right\} dk_x.$$
(2)

where integration over k_x gives the total power emitted by the emitter. Here k_0 is the photon k-vector, h is the distance between an emitter and metal, \mathbf{p} and \mathbf{m} are correspondingly electric and magnetic dipole moments and subscripts // and \perp correspond to the parallel and perpendicular orientation v_s the plane interface. R_p and R_s are Fresnel coefficients for p- and s-polarizations respectively, and z-axis is normal to the interface. Modes with $k_x < k_0$ are propagating modes and contribute to far field emission while modes with higher k_x are not radiative. Calculations made in [26] show that for flat metal, the ratio of the far-field radiated power to the total power for the electric dipoles is close to zero at the distances <10 nm for thick metal. Quenching is even stronger for thin metal films. Note that in Eu³⁺ both electric and magnetic emission is originated from the same energy state. Thus, magnetic emission is expected to be fully quenched as well.

Note that in our LB films, we have emitters closely packed to each other. One can hypothesize that a dense arrangement of emitters results in different near fields in comparison with widely spaced individual emitters and may lead to a different excitation probability of high-k modes. For simplicity let us consider only electric dipoles of a certain orientation and describe the emitting surface in terms of dipole density π , which corresponds to a single dipole **p** spread over area da=dxdy; $p = \pi dxdy$. Taking into account the emitting surface and its image, the potential reads

$$V = -\int \frac{4\pi i}{k^2} (\mathbf{k} \cdot \mathbf{p}) e^{i\mathbf{k}\mathbf{r}} \{ e^{-ik_z h} + \alpha e^{ik_z h} \} \frac{d^3 k}{(2\pi)^3} , \qquad (3)$$

where $\alpha = (1 - \varepsilon_m)/(1 + \varepsilon_m)$ is the magnitude of the image dipole and ε_m is the permittivity of metal. Since emitters are not emitting in phase, let us consider a dipole density wave with the wave-vector $\mathbf{q} = (q_x, q_y) \ \boldsymbol{\pi}(\mathbf{r}') = \boldsymbol{\pi}_0 e^{iq_x x'} e^{iq_y y'}$. Substituting this expression into Eq. 3,

$$V = -\int \frac{d^3k}{(2\pi)^3} \frac{4\pi i}{k^2} (\mathbf{k} \cdot \mathbf{\pi_0}) e^{i\mathbf{k}\mathbf{r}} (2\pi)^2 \,\delta(k_x - q_x) \delta(k_y - q_y) \{ e^{-ik_z h} + \alpha e^{ik_z h} \},\tag{4}$$

$$V = -e^{-iq_x x} e^{iq_y y} \int \frac{dk_z}{2\pi} \frac{4\pi i}{q_x^2 + q_y^2 + k_z^2} (\boldsymbol{q} \cdot \boldsymbol{\pi}_0 + k_z \cdot \pi_{0z}) e^{ik_z z} \{ e^{-ik_z h} + \alpha e^{ik_z h} \}.$$
(5)

Eq. 5 means that each plane wave in the emitted far-field corresponds to a wave of dipole density oscillations in the dipole arrays. Full absence of quenching would mean that there are no high-k oscillations in the emitting plane. A reduced quenching as in our case may indicate a certain degree of coherence between emitting dipoles. For large number of emitters oscillating in phase, the near field distribution is considerably more uniform than that for an individual emitter due to the cancellation of high momentum harmonics. This results in a suppression of energy transfer from emitters to plasmonic excitations with high k-vectors, and correspondingly, a reduced quenching.

On the other hand, our experiments point to the efficient excitation of surface plasmon polaritons, which are decoupled at the certain angle in grating structures. In periodic DVD-based structures having modulation period, d, of 740 nm, the decoupling is expected at [30]

$$k_{spp} = k_0 \sin \theta + \frac{2\pi}{d},\tag{6}$$

where θ_{spp} is the resonance angle, k_{spp} is the SPP wave-vector determined by the permittivity of metal, ε_m , and dielectric, ε_d , as

$$k_{spp}/k_0 = \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \ . \tag{7}$$

For a rough estimate, let us assume the wavelength $\lambda = 600$ nm (between MD and ED peaks), $\varepsilon_d = 1$ and the permittivity of silver, $\varepsilon_m = -16$. Estimations show that $\theta_{spp} = 22$ deg at $\varepsilon_d = 1.3$. This is consistent with the fact that the dielectric film is very thin and the effective permittivity of it is closer to that in air than in organic material.

Note that in our DVD-based gratings, the efficiency of SPPs coupling to far-field is not expected to be optimal due to a strong profile-modulation of the structure [28]. Nevertheless, the SPP-related emission peak at 22 deg, Fig. 4 (b), is very prominent in comparison to the non-SPP related emission. It is much higher than the SPP-related peak observed in a similar experiment [23] with 60 nm thick films having Eu^{3+} emitters diluted in polyvinylpyrrolidone (PVP) matrices. In the experiment of Ref. [23] the p-to-s ratio was only ~ 1.8 at the SPP resonance angle. In our samples, the ratio is higher than 5. Thus, densely packed emitters in our ultra-thin films deposited directly on metal efficiently emit to far-field and propagating surface plasmons. However, they do not efficiently excite lossy plasmonic modes with high k-vectors, which is expected from individual emitters at such close distances.

A possible explanation of such a behavior can be the emergence of a collective state due to emitters' coupling to the SPP, as indicated by the large p-to-s polarization ratio of the emitted light. An analogous phenomenon was reported in modeling of emitters distributed on top of a metal nanoparticle supporting localized surface plasmons [31]: At a close distance to the nanoparticle surface, the radiation of an individual emitter resonantly coupled to the dipole plasmon is strongly quenched due to excitation of off-resonance plasmons with high angular momenta l. However, for large number of emitters oscillating coherently, as they form a collective state via near-field coupling with the dipole plasmon, the quenching due to excitation of high-k plasmons is suppressed due to much weaker field variation as compared to that of individual emitters [31]. Long range cooperative behavior of emitters has been recently reported [32] in micro-ring resonators as well, leading to modification in the emission pattern and kinetics.

At the current stage we could not exclude other mechanisms for reduced quenching such as cooperative behavior via dipole-dipole interactions and coupling with nano-size features [33-36] associated with metal roughness. Nano-size features can also serve as scattering centers for plasmonic modes contributing the far-field radiation. In order to fully explain this

interesting result, more theoretical and experimental studies are needed including kinetics measurements and experiments with partially diluted systems, structures with intermediate dielectric layers, and structures with nanopatterns of a luminescent layer. This will be a subject of further study.

In conclusion, the amphiphilic complexes with luminescent rare earth ions are synthetized and shown to be suitable for Langmuir-Blodgett deposition, which produces closely packed assembles of luminescent molecules. Anomalously strong spontaneous emission and seemingly weak luminescence quenching in vicinity of metal are among the central results of this study. As it was discussed above, one possible reason for the disagreement between the experiment and the theoretically predicted low quantum yield of emission is the discussed above collective behavior of Eu³⁺ emitters in the LB film mediated by SPP. Alternative mechanisms can involve nano-size features due to film roughness serving as nanoantennas or scattering centers for plasmonic modes. The thorough study of this phenomenon is the subject of the future study to be published elsewhere. We believe that such highly luminescent films with densely packed emitters can find various applications in nanophotonics and plasmonics.

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Disclosures

The authors declare no conflict of interest.

Data availability

Data supporting the results presented in this paper can be obtained from the authors upon reasonable request.

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