Published in final edited form as:

Chem Commun (Camb). 2014 August 18; 50(64): 9010–9013. doi:10.1039/c4cc03633f.

Surface-Plasmon Induced Polarized Emission from Eu(III) – A Class of Luminescent Lanthanide Ions

Sharmistha Dutta Choudhury^a, Ramachandram Badugu^b, Krishanu Ray^b, and Joseph R. Lakowicz^b

Sharmistha Dutta Choudhury: sharmidc@barc.gov.in; Joseph R. Lakowicz: jlakowicz@umaryland.edu

^aRadiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India.
Fax: 91 2225505151; Tel: 91 22 25590296

^bCenter for Fluorescence Spectroscopy, Department of Biochemistry and Molecular Biology, University of Maryland Baltimore, 725 West Lombard Street, Baltimore, Maryland 21201, USA.
Fax: 410 706 8408; Tel: 410 706 8409

Abstract

The intrinsically unpolarized emission from luminescent Eu(III) ions is transformed to wavelength-resolved and sharply directional polarized emission by coupling with plasmonic and photonic modes present in metal-dielectric layered substrates. This nanoscale control over lanthanide luminescence can facilitate the design of novel emissive structures with potential technological applications.

Lanthanide ions possess unique optical properties that have led to development of novel luminescent probes, tags and smart photonic materials.¹ The most prominent attributes of luminescent lanthanide ions (Ln(III)) that make them suitable for many applications are; the large Stokes' shifts, the multiple narrow emission lines and the long emission lifetimes.¹ Further, unlike organic fluorophores, the emission from lanthanide ions results from high-spin to high-spin transitions involving multiple transition dipole moments. The combination of the many energetically degenerate transitions that have similar transition probabilities but differently oriented dipole moments, often leads to unpolarized emission from the lanthanides.^{1,2}

The intrinsically unpolarized luminescence of lanthanides is useful in resonance energy transfer studies to measure conformations of biomolecules without concern for the orientation dependence. However, polarized emission from lanthanides could be valuable for many other applications such as, measuring rotational motions in the millisecond time scale or improving the performance of optical displays, polarized LEDs and optoelectronic devices.³ Controllable, polarized emission is important for future advanced emissive devices, and lanthanide based materials are expected to be especially significant because their unique optical characteristics can provide high efficiency, photostability and good monochromatic properties.

Correspondence to: Sharmistha Dutta Choudhury, sharmidc@barc.gov.in; Joseph R. Lakowicz, jlakowicz@umaryland.edu.

Most of the earlier efforts to obtain polarized emission from lanthanides are based on specially synthesised, oriented molecular systems.⁴ In recent years, plasmonics has provided us with alternative methodologies for controlling light emission in ways that are fundamentally different from conventional approaches.⁵ The ability of surface-plasmons to engineer radiative properties of an emitter placed in close vicinity of metallic nano-substrates is being increasingly exploited for developing new nanophotonic systems for concentrating and delivering light.⁶ These effects are based on the near-field coupling of emission with surface-plasmon oscillations in metal nanostructures, and can provide significant improvements in the emission intensities, reduced emission lifetimes and/or directional and polarized emission.^{5,7} This offers interesting new prospects for technological applications, sensing, bio-assays or diagnostics. Not surprisingly, metallic nanostructures are also being investigated for improving the emission of luminescent lanthanides.⁸ This Communication describes the transformation of the intrinsically unpolarized emission from luminescent Eu(III) ions to wavelength-resolved and sharply directional polarized emission by coupling with the propagating surface-plasmon oscillations in metal-dielectric layered substrates. Basic principles of this phenomenon and substrate parameters that determine and endow specific and controllable polarization to luminescent lanthanide ions are discussed, to facilitate design of emissive structures with desired polarization functionalities.

Metal-dielectric substrates were prepared by thermal vapour deposition of silver on glass slides (Ag film ~50 nm) followed by spin coating an aqueous solution of poly(vinyl alcohol) (PVA) containing europium(III)acetate. Weight percentages of PVA were varied to obtain desired thickness of the dielectric layer (details in ESI[†]). The Ag-PVA substrates were illuminated in the Reverse Kretschmann (RK) configuration with light from a 375 nm laser source incident normally on the PVA layer, containing europium(III) acetate (Fig. 1). The emission from Eu(III) was collected on the glass side at different angles and was monitored through a compact fiber optic spectrometer (ESI[†]).

The emission spectrum of europium(III) acetate in aqueous PVA solution (1% PVA), shows three sharp bands corresponding to $^5D_0 \rightarrow ^7F_1$ (590 nm), $^5D_0 \rightarrow ^7F_2$ (615 nm) and $^5D_0 \rightarrow ^7F_4$ (695 nm) transitions of Eu(III) (Fig. S2, ESI[†]).¹ To understand the emission properties of Eu(III) embedded in metal-dielectric substrates, control experiments were first carried out by spin coating the aqueous PVA solution (1% PVA) of europium(III) acetate on a bare glass slide without any Ag film, to obtain ~50 nm PVA layer containing the luminescent Eu(III) ions. Although the characteristic emission bands of Eu(III) are clearly observed with this substrate, the emission is no longer isotropic as in homogeneous medium. It is known that excited fluorophores, which are in close proximity to the interface between two dielectric media, emit a large proportion of their radiation into the environment with higher index of refraction. In the present case, due to discontinuity of refractive indices (n) at the glass(PVA)/air interface ($n_{\text{glass}} = n_{\text{PVA}} \sim 1.52$), the emission is preferentially directed toward glass and a significant portion of emission occurs above the critical angle of the interface, leading to characteristic angular emission patterns, as described in the literature.⁹ Representative emission spectra (collected on the glass side, as indicated in Fig.1) and

[†]Electronic Supplementary Information (ESI) available: [Substrate preparation, experimental methods]. See DOI: 10.1039/b000000x/

angular distribution of emission at 590, 615 and 695 nm (three bands of Eu(III)), are depicted in Fig. 2. For clarity of presentation of the angular emission patterns, the maximum intensities of all three bands have been normalized to unity. This experiment shows that the three emission wavelengths have similar angular emission patterns. Furthermore, the Spolarized emission (emission polarizer oriented vertically) and the P-polarized emission (emission polarizer oriented horizontally) are comparable and have nearly identical angular distributions. This clearly indicates that emission from Eu(III) is unpolarized, as typically expected for most lanthanides.

A remarkably different effect is observed when the above PVA solution of europium(III) acetate is spin coated on a glass slide covered with 50 nm Ag film (Ag-PVA). Interestingly, the emission pattern of Eu(III) on this substrate is strongly dependent on the observation angle. Each of the three emission bands appears to be most intense in a specific direction, leading to wavelength dependent angular distribution patterns. For example, the emission intensity at 590 nm is largest at 53° (also at 307° due to symmetry) and falls away rapidly at other observation angles. Similarly, the intensity at 615 nm is largest at 52° (and 308°) and the intensity at 695 nm is largest at 49° (and 311°). Most importantly, all the emissions are completely P-polarized. Representative emission spectra and polarization-resolved, angular emission patterns for Eu(III), are shown in Fig. 3.

These exciting observations can be interpreted from the principles of surface-plasmon coupled emission (SPCE), as explained below in the context of the present system.¹⁰ SPCE involves two effects. First, the emission arising from Eu(III) excites propagating surface-plasmons in the Ag-PVA substrate by near-field coupling. Interestingly, this coupling takes place irrespective of the fact that the effective emission of Eu(III) is unpolarized. The activated surface-plasmons then radiate into the substrate with their own characteristic properties, determined by the surface-plasmon resonance conditions, which depend on the emission wavelength and geometry of the substrate. This is equivalent to the leakage radiation (LR) that is emitted into the higher refractive index medium (glass substrate) when surface-plasmon polariton fields propagating along the metal-air interface leak through the metal film and reach the substrate. The LR is emitted in a narrow range around a characteristic angle with respect to the interface normal.¹¹ Therefore, although the emission originates from Eu(III), observed dispersion and polarization properties are those of the surface-plasmons. Since coupling between surface-plasmons and light of a particular wavelength can take place only at a specific angle at the glass/metal interface, each of the three emission bands of Eu(III) appears to be most intense at a certain angle. Similarly, since wavevector matching conditions require the radiating surface-plasmons to be P-polarized, the emission from Eu(III) appears to be completely P-polarized. Surface-plasmon mediated polarization of Eu(III) luminescence is further substantiated from reflectivity simulations for the Ag-PVA substrate. Angle-dependent reflectivity curves for S- and P-polarized light of wavelengths, 590 nm, 615 nm and 695 nm (corresponding to the emission bands of Eu(III)), have been calculated on the basis of the transfer matrix formalism using TF Calc software (ESI[†]). Simulated angle dependent reflectivity plots are presented in Fig.3 along with the emission spectra and angular distribution patterns, for easier comparison.

For an Ag-PVA substrate with 50 nm PVA, calculations show that S-polarized light of wavelengths, 590, 615 or 695 nm, is completely reflected back from the substrate at all incidence angles. On the other hand, for P-polarized light, dips in the reflectivity are observed at specific angles ($\theta_{sp,\lambda}$) depending on wavelength, λ . For instance, the reflectivity dip for P-polarized light of wavelength 590 nm occurs at 54°(and 306°), the reflectivity dip for 615 nm occurs at 52°(and 308°) and the reflectivity dip for 695 nm occurs at 48°(and 312°). These dips arise because P-polarized light of these wavelengths can excite propagating surface plasmons in the Ag-PVA substrate, when the incidence angle matches the surface-plasmon resonance angle ($\theta_{sp,\lambda}$).¹⁰ Close agreement of the reflectivity simulations with experimentally measured polarization and angular emission patterns, confirms that polarized emission from Eu(III) is induced by the propagating surface-plasmon mode in Ag-PVA substrate.

Metal-dielectric substrates with thick dielectric layers can support multiple photonic modes in the dielectric layer, in addition to the existing surface-plasmon mode.¹⁰ Considering that the unpolarized lanthanide luminescence can be converted to completely P-polarized luminescence by the surface-plasmons in a simple metal-dielectric substrate, we investigated the possibility of selective and independent polarization tuning of the three bands of Eu(III) by coupling with multiple modes present in Ag-PVA substrates with thicker PVA layers. The emission spectral features and polarization characteristics of Eu(III) in representative metal-dielectric substrates, differing in thickness of the PVA layer above the Ag film, are presented in Fig. 3.

When the PVA thickness is increased from 50 nm to ~95 nm, the angular emission patterns of Eu(III) are observed to be different. Nevertheless, the emissions at all three wavelengths are completely P-polarized, as in the case of the Ag-PVA substrate with 50 nm PVA layer. With further increase in the PVA thickness (~125 nm), the polarization property of Eu(III) emission turns out to be quite intriguing. Each of the emission bands carries distinctive polarization characteristics, depending on the wavelength. More specifically, the 590 nm emission band is completely S-polarized and is observed to have the largest intensity at an angle of 44° (and 316°). The emission band at 695 nm is completely P-polarized and has the largest intensity at an angle of 72° (and 288°). On the other hand, the emission band at 615 nm has both S- and P-polarized components that appear at different observation angles. At higher PVA thickness (~300 nm), all three emission bands of Eu(III) exhibit polarized emission, having both S- and P-polarized components, that appear in different directions.

In all Ag-PVA substrates considered above, the experimentally observed polarization matches with the reflectivity simulations, for the corresponding PVA thickness. It appears as if the emission from Eu(III) senses the electromagnetic modes present in the respective metal-dielectric substrate, and gets modified accordingly by the characteristics of these modes. To illustrate this point, the polarization properties of electromagnetic modes of wavelengths 590 nm, 615 nm and 695 nm (corresponding to the emission bands of Eu(III)), that exist in the Ag-PVA substrates having different PVA thickness are collectively presented in Fig. 4. This figure summarizes data obtained from several reflectivity simulations. For simplicity, calculations for only one half-space on the glass side, (i.e. 0° to

90°) are depicted. Experimentally observed results are superimposed on the calculated graph to reinforce the excellent agreement between theory and experiment.

Fig. 4 shows the various electromagnetic modes that are available for coupling with the three emission wavelengths of Eu(III), in Ag-PVA substrates with different PVA thicknesses. At a PVA thickness of 50 nm (or 95 nm), the only available mode that can couple with all the three emission wavelengths is the P-polarized surface-plasmon mode. This results in P-polarized emission from Eu(III). However, at a PVA thickness of 125 nm, an interesting situation prevails. In this substrate, both P-polarized surface-plasmon mode as well as S-polarized photonic mode is available to interact with the 615 nm emission. However, only the S-polarized photonic mode is available for coupling with the 590 nm emission and only the P-polarized surface-plasmon mode is available for coupling with the 695 nm emission of Eu(III). At higher PVA thickness (300 nm), the P- and S-polarized photonic modes become available for coupling with all the three emission wavelengths of Eu(III). The ultimate outcome of the near-field coupling with various electromagnetic modes present in Ag-PVA substrates, is the creation of selective, polarized and directional emission for each band of Eu(III).

These results demonstrate the ease with which the unpolarized emission from Eu(III) can be converted to controllable polarized emission using simple metal-dielectric layered substrates. This approach has several advantages: it is very general and will be applicable for any luminescent lanthanide; substrates can be fabricated easily and readily adapted for use in device formats; substrate dimensions can be selected from reflectivity simulations to obtain desired emissive structures. Typically, SPCE does not lead to significant changes in the emission intensities or lifetimes. However, the unique features of high directionality and the ability to transform the unpolarized emission from lanthanide ions to wavelength-resolved polarized emission, makes it an attractive phenomenon with many potential applications. We believe plasmonic-photonic hybrid metal-dielectric layered structures will be important in the next generation of devices and will offer a range of opportunities for control of luminescence at nanoscale dimensions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by NIH grants HG002655, AI087968 and EB006521. SDC acknowledges Indo-US Science and Technology Forum for IUSSTF Fellowship.

Notes and references

1. Bünzli J-CG, Eliseeva SV. Chem Sci. 2013; 4:1939. Bünzli J-CG, Piguet C. Chem Soc Rev. 2005; 34:1048. [PubMed: 16284671] Heffern MC, Matosziuk LM, Meade TJ. Chem Rev. 2014; 114:1021/cr400477t Richardson FS. Chem Rev. 1982; 82:541.
2. Reifengerger JG, Snyder GE, Baym G, Selvin PR. J Phys Chem B. 2003; 107:12862.

3. Gao R, Lei X, Chen M, Yan D, Wei M. *New J Chem*. 2013; 37:4110. Matioli E, Brinkley S, Kelchner KM, Hu Y-L, Nakamura S, DenBaars S, Speck J, Weisbuch C. *Light: Science & Applications*. 2012; 1:e22.
4. Galyametdinov YG, Knyazev AA, Dzhabarov VI, Cardinaels T, Driesen K, Görrler-Walrand C, Binnemans K. *Adv Mater*. 2008; 20:252. Driesen K, Vaes C, Cardinaels T, Goossens K, Görrler-Walrand C, Binnemans K. *J Phys Chem B*. 2009; 113:10575. [PubMed: 19601595] Yang CY, Srdanov V, Robinson MR, Bazan GC, Heeger AJ. *Adv Mater*. 2002; 14:980. Wu S, Yu X, Huang J, Shen J, Yan Q, Wang X, Wu W, Luo Y, Wang K, Zhang Q. *J Mater Chem*. 2008; 18:3223.
5. Lakowicz JR, Ray K, Chowdhury M, Szmajcinski H, Fu Y, Zhang J, Nowaczyk K. *Analyst*. 2008; 133:1308. [PubMed: 18810279] Cao S, Cai W, Liu Q, Xie K, Weng Y, Li Y. *Chem Commun*. 2014; 50:518. Liu J, Li A, Tanq J, Wang R, Kong N, Davis TP. *Chem Commun*. 2012; 48:4680.
6. Schuller JA, Barnard ES, Cai W, Jun YC, White JS, Brongersma ML. *Nature Materials*. 2010; 9:193. [PubMed: 20168343] Dutta Choudhury S, Badugu R, Nowaczyk K, Ray K, Lakowicz JR. *J Phys Chem Lett*. 2013; 4:227. [PubMed: 24013521]
7. Ming T, Zhao L, Chen H, Woo KC, Wang J, Lin H. *Nano Lett*. 2011; 11:2296. [PubMed: 21568320] Ming T, Chen H, Jiang R, Li Q, Wang J. *J Phys Chem Lett*. 2012; 3:191. Tam F, Goodrich GP, Johnson BR, Halas N. *Nano Lett*. 2007; 7:496. [PubMed: 17256995]
8. Zhang J, Fu Y, Lakowicz JR. *J Phys Chem C*. 2009; 113:19404. Deng W, Jin D, Drozdowicz-Tomsia K, Yuan J, Wu J, Goldys EM. *Adv Mater*. 2011; 23:4649. [PubMed: 21913234] Dolgov L, Kiisk V, Matt R, Pikker S, Sildos I. *Appl Phys B*. 2012; 107:749. Buch Z, Kumar V, Mamgain H, Chawla S. *Chem Commun*. 2013; 49:9485. Zhang J, Fu Y, Ray K, Wang Y, Lakowicz JR. *J Phys Chem C*. 2013; 117:9372.
9. Enderlein J, Ruckstuhl T. *Optics Express*. 2005; 13:8855. [PubMed: 19498918]
10. Gryczynski I, Malicka J, Nowaczyk K, Gryczynski Z, Lakowicz JR. *J Phys Chem B*. 2004; 108:12073. Calander N. *J Phys Chem B*. 2005; 109:13957. [PubMed: 16852751]
11. Hecht B, Bielefeldt H, Novotny L, Inoué Y, Pohl DW. *Phys Rev Lett*. 1996; 77:1889. [PubMed: 10063197] Drezet A, Hohenau A, Stepanov AL, Detlbacher H, Steinberger B, Galler N, Aussenegg FR, Leitner A, Krenn JR. *Appl Phys Lett*. 2006; 89:091117. Zhao C, Liu Y, Zhao Y, Fang N, Huang TJ. *Nature Communications*. 2013; 4:2305. Zhao C, Zhang J. *ACS Nano*. 2010; 4:6433. [PubMed: 20925325]

Fig. 1. The illumination geometry (Reverse Kretschmann), angle notations and emission polarizer orientations for recording the S- and P-polarized components of Eu(III) luminescence.

Fig. 2.

Representative spectra (A) and angular distributions (B) for S-(dotted) and P-polarized (solid lines) emission of Eu(III) at 590 nm (black), 615 nm (green) and 695 nm (red), embedded in 50 nm PVA layer coated on glass. The maximum intensities of the three emission wavelengths for each polarization are normalized to unity in (B).

Fig. 3. Representative spectra (A) and angular distributions (B) for S- (dotted) and P-polarized (solid lines) emission of Eu(III) at 590 nm (black), 615 nm (green) and 695 nm (red) on Ag-PVA substrates with different PVA thickness. Reflectivity calculations for the corresponding wavelengths and polarizations, for each substrate are shown in (C).

Fig. 4. Reflectivity simulations for S- (dotted lines) and P-polarized (solid lines) light of wavelengths, 590 nm (black), 615 nm (green) and 695 nm (red), showing the dependence of angle of minimum reflectivity on the PVA thickness. Experimentally determined angles at which maximum intensity of S- (hollow circles) and P-polarized emission (solid circles) can be observed from Eu(III) embedded in Ag-PVA substrates with PVA thicknesses of 50, 95, 125 and 300 nm, are indicated on the graph.