Supporting Information

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

Sharmistha Dutta Choudhury[*a], Ramachandram Badugu[b], Krishanu Ray[b], Joseph R. Lakowicz*[*b]*

[a]Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

[b]Center for Fluorescence Spectroscopy, Department of Biochemistry and Molecular Biology, University of Maryland Baltimore, 725 West Lombard Street, Baltimore, Maryland 21201, USA

Materials and Methods

Silver wire (99.999%), poly(vinylalcohol) (PVA, MW 13000-23000) and europium(III) acetate were purchased from Sigma-Aldrich. Glass microscope slides were obtained from VWR.

Preparation of the metal-dielectric layered substrates

The glass slides were cleaned with "piranha solution" (35% H_2O_2/H_2SO_4, 1:3) overnight, washed thoroughly with distilled deionized water and dried with air stream (*Caution*: *piranha solution reacts strongly with organic compounds and should be handled with extreme caution. Do not store the solution in a closed container.*) Metallic silver (thickness ~50 nm) was deposited on the cleaned glass slides using an Edwards Auto 306 Vacuum evaporation chamber under high vacuum (< 5×10^{-7} Torr). The deposition rate (~1.0 nm/min) was adjusted by the filament current. The thickness of the Ag film was determined with a built-in quartz crystal microbalance. The Ag film thickness was further measured using n&k Model 1200 Analyzer (n&k Technology Inc.) and was found to be 50 nm, as expected. Moreover, the close resemblance between the experimentally observed angular emission patterns and the reflectivity calculations on the metal-dielectric layered substrates (discussed later) also match with Ag film thickness of 50 nm. The optical absorption and SEM image of the Ag film are presented in Fig.

S1. The absorption spectrum displays a non structured profile in the 350-800 nm wavelength range indicating a smooth Ag film. The SEM image also shows the presence of continuous metal film with minor surface roughness.

The surface of the Ag film was spin coated (at 3000 rpm) with an aqueous solution of PVA, containing europium(III) acetate to obtain the final Ag-PVA substrates. The weight percentages of PVA were varied to obtain various thicknesses of the dielectric, PVA layer, keeping the Ag layer thickness constant at 50 nm. The PVA film thicknesses after spin coating were measured with a Tencor Alphastep 200 Profilometer. The film thickness corresponding to different PVA concentrations and the calibration curve for the same is discussed in detail in our previous paper (*J. Phys. Chem. Lett.*, 2013, **4**, 227).

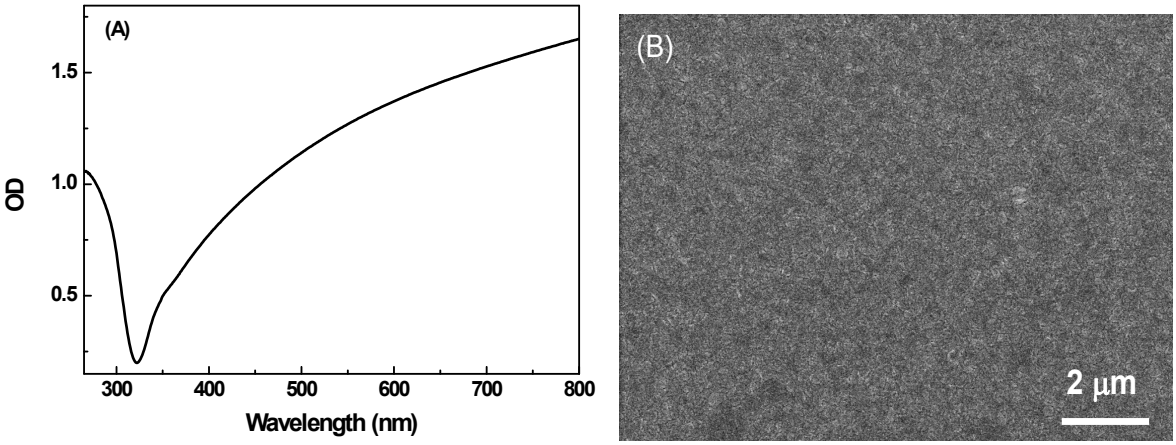


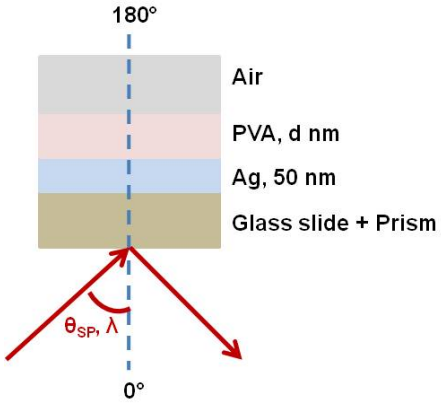
Figure S1. (A) Absorption spectrum and (B) SEM image of 50 nm thick Ag film.

Angle-dependent Emission measurements

The Ag-PVA samples on glass slides were fixed to a hemispherical BK7 glass prism with glycerol, for refractive index matching. The prism along with the attached sample was placed on a precise rotary stage that allows excitation and observation at any angle relative to the vertical axis of the cylinder. The samples were directly illuminated from the air side in the Reverse Kretschmann (RK) configuration, with vertically polarized light from a 375 nm diode laser source (PicoQuant, Germany) incident normally on the PVA layer, containing europium(III) acetate (Fig. 1). The light from this 375 nm laser was already collimated. No additional collimating or objective lens was used. The emission was collected with an Ocean Optics optical fiber (with diameter 1 mm and NA 0.22). The output of the fiber was connected to a compact fiber optic spectrometer (Ocean Optics SD2000) for recording the emission spectra. Both the

detector and the sample were placed on a rotation stage to enable excitation and detection at different angles. The emission observed from 0° to 90° and 270° to 360° on the glass side, is designated as SPCE. The S- and P-polarized emissions from Eu(III) were observed by changing the polarizer orientation in front of the fiber optic cable; vertical for S-polarization and horizontal for P-polarization.

Reflectivity calculations



Scheme S1. A schematic of the sample configuration used for the reflectivity simulations.

The reflectivity calculations were performed using the TF Calc software package (Software Spectra, Inc., Portland, Oregon) that is used to design multilayer optical filters. A schematic representation of the sample configuration used for the calculations is shown in Scheme S1. For simplicity the prism and the glass slide were considered as a single phase with the same refractive index (n = 1.52). The wavelength dependent optical constants of silver were considered for calculating the reflectivity at different emission wavelengths; 595 nm, 615 nm and 695 nm, corresponding to the three emission bands of Eu(III). The thickness of the PVA layer (refractive index, n = 1.52) was varied during the calculations to match the measured angular emissions for the respective Ag-PVA structures shown in Fig. 3. The calculated PVA thicknesses were consistent with the known film thicknesses at various weight percentages of PVA. Some differences from the calculated curves may be expected due to the variations in the thicknesses of the spin coated PVA films and the deposited Ag layer.

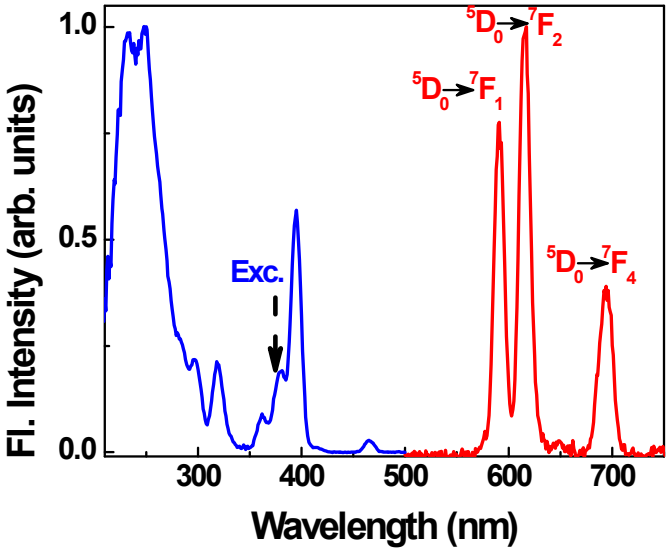


Figure S2. Excitation and emission spectra of 0.1 M europium(III) acetate in 1% aqueous PVA. For recording the emission spectrum, Eu(III) was excited directly at 375 nm (wavelength indicated by an arrow in the excitation spectrum).