Supporting Information

Tuning Fluorescence Direction with Plasmonic Metal-Dielectric-Metal Substrates

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Materials and Methods

Silver wire (99.999%), poly(vinylalcohol) (PVA, MW 13000-23000), sulforhodamine101 (S101), rhodamine6G (Rh6G) and tris-(8-hydrxyquinoline)aluminium (AlQ_3) were purchased from Sigma-Aldrich. The dye, Cy5 was procured from Invitrogen. Glass microscope slides were obtained from VWR.

Preparation of the metallo-dielectric 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 and the thickness of the Ag film was measured with a built-in quartz crystal microbalance. The surface of the Ag film was then spin coated (at 3000 rpm) with an aqueous solution of PVA, containing the dyes (~100 μM). This was followed by the thermal vapor deposition of a second 50 nm layer of Ag, to get the final Ag-PVA-Ag metallo-dielectric substrates. The weight percentages of PVA were varied to obtain various thicknesses of the dielectric, PVA layer.

For the surface plasmon polariton mediated energy transfer (SPP-ET) studies, the donor (AlQ_3) was spin coated above the top Ag layer using a poly(methyl methacrylate) (PMMA) solution in chloroform, containing the dye. The configuration of the substrate in this case was PMMA(4% containing AlQ_3)-Ag-PVA(4% containing Rh6G)-Ag. Control donor-only and acceptor only samples were made with the same configuration.

Fluorescence measurements

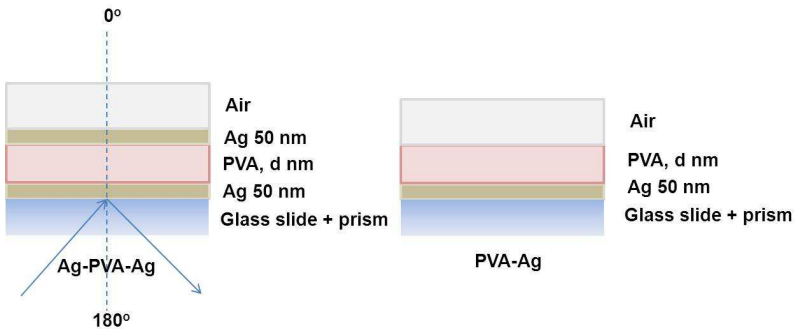
The Ag-PVA-Ag samples on glass slides were fixed to a hemispherical BK7 glass prism with glycerol, for refractive index matching. The prism along with the attached sample was placed on a precise rotary stage that allows excitation and observation at any angle relative to the vertical axis of the cylinder. The samples were illuminated in the reverse Kretschmann configuration, from the air side (Figure S1). Unless otherwise mentioned, the excitation was always normal to the sample surface. 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 spectrofluorometer (Ocean Optics SD2000) for recording the emission spectra and to a TCSPC instrument (PicoQuant, Fluotime 100) for time-resolved measurements. The emission observed from 90^o to 270^o is designated as SPCE while the emission from 0^o to 90^o and 270^o to 360^o is designated as the free space emission.

A 532 nm continuous wave diode pumped solid state laser (CNI, China) was used as the excitation source for the steady-state measurements with S101. Time-resolved measurements for S101 were performed with a pulsed laser (510 nm, 130 ps, 10 MHz, Picoquant). Pulsed laser diodes were used as the excitation sources for studies with AlQ_3 (470 nm, 100 ps, 40 MHz) and Cy5 (635 nm, 100 ps, 40 MHz). The excitation light was passed through laser clean-up filters and the emission was observed through suitable long pass filters to suppress any scattered light. The s- and p-polarized emissions were observed by changing the polarizer orientation in front of the fiber optic cable. The emission intensities at each observation angle were obtained by integrating the area under the emission spectra at the corresponding angles. Lifetimes were estimated by fitting to a χ_r^2 value of less than 1.2 and a residual trace that was symmetrical about the zero axis.

For the photographs, the samples were attached to a hemispherical prism instead of a hemicylinder.

Reflectivity calculations

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 configurations 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; 600 nm (corresponding to the emission maximum of S101) and 670 nm (corresponding to the emission maximum of Cy5). The thickness of the PVA layer (refractive index, n = 1.52) was varied during the calculations to match the measured angular emissions shown in Figure 1 and Figures S3, S4, S9. We found reasonable agreement between the observed angular emissions and the calculated angles and polarizations of the reflectivity minima. The calculated PVA thicknesses were also consistent with the measured thicknesses of the PVA film (discussed below). Some differences from the calculated curves may be expected due to the variations in the thicknesses of the spin coated PVA films. Moreover, a fluorophore emits with a finite bandwidth, so that in reality the angular emission distributions are expected to be wider than the theoretically calculated values for a single emission wavelength. It should also be mentioned that the positions and polarizations of the reflectivity minima are very sensitive to even slight changes (nanometer range) in the thicknesses of the layers.



Scheme S1. A schematic of the sample configurations used for TF Calc. The refractive indices of Ag, used in the calculations are as follows; $n_{600\ nm} = 0.06+i3.75$ and $n_{670\ nm} = 0.069+i4.39$

PVA Film Thickness measurements

The PVA film thicknesses after spin coating were measured with a Tencor Alphastep 200 Profilometer. The measured thicknesses were found to be in reasonable agreement with those

obtained from TF Calc. Figure S1 shows the dependence of film thickness on the weight percentage of PVA used.

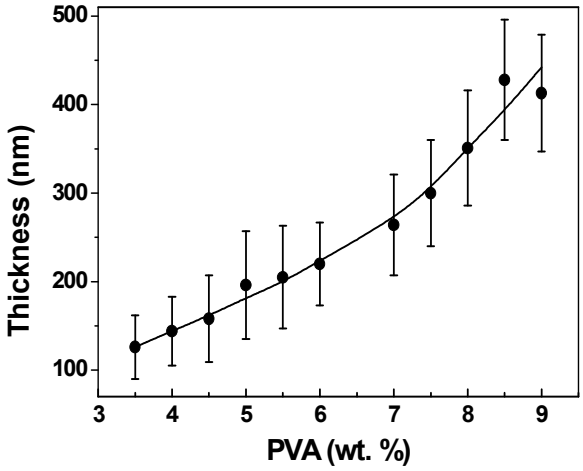


Figure S1. Thicknesses of PVA films as obtained from profilometer measurements. The solid line is shown as a guide for the eye.

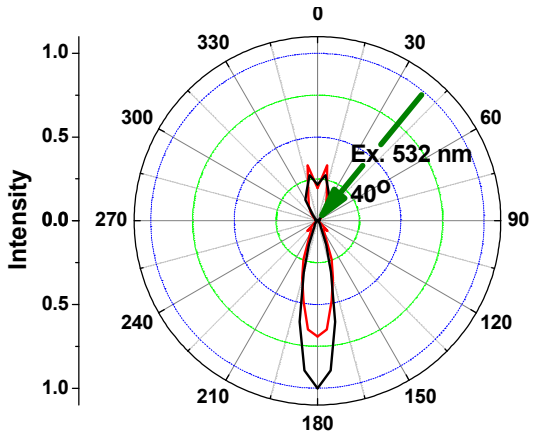


Figure S2. Measured angular distributions of the s- (black) and p-polarized (red) emissions of S101 embedded in the metallo-dielectric Ag-PVA(4%)-Ag substrate, with 532 nm excitation at 40^{o} from the normal.

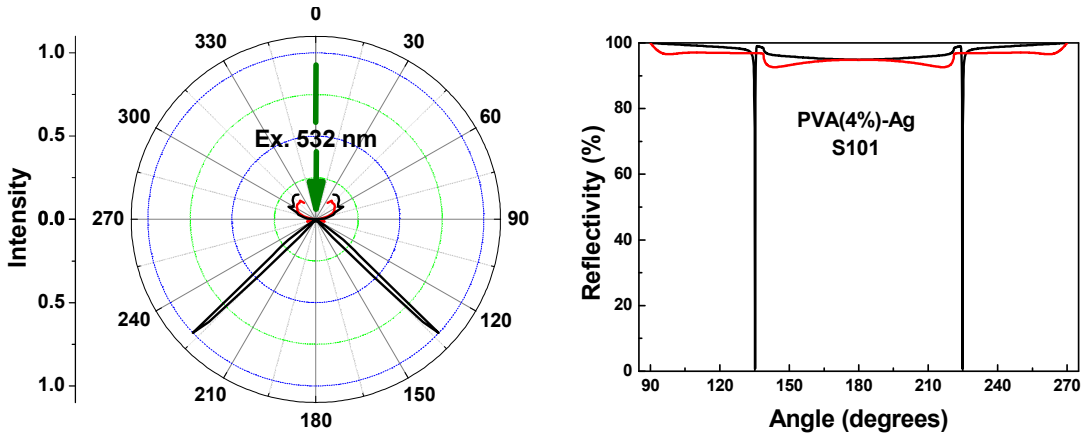


Figure S3. Measured angular distributions and the corresponding reflectivity calculations of the s- (black) and p-polarized (red) emissions for S101 in the PVA(4%)-Ag substrate

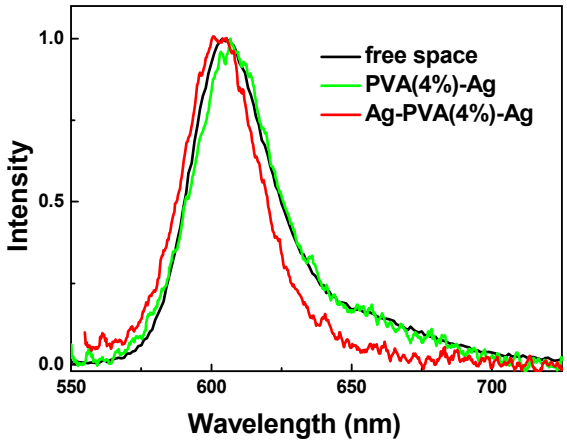


Figure S4. Comparison of the free space emission spectra of S101 with the SPCE emission in PVA(4%)-Ag and Ag-PVA(4%)-Ag substrates. The emission spectra for the metallo-dielectric substrates have been obtained by combining the spectra recorded at all observation angles. The slight blue shift in the spectra observed with the MDM substrate might be due to a small contribution of the direct excitation light, for measurements normal to the substrate.

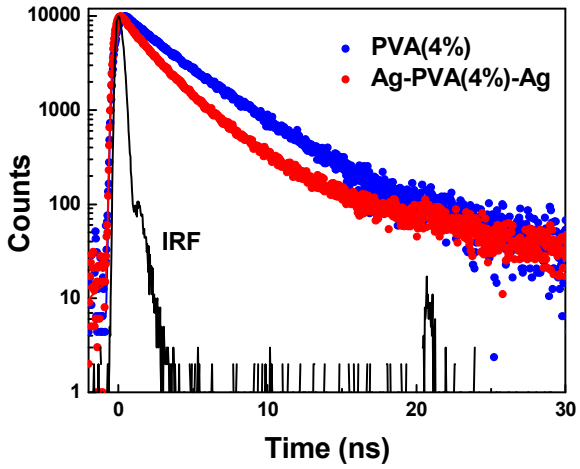


Figure S5. Fluorescence intensity decays of S101 in PVA(4%) and Ag-PVA(4%)-Ag substrates.

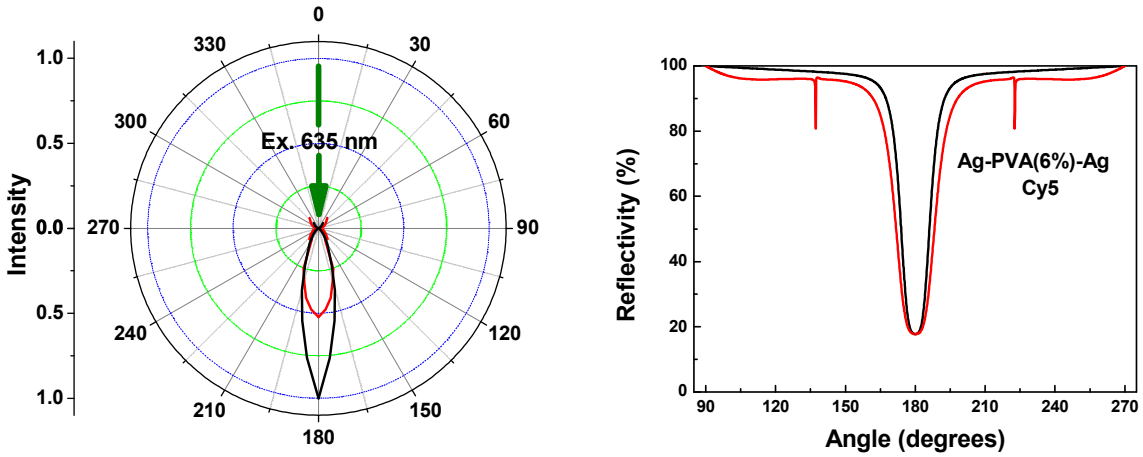


Figure S6. Measured angular distributions and reflectivity calculations of the s- (black) and p-polarized (red) emissions for Cy5 in Ag-PVA(6%)-Ag substrate, PVA thickness 175 nm.

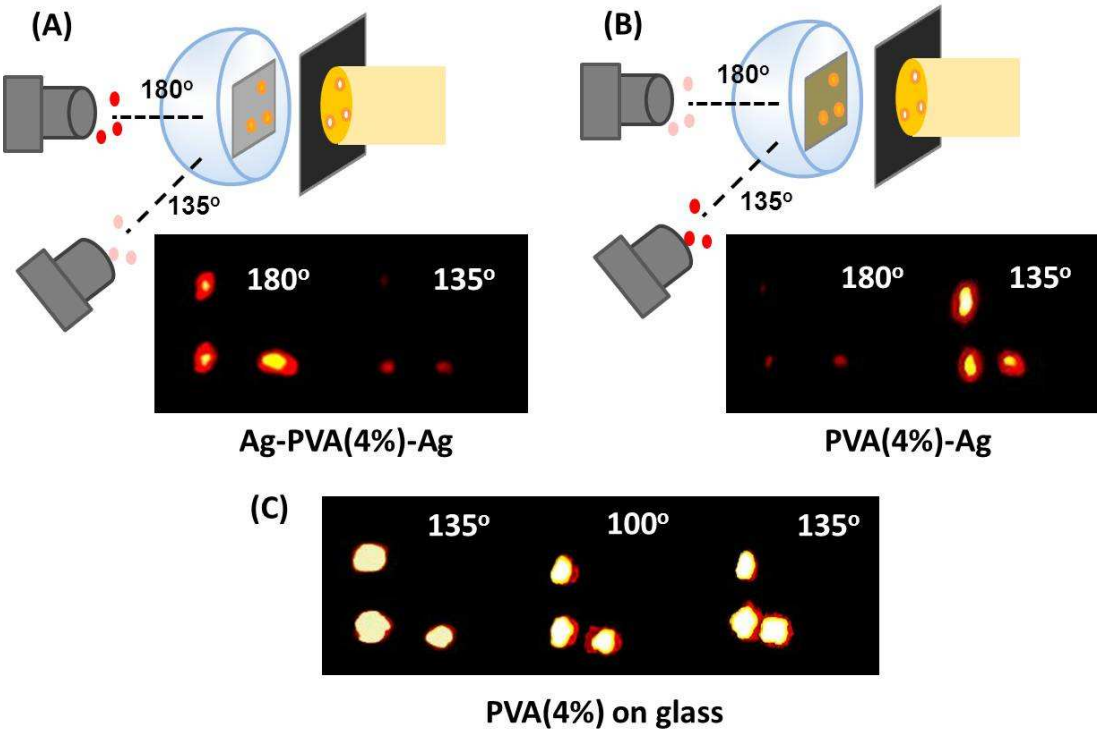


Figure S7. Fluorescence images of S101 captured on a camera at different observation angles using the metallo-dielectric substrates (A) Ag-PVA(4%)-Ag and (B) PVA(4%)-Ag. The emission pattern from S101 in PVA(4%) spin coated on glass is also shown for comparison (C). The illumination was performed through a patterned, perforated screen using a 532 nm laser beam. The beaming emission at 180^{o} is clearly observed for the Ag-PVA(4%)-Ag substrate in contrast to emission at 135^{o} with the PVA(4%)-Ag substrate and the nearly isotropic emission on glass.

Table S1. Fluorescence intensity decay parameters[a] for the SPP-ET system.

System	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)
AlQ_3/PMMA(4%)-Ag-PVA(4%)-Ag (Donor only)[b]	6	1.1	94	15.4	-	-
PMMA(4%)-Ag-PVA(4%)/Rh6G-Ag (Acceptor only)[c]	43	0.6	57	2.5	-	-
AlQ_3/PMMA(4%)-Ag-PVA(4%)/Rh6G-Ag (Donor-Acceptor)[c]	35	0.6	49	2.1	16	15.2

[a]The intensity decays were fitted according to, $I(t) = \sum_i a_i \exp(-t/\tau_i)$, χ_r^2 values in all the cases was less than 1.2. The relative contributions were estimated as $A_i = \frac{a_i \tau_i}{\sum_i a_i \tau_i}$.

[b]Observed with 500 nm long pass filter at 180^o

[c]Observed with 550 nm long pass filter at 180^o