Purcell Factor Based Understanding of Enhancements in Surface Plasmon-Coupled Emission with DNA architectures

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Electronic Supplimentary Information

Materials and Methods:

Rhodamine 6G (Rh6G), poly vinyl alcohol (PVA), Calf Thymus DNA were procured from Sigma-Aldrich. 50nm silver thin film coated on pyrex with 5 nm silica top layer were purchased from EMF Corp, USA. DNA thin film was obtained by spin-coating aqueous solution of calf thymus DNA. Decoration of silver and carbon dots (DNA-Ag and DNA-CD) on DNA were achieved with suitable modifications to earlier reported procedures.[S1] Hydrothermal synthesis of DNA-CD was achieved by incubating DNA (4mg/mL in MilliQ water) with CD at 180°C for 12h. The resulting DNA-CD was centrifuged at 11000g for 30min followed by dialysis[S1]. DNA-CD (4mg/mL in MilliQ water) was then mixed with 1:1 w/w $AgNO_3$ and UV-irradiated (254nm) for 20min[S1]. 1mM concentration of Rh6G was used for all the experiments, enabling correlation with our previous works[S2]. The SPCE substrate with each of the bio-spacer was then attached to a hemi-cylindrical prism mounted on a rotating stage. The substrates were illuminated with a 532 nm c.w. laser (5 mW) and the emission was passed through a 540 nm long-pass filter, before collecting into a fiber coupled to an Ocean Optics USB 2000+ fiber optic spectrometer. The angularity and enhancements were measured with the help of a rotating stage. Polarization measurements were carried out by placing a polarizer between the prism and the collection fiber.

Commercially available Lumerical FDTD solutions and TfCalc softwares were used for complimenting the experimental results with the simulation studies. The TfCalc simulations were carried out for PVA overcoats (n_s = 1.50) on 50nm silver thin film (ϵ_m=-14.06 + 0.45i) on 0.7mm BK7 glass (n_g= 1.518), for the respective emission wavelength maxima corresponding to each nanocavity. 3D FDTD simulations were carried out using a point source (560nm) as the radiating dipole placed in the nanocavity. Time Correlated Single Photon Counting (TCSPC) studies were carried out to determine the time resolved fluorescence decay profiles. The excitation source used was 490 nm LED with 1 ns pulse. The emission intensities were counted by Horiba Jobin Yvon TCSPC system and the fluorescence decay was analyzed using IBH- DAS V6.2.

SPCE Platform:

As shown in figure S1, the SPCE platform consists of: light source, aperture, substrate mounted on prism with filter and optic fiber attached to a rotating stage. The optic fiber is coupled to spectrometer for data collection. The inset in figure S1 shows the microscopic image of the substrate having Rh6G trapped between the nanomaterial and the silver thin film (for simplicity only the Rh6G trapped in the cavity is shown).

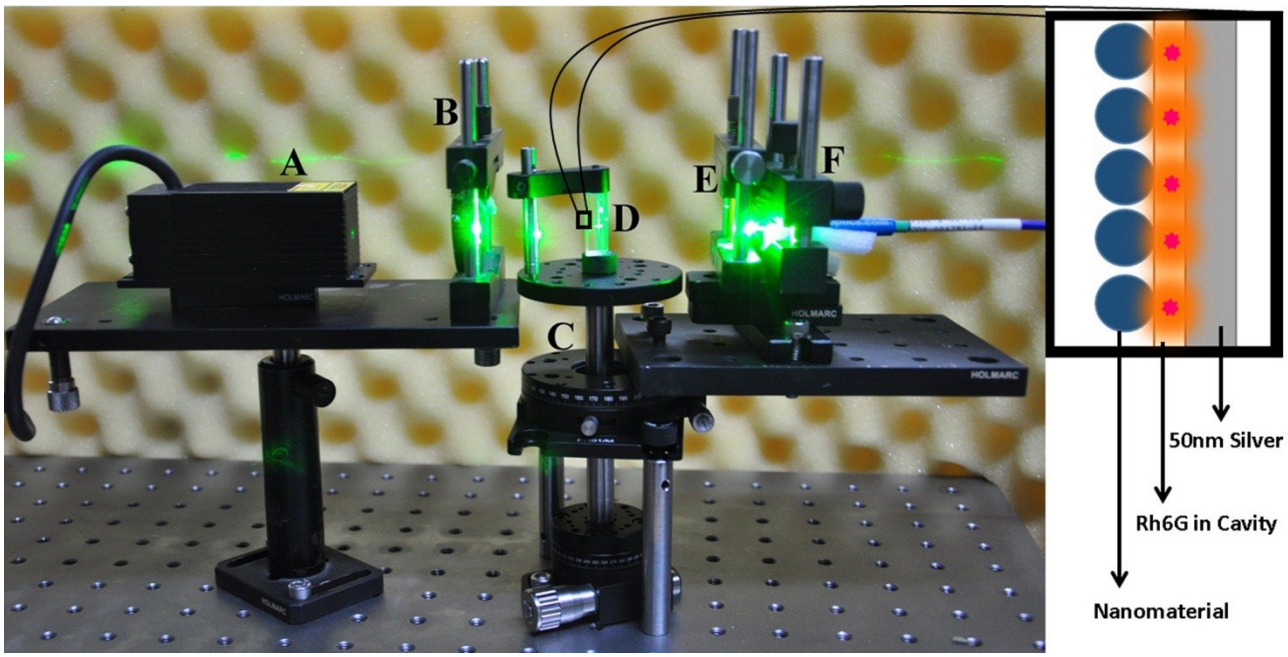

Figure S1. High definition image of the plasmonic platform with (A) Laser, (B) Aperture, (C) Rotating stage, (D) Substrate and prism, (E) Filter, (F) Optic fiber. (inset) Microscopic representation of the substrate showing Rh6G trapped between 50nm silver thin film and the nanomaterial.

DNA Thin Film: The DNA thin film was spin coated on a glass slide and its absorption and fluorescence emission was studied in the spectral range of interest. In figure S2 (a) it can be seen that the DNA thin film does not absorb between 530-650nm. Further with 530nm excitation (the excitation wavelength of the source, used for SPCE studies), the DNA thin film showed no fluorescence emission (Figure S2 (b)).

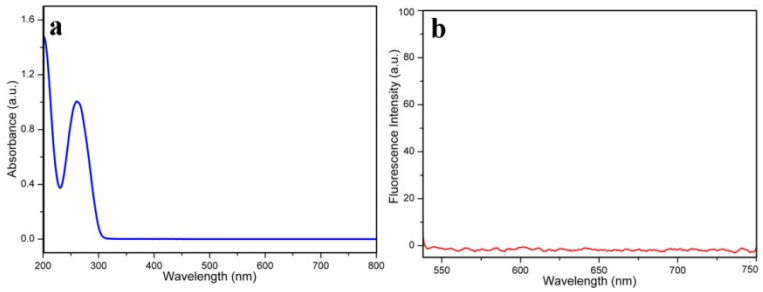

Figure S2. (a) Absorbance spectrum of 30nm DNA thin film on glass slide, (b) Emission spectrum of 30nm DNA thin film on glass slide, with 530nm excitation.

Surface Plasmon Resonance dips simulations:

We carried out TfCalc simulations[S3] to predict the minimum reflectivity curves with both the SPCE and MDM substrates with different metal composition and bio-spacer thickness. The SPR angle / minimum reflectivity curve correlates with directionality of fluorescence in the SPCE platform. The reflectivity plots show both the s-polarized (red line) and p-polarized light (green line). Figure S3 shows the comparative reflectivity minimum plot of varying thickness of DNA bio-spacer and PVA. On closer observation, the DNA spacer shows wider angle of minimum reflectivity compared to the respective PVA thickness which in turn results in the desired angularity at lower thickness of DNA than PVA. This could offer greater sensitivity with DNA based sensing technologies.

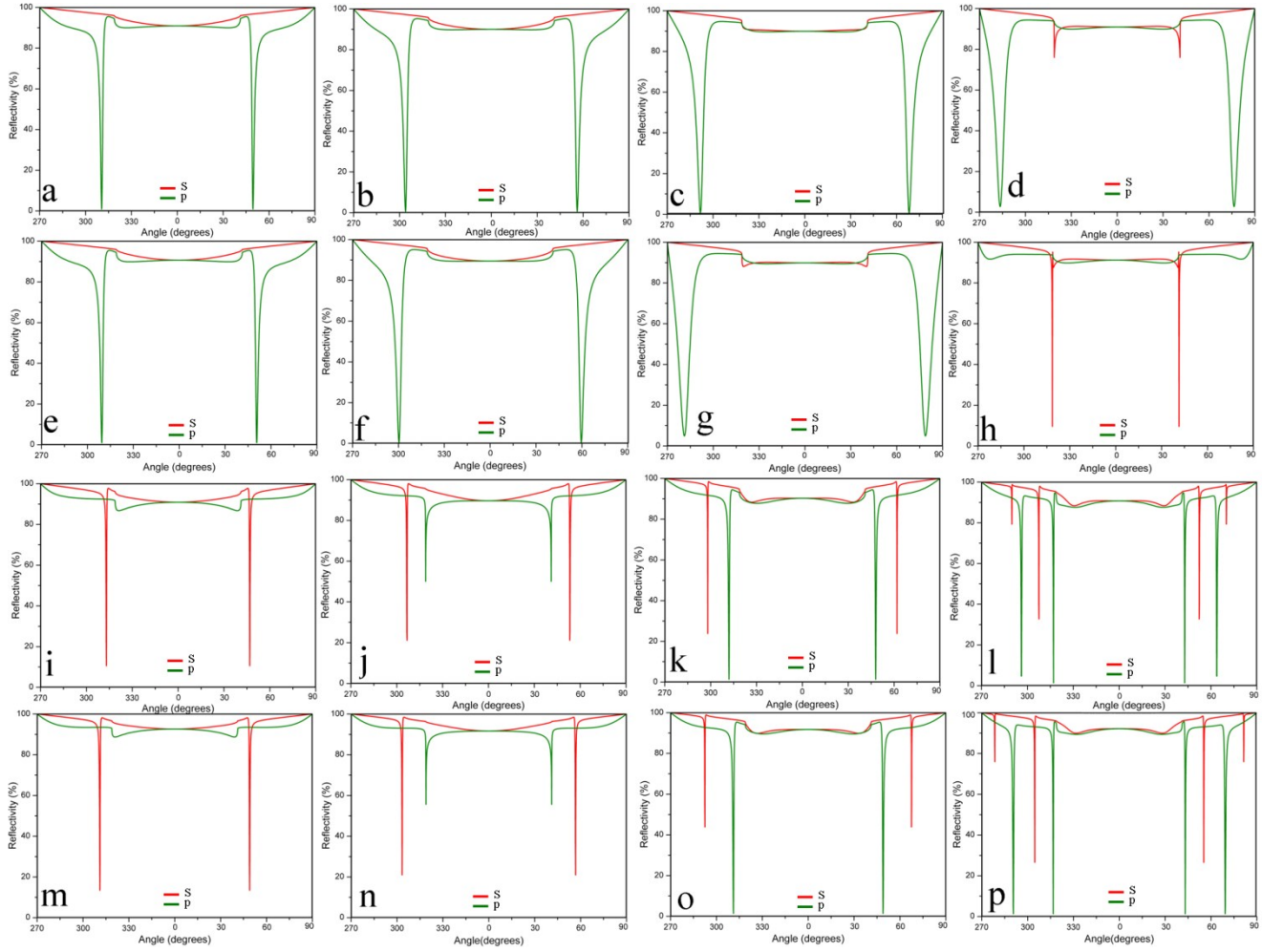

Figure S3. Plasmon resonance dips for different thickness of PVA (a-d, i-l) and DNA (e-h, m-p); (a,e) 30nm, (b,f) 50nm, (c,g) 80nm, (d,h) 100nm, (i,m) 150nm, (j,n) 200nm, (k,o) 300nm, (l,p) 500nm.

Reflectivity minimum plots for MDM structures with different metals are shown in Figure S4 and S5. Figure S5 presents a combination of silver and gold with non-conventional metal films for SPCE studies. These plots show the potential of the DNA bio-spacer for use not only in SPCE but also in MDM structures towards beaming emission.

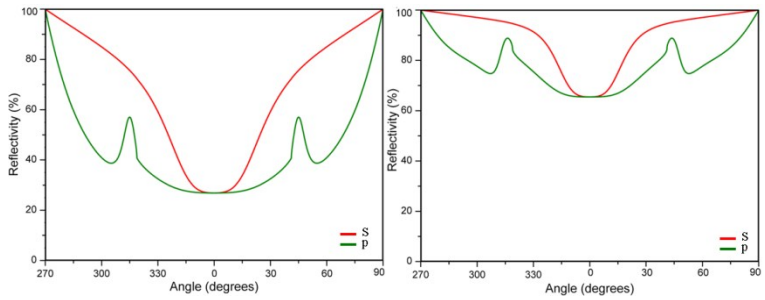

Figure S4. Reflectivity minima curve for s- (red) and p- polarized light (green) presenting the difference in the percentage of reflectivity at normal incidence for MDM structures: Ag-DNA-Au (left) and Au-DNA-Au (right).

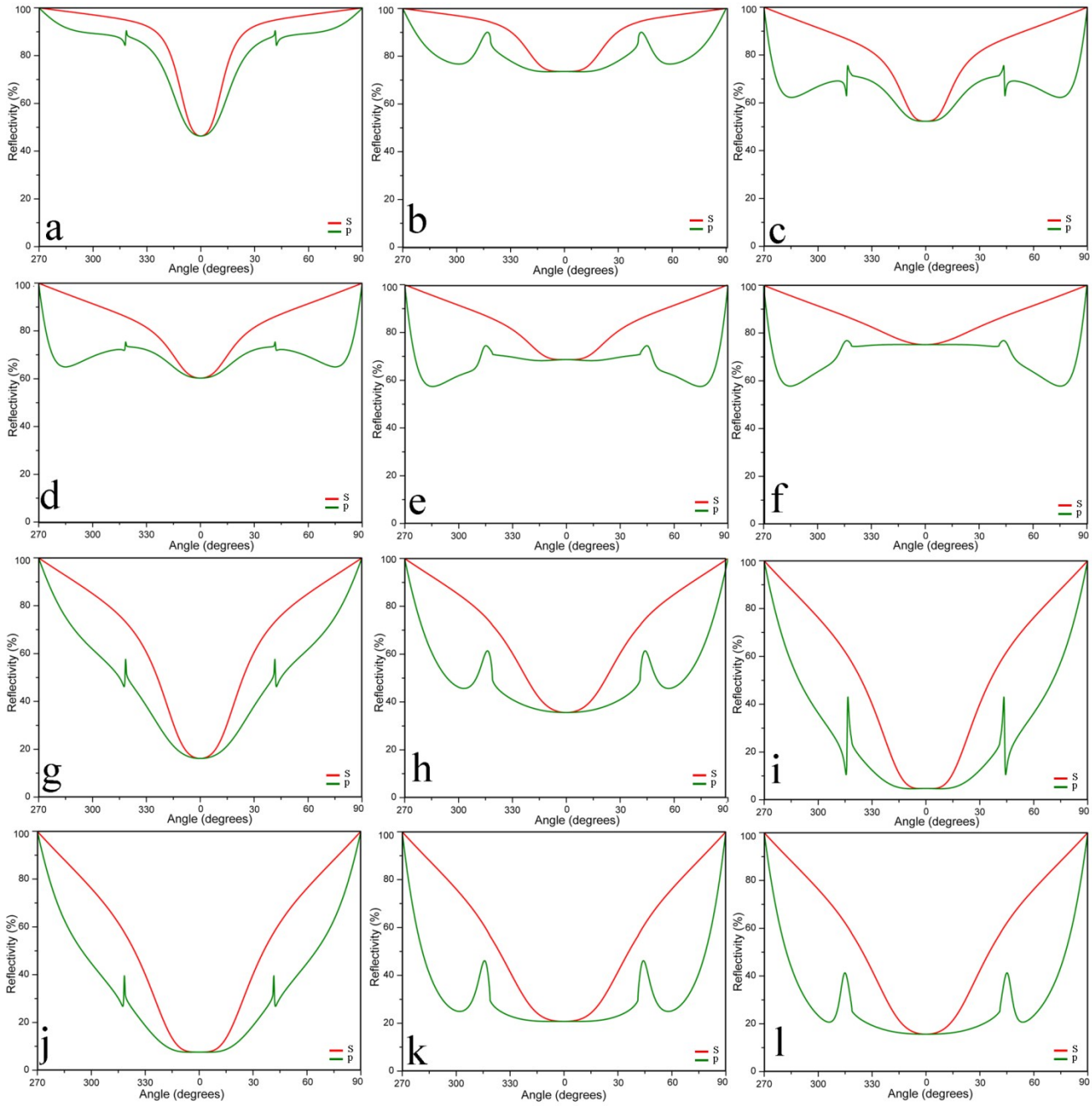

Figure S5. Reflectivity minima curve for s- (red) and p- polarized light (green) with optimum DNA bio-spacer thickness for the lowest dip percentage/high coupling at normal incidence for MDM structures- [MDM stack (Optimal DNA thickness)]: (a) Ag-DNA-Al (137nm), (b) Ag-DNA-Cu (121nm), (c) Al-DNA-Ag (136nm), (d)

Al-DNA-Al (146nm), (e) Al-DNA-Au (127nm), (f) Al-DNA-Cu (137nm), (g) Au-DNA-Al (137nm), (h) Au-DNA-Cu (137nm), (i) Cu-DNA-Ag (137nm), (j) Cu-DNA-Al (137nm), (k) Cu-DNA-Cu (137nm) and (l) Cu-DNA-Au (137nm).

FDTD Simulations:

We carried out a series of 3D FDTD simulations to study the orientation effect of a radiating dipole in bio-nanocavities (nanomaterial on modified DNA-fluorophore-Silver thin film) and its effect on Purcell factor. Based on the earlier reports[S4], we present the case where the intercalated fluorophore would be at an orientation angle that is non-perpendicular to the nanocavity, while the minor groove bound fluorophore would be oriented at 90° (perpendicular) to the nanocavity. Hence the intercalated fluorophore would radiate transverse electric polarized waves (s-polarized) with respect to the plane of the nanocavity, while for the minor groove bound radiating dipole, it would be transverse magnetic polarized waves (p-polarized). The hotspot intensity and Purcell factors were extracted from the simulation result. The observed trend correlated well with that of the fluorescence enhancements and experimentally obtained Purcell factors. Figure S6 illustrates the fluorophore binding with the DNA and Table.S1 presents the theoretical Purcell factors calculated for the two different orientations of the radiating dipole.

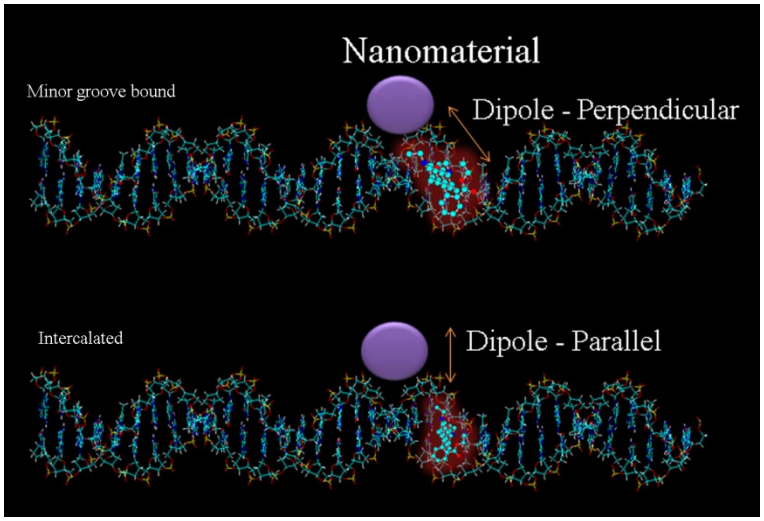

Figure S6. Different orientation angles of the radiating dipole with respect to the nanomaterial surface.

Bio-Nanocavity	**Site/type of fluorophore binding**	**Purcell factors** (from simulations)
DNA-CD	Intercalation	0.037
	Minor groove	4.440
DNA-AgCD	Intercalation	1.090
	Minor groove	8.060

Table S1. Theoretical Purcell factors for different bio-nanocavities

References:

S1. H. Ding, F. Du, P. Liu, Z. Chen and J. Shen, ACS Appl. Mater. Interfaces. 2015, 7, 12, 6889-97; H. Choi *et al*. Nature Photon. 2013, 7, 732-738.

S2. S. Venkatesh, P. K. Badiya and S. S. Ramamurthy, Chem. Commun., 2015, 51, 7809.

S3. T. Inagaki, R. N. Hamm, L. R. Painter and E. T. Arakawa, J. Chem. Phys., 1974, 61, 4246.

S4. P. H. Doan, D. R. G. Pitter, A. Kocher, J. N. Wilson and T. Goodson, J. Am. Chem. Soc. 2015, 137, 9198-9201

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